The Separation of Titanium, Zirconium and Thorium by Ion Exchange[1,2]

BY WILLIAM E. BROWN AND WILLIAM RIEMAN III

A method has been developed for the quantitative separation of titanium, zirconium and thorium by ion-exchange technique. The nature of the complexes between metal and citrate ions has been investigated and some probable complexes given. Radiochemical work with titanium-51 showed that the radioactive isotope was, to a certain extent, separated from the normal isotopes. It is believed that partial separation of the natural isotopes of titanium was achieved and that this separation accounts for the unusual shape of the elution curve of this element.

I. Introduction

The purpose of this work was to effect a separation of titanium, zirconium and thorium by ion-exchange techniques.

Proof of the value and versatility of the ion-exchange techniques has been provided in numerous recent articles. A separation of the rare earths has been developed[3-8] and pilot-plant operations have proved the method practical.[9] Zirconium and hafnium have been separated with an anion-exchange resin.[10] The separation of columbium and tantalum[11] has been achieved by application of the ion-exchange technique. These examples illustrate the power of this technique in achieving difficult separations.

II. Theory of Elution

The work of Mayer and Tompkins[12] concerning the theoretical aspect of ion-exchange separation indicates the importance of the distribution ratio C, which is defined as the quantity of metal in the resin of any plate divided by the quantity of metal in the interstitial solution of the same plate. They derived equations relating C to the elution curve by assuming that an ion-exchange column consists of a number of theoretical plates in analogy with a plate distillation column. The point of maximum concentration of the cation being eluted was found to be related to C by the equation

$$F_{max} = C$$

where F_{max} is that volume of eluate, expressed in "V units," at which the maximum concentration of the cation being eluted appears in the eluate. The V unit is the volume of the interstitial space in the resin bed. Thus, the degree of separation of two cations depends on the difference of their C values.

The presence of a complexing agent, such as citrate ions, lowers the value of C by competing with the resin for the cation, for example

Th-Complex $+ 4 HR \rightleftarrows ThR_4 + 4 H^+ +$ Complexing agent
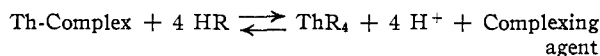
(1) Part of a thesis submitted by William E. Brown to Rutgers University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) The authors wish to express their appreciation to the Titanium Alloy Manufacturing Division of the National Lead Company, for financial assistance and for some of the chemicals used in this work.

(3) E. R. Tompkins, J. X. Khym and W. E. Cohn, THIS JOURNAL, **69**, 2769 (1947).

(4) F. H. Spedding, A. F. Voight, E. M. Gladrow and N. R. Sleight, ibid., **69**, 2777 (1947).

(5) J. A. Marinsky, L. E. Glendenin and C. D. Coryell, ibid., **69**, 2781 (1947).

(6) F. H. Spedding, A. F. Voight, E. M. Gladrow, N. R. Sleight, J. E. Powell, J. M. Wright, T. A. Butler and P. Figard, ibid., **69**, 2786 (1947).

(7) D. H. Harris and E. R. Tompkins, ibid., **69**, 2792 (1947).

(8) B. H. Ketelle and G. E. Boyd, ibid., **69**, 2800 (1947).

(9) F. H. Spedding, E. I. Fulmer, T. A. Butler, E. M. Gladrow, N. Gobush, P. E. Porter, J. E. Powell and J. M. Wright, ibid., **69**, 2812 (1947).

(10) E. H. Huffman and R. G. Lilly, ibid., **71**, 4147 (1949).

(11) K. A. Kraus and G. E. Moore, ibid., **71**, 3855 (1949).

(12) S. W. Mayer and E. R. Tompkins, ibid., **69**, 2866 (1947).

III. Materials, Apparatus and General Procedure

(1) **Preparation and Purification of Buffers.**—All reagents used were of C.P. grade. The 1% citric acid (0.0520 M) eluant solution was prepared in 12-liter batches at various pH values from crystals of Merck and Co., Inc., citric acid monohydrate, concentrated hydrochloric acid, and distilled water. The pH was checked with a pH meter which had been calibrated with a standard buffer. If the pH of the solution was not at the desired value, it was adjusted with small portions of concentrated hydrochloric acid or 0.0520 M citric acid. A small crystal of thymol was added to prevent growth of mold. For some of the following work, this buffer was treated to remove traces of iron introduced with the citric acid by passing the solution through a 15-cm. bed of hydrogen-form Dowex-50.

(2) **Preparation of Standard Solutions of Titanium, Zirconium and Thorium.**—The standard titanium solutions were prepared from double-distilled C.P. titanium tetrachloride. About 15 ml. of this titanium tetrachloride, cooled to 0°, was slowly added to 15 ml. of concentrated hydrochloric acid with continuous stirring. A deep red-orange viscous liquid was produced. Portions of this liquid were used to prepare standard solutions by dilution with 1% citric acid. The pH was adjusted by adding either concentrated hydrochloric acid or ammonia water which were 0.0520 M with respect to citric acid or citrate ion, respectively. Zirconium oxychloride was dissolved in 0.0520 M citric acid and the pH adjusted as above. The thorium standard was prepared similarly from thorium nitrate. The titanium and zirconium solutions were found to be unstable and slowly changed to colloidal solutions at pH values below 3.50. For this reason the titanium and zirconium standards were made up at a pH near 4.0 and the pH of each sample adjusted to the required value with concentrated hydrochloric acid immediately before use.

(3) **Preparation of a Solution of Radioactive Titanium-51.**—A solution containing radioactive titanium-51 was prepared from a sample of titanium dioxide which had been bombarded in the pile at Oak Ridge, and contained titanium-51. This titanium dioxide was very resistant to solution by the usual methods. It was treated with carbon tetrachloride vapor at 500° in an all-glass apparatus. The reaction products were collected and treated with concentrated hydrochloric acid. The solution was subsequently made 0.0520 M with citric acid and adjusted to a pH of 2.0 with concentrated ammonia.

(4) **Apparatus.**—The ion-exchange resin was held in a glass tube provided with a sintered-glass disc of medium porosity. It was surrounded by a jacket through which water from a constant-temperature bath was pumped.

The eluate from the column flowed into a siphon pipet which delivered fractions of constant volume into beakers. These beakers stood on the turntable of an automatic sample collector, which is described in detail elsewhere.[1]

(5) **Preparation of the Resin.**—Dowex-50 was chosen as the ion-exchange resin[13] for this work because of its fast action and single active group. The sodium form of spherical Dowex-50 as received from the manufacturer was dry-screened, the 80-to-100 mesh fraction washed, and suspended matter decanted off until a clear supernatant liquid remained. The settled resin was slurried into a column and washed exhaustively with 5% triammonium citrate solution, then washed with M hydrochloric acid to convert it to the hydrogen form. Washing was continued with distilled water until a negative chloride test was obtained. The resin was removed, air-dried, and used in the equilibrium studies.

(13) W. C. Bauman and J. Eichhorn, ibid., **69**, 2830 (1947).

Colloidal Dowex-50 became available and was used for later work. Preliminary studies showed that the large aggregates (about 2 to 3 mm.) in the resin as received from the manufacturer did not reach equilibrium with the solution as rapidly as the smaller particles. Therefore the resin was treated as follows. The sodium resin was wet-screened. The 100-to-120 mesh fraction was placed in a long column, and fines were removed by back washing for several hours with tap water at a flow rate which extended the resin to about three times the settled bed volume. Exhaustive backwashing with 1% diammonium citrate converted the resin to the ammonium form. It was backwashed further with M hydrochloric acid, and finally with a 1% citric acid–HCl buffer at pH 1.00. This resin was then used in column work.

IV. Experimental

(1) **Equilibrium Experiments.**—A series of equilibrium studies was made to determine the distribution ratios. To each of a number of 100-ml. volumetric flasks containing 5.00 g. of air-dried Dowex-50 (12.9 meq.) and 0.466 mmole. thorium nitrate, varying amounts of 3.17 M ammonia (which was 0.0520 M with respect to citrate) were added, plus enough 0.0520 M citric acid to make 100 ml. It was found that equilibrium was reached in less than 24 hours. However, all the equilibrium studies were allowed to stand for at least 48 hours before sampling. Temperature control was found to be necessary to give reproducible results. Therefore all the equilibrium studies were made in a bath at 25.0 ± 0.1°. Samples of the supernatant liquid were withdrawn for pH measurement and determination of thorium. Under these conditions the resin had a settled volume of 7.50 ml. and an interstitial volume of 1.10 ml. This furnished the data for the calculation of the distribution ratios for thorium. Similar experiments were performed with titanium and zirconium.

The results are plotted in Fig. 1. The large difference in the C values for the various cations at pH values below 2.00 indicates that a good column separation is possible.

(2) **Elution Experiments.**—The possibility of the separation of titanium, zirconium and thorium cations with a column containing Dowex-50, was investigated as follows:

Preliminary work with conditions similar to those applied in the rare-earth separation[14] produced a poor separation of titanium, zirconium and thorium. With 5% citric acid–ammonium citrate as the complexing agent at room temperature and with pH values from 2 to 4, no separation was observed; and only when hydrochloric acid was added to lower the pH to 1.0 was thorium separated from titanium and zirconium.

From the results of the equilibrium work it was decided to begin column operation with 1% citric acid buffer at pH 2.00. With a resin bed 28 cm. deep having a cross section area of 1.04 cm.², separate elutions were run for titanium, zirconium and thorium at a flow rate of approximately 0.2 ml./cm.²/min.

(a) **Addition of Samples to the Column.**—For some of the work, a pipet was used to add 10.00-ml. volumes of a standard solution of titanium, zirconium or thorium to the top of the resin bed. These solutions were made up at a pH of 2.00, and the resin bed had previously been washed with 1% citric acid buffer at pH 2.00.

In later work, to further assure equilibrium conditions when adding the sample to the top of the bed, the stand-ard solutions were equilibrated with 10.0-ml. (settled volume) portions of Dowex-50 in a small flask. The pH of the resin and solution was adjusted to the desired value with concentrated hydrochloric acid or ammonia. The flask was shaken occasionally during a period of about one hour to attain equilibrium. The entire contents of the flask were transferred carefully to the top of the resin bed, the flask rinsed several times, and the washings added to the top of the bed. The entire elution was run at the full flow rate. This method gave results which could be reproduced accurately.

(b) **Qualitative Tests.**—A literature search revealed no qualitative test for titanium, zirconium and thorium which could be applied in the 1% citrate buffer. A qualitative test was developed with oxine (8-hydroxyquinoline) as
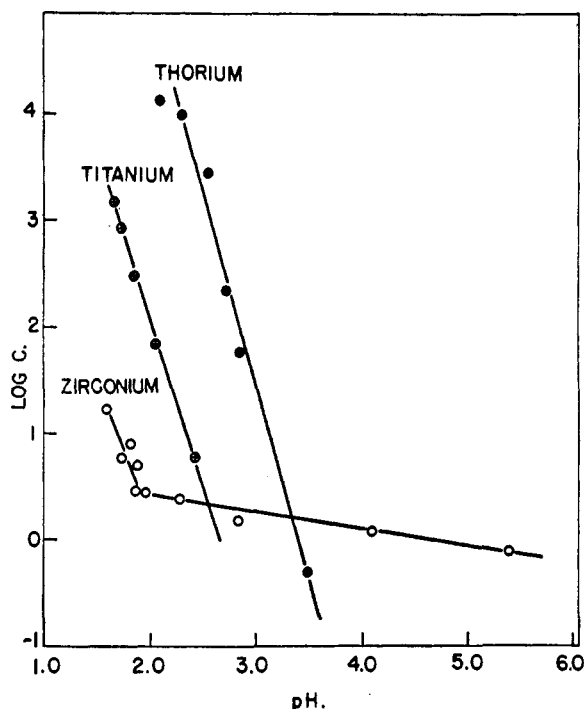
(14) E. R. Tompkins, J. X. Khym and W. E. Cohn, This Journal, 69, 2769 (1947).

Fig. 1.

follows. About 0.4 to 0.5 ml. of a 5% solution of oxine in 2 M acetic acid was added to a 25-ml. sample of 1% citrate solution containing titanium, zirconium or thorium, and the solutions were mixed by swirling. The solution was then made basic by the addition of about one ml. of concentrated ammonia. The light yellow color of the oxine turns to a deeper shade upon addition of the excess ammonia. A positive test gives a very fine, light-yellow precipitate which slowly settles on standing. Under these conditions a negative test will be a clear yellow solution. If too much oxine is used, the ammonia may cause the precipitation of fine needles of oxine, which in the case of a large excess of oxine may form a pulp-like mat completely obscuring any other precipitate. Incomplete mixing of the oxine and the 25-ml. sample may produce a flaky oxine precipitate in the areas of high oxine concentration when the ammonia is added. Table I gives the limiting values for detection of titanium, zirconium and thorium. This test has the added advantage that no non-volatile materials are added, thus eliminating interference with the quantitative analysis to be performed later.

Table I

Cation in 1% citrate	Ti	Zr	Th
Concentration giving instantaneous positive test	$3 \times 10^{-4} M$	$4 \times 10^{-5} M$	$3 \times 10^{-5} M$
Concentration giving unmistakable positive test in less than five minutes	$2 \times 10^{-4} M$	$4 \times 10^{-6} M$	$3 \times 10^{-6} M$

(c) **Quantitative Determinations.**—Titanium, as well as zirconium and thorium, was determined quantitatively by removing the citric acid in the following manner. One ml. of concentrated sulfuric acid was added for each 100 ml. of eluate. The solution was evaporated until it began to turn dark. Then concentrated nitric acid was added until the solution remained colorless when evaporated to the point where fumes of sulfur trioxide were evolved. In some cases it was necessary to add more sulfuric acid and repeat the treatment with nitric acid before a colorless product was obtained. The residue was cooled, diluted with water to about 100 ml., and excess ammonia was added. The hydroxide precipitate was filtered on ashless paper, ignited in a platinum crucible, and weighed as the oxide.

Radioactivity measurements were made with a well shielded bell-type thin-mica-window Geiger–Mueller tube and a Tracerlab Autoscaler. All determinations were cor-

TABLE II

TOTAL RECOVERY RESULTS, pH 1.75

Elution number	Zirconium			Titanium			Thorium		
	Mmole added	Mmole found	Recovery, %	Mmole added	Mmole found	Recovery, %	Mmole added	Mmole found	Recovery, %
1	0.4004	0.4004[a]	100.0	0.0000			0.0000		
2	.0000			.3460	0.349[b]	100.8	.0000		
3	.0000			.0000			.2802	0.281	100.3
4	.4004	.402	100.3	.3460	.348	100.6	.2802	.281	100.3
5	.4004	.402	100.3	.3460	.344	99.4	.2802	.278	99.2
6	.4004	.401	100.1	.3460	.352	101.7	.2802	.281	100.3

[a] Average of three results.   [b] Average of two results.

rected for background, counter efficiency, and sample decay. The number of counts was such that the probable error in the determinations was of the order of one per cent.

(d) **Separation of Eluate into Fractions.**—The siphon pipet used in most of the elutions delivered 26.56 ml. Qualitative tests were applied to frequent 26.56-ml. portions of eluate. In some cases, each 26.56-ml. sample was quantitatively analyzed. For most of the work, groups of up to ten 26.56-ml. portions were combined for analysis. The results of these individual and group analyses were used to establish the elution curves. In the case of the total recovery analyses, all the fractions containing any one metal were combined for the quantitative determination.

(e) **Elution of Individual Metals.**—In order to determine the behavior of titanium, zirconium and thorium in an ion-exchange column, the elements were eluted separately at various pH values. Because a bed depth of about 30 cm. gave a long elution with the attendant large volume of eluate, it was decided to investigate the feasibility of using a shorter bed. A 7-cm. bed with a cross section area of 7.07 cm.² was used in the following work. A 10.00-ml. volume of the standard solution was equilibrated with a small amount of resin and added to the top of the resin bed as described previously. The elution was carried out with 1% citric acid buffer at a flow rate of about 0.85 ml./cm.²/min. At pH 2.00, there was a considerable area where the titanium and zirconium elution curves overlapped. At pH 1.50, the titanium curve no longer overlapped the zirconium curve, but titanium appeared in the eluate in very small concentrations spread over a large volume. At a pH of 1.75, titanium and zirconium were completely separated and within a volume of three liters.

Thorium is very strongly held by the resin and does not appear in the eluate even after ten liters of eluant at pH 2.00 have been passed through the bed. For this reason, after the zirconium and titanium were completely eluted, the eluant was changed to 0.0520 M diammonium citrate which has a pH of 4.98. This solution immediately eluted the thorium from the resin bed.

The titanium elution curve at pH 1.50 was interesting because it showed that the titanium appeared in a much
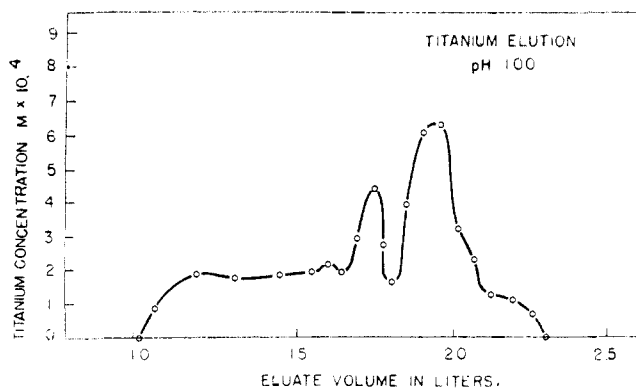

Fig. 2.

wider band than anticipated and in irregularly varying concentration. The elution curves given by gravimetric analysis of portions of the eluates, while not exactly reproducible, always had a characteristic two-step rise followed by a drop, then a point of maximum concentration followed by a two-step drop.
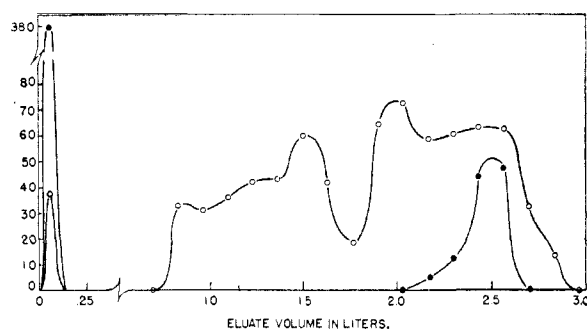

Fig. 3.—Elution, titanium-51, pH 1.00: O, gravimetric analysis, $M \times 10^4$; ●, radioactivity, counts × 100/sec. ml.
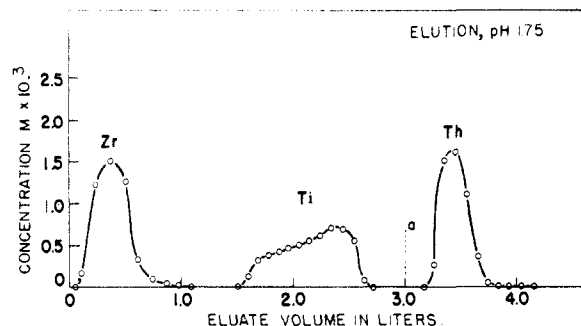

Fig. 4.—Eluant changed to 0.0520 M di-ammonium citrate.

Several titanium elutions were made at a pH of 1.0, the lower pH serving to accentuate the pattern. A typical curve is shown in Fig. 2. This behavior was obtained in elutions with different batches of resin and in various columns with different standard solutions.

(f) **Elution of Radioactive Titanium.**—A solution containing both radioactive titanium-51 and normal titanium was eluted through a 35-cm. bed with a cross section area of 1.04 cm.² in order to determine if the unusual behavior of titanium was an isotope effect. Five ml. of the standard radioactive titanium solution was added to the top of the column and allowed to drain into the bed. This was eluted with a 1% citric acid buffer at pH 1.00. At the start of the elution, radioactivity appeared in the eluate, followed by an inactive volume giving a negative test for titanium. Titanium again appeared in the eluate at about the point where it would normally be expected. Gravimetric analysis gave a curve somewhat similar to the other titanium elution curves. However, radio-analysis of the precipitates showed that the radioactivity was confined to about 20% of the titanium-containing eluate volume. Figure 3 shows the gravimetric and radioactivity curves for this elution.

(g) **Elution of Mixture.**—Ten-ml. portions each of the titanium, zirconium and thorium standard solutions were equilibrated with resin and added to the top of a 7-cm. resin bed with a 7.0-cm.² cross section. The elution was continued at a pH of 1.75. The three elements appeared in the eluate in the order zirconium, titanium, thorium, which agrees with the result expected from the C values. The thorium is eluted after titanium has ceased to appear in the eluate by changing the eluant to 0.0520 M di-

ammonium citrate. A typical elution curve is shown in Fig. 4.

At pH 1.75 the multiple peaks for titanium are not as well defined as at pH 1.00. In Fig. 4 not enough points were taken to develop fully the elution curve for titanium. For each of the metals, both singly and in mixtures, total recovery analyses of the entire volume which gave a positive qualitative test were made. The results of the analyses are listed in Table II.

V. Discussion

(1) Nature of the Complex as Deduced from Equilibrium Experiments.—The nature of the complex can be deduced from the equilibrium experiments by a process of trial and error. Various complexes, such as $ThCi^+$, $ThCi_2^{-2}$, $Th(HCi)_2^0$, were assumed to exist in the solution. The complex constant was evaluated in each case for all the equilibrium studies. The complex whose constant shows the least variation throughout the series of experiments is probably the predominant complex.

It is assumed that the activity coefficient of hydrogen-ion, f_H, is 0.86 and that the classical ionization constants of citric acid[15] are

$$K_1 = 1.00 \times 10^{-3}$$
$$K_2 = 3.55 \times 10^{-5}$$
$$K_3 = 5.01 \times 10^{-6}$$

These values apply for an ionic strength of 0.050 which is about the average value for the thorium equilibrium studies. The effect of variation in ionic strength was not included in the calculations because the experimental data did not warrant it. A small error in the determination of pH or concentration of metal in the equilibrium solution results in a large error in the calculated pK value.

As an example, the equilibrium data for thorium at pH 2.85 may be considered. Let us assume that the complex has the formula $ThCi_2^{-2}$, where Ci represents the tertiary citrate radical. The calculations are

$$(H^+) = 1.41 \times 10^{-3}$$
$$\frac{(H^+)}{f_{H^+}} = \frac{1.41 \times 10^{-3}}{0.86} = 1.64 \times 10^{-3} = [H^+]$$

where the parentheses denote activity. Let A, P, S, T and X denote respectively the molar concentrations of free citric acid, primary, secondary and tertiary citrate ions, and the complex ion $ThCi_2^{-2}$. Assume that $A = 0.0290$.

$$P = \frac{K_1A}{[H^+]} = \frac{1.00 \times 10^{-3} \times 2.9 \times 10^{-2}}{1.64 \times 10^{-3}} = 1.77 \times 10^{-2}$$

and

$$S = \frac{K_2P}{[H^+]} = \frac{3.55 \times 10^{-5} \times 1.77 \times 10^{-2}}{1.64 \times 10^{-3}} = 3.83 \times 10^{-4}$$

and

$$T = \frac{K_3S}{[H^+]} = \frac{5.01 \times 10^{-6} \times 3.83 \times 10^{-4}}{1.64 \times 10^{-3}} = 1.17 \times 10^{-6}$$

X was found to be 0.00290.

A 1% solution of citric acid is 0.0520 M. Then to account for all of the citric acid present

$$A + P + S + T + 2X = 0.0520$$

(15) W. Rieman, J. Neuss and B. Naiman, "Quantitative Analysis," Third Edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1951 pp. 467-469.

and

$$A + P + S + T = 0.0520 - 2X = 0.0462$$

Adding the calculated values, we find

$$A + P + S + T = 0.0290 + 0.0177 + 0.0004 + 0.0000 = 0.0471$$

The assumed value of A was greater than the correct value, and must be decreased by the factor 0.0462/0.0471. Since a change in the value of A is linearly related to changes in P, S and T, simple multiplication of all four quantities by the same factor will give the corrected result.

$$A = 0.0284 \qquad T = 0.0000$$
$$P = 0.0174 \qquad X = 0.0260$$
$$S = 0.0004$$

A total of 12.9 meq. of hydrogen resin was used for each of the equilibrium studies. Experimentally 0.195 mmole of thorium was found to be held by the resin. The equivalent fraction of thorium resin, N_{Th}, may be written

$$N_{Th} = \frac{4 \times 0.195}{12.9} = 0.0604$$

The equivalent fraction of hydrogen resin may be written

$$N_H = 1.000 - N_{Th} = 0.940$$

If K is the equilibrium constant of the reaction

$$ThCi_2^{-2} + 4HR \rightleftarrows ThR_4 + 4H^+ + 2Ci^{-3}$$

$$K = \frac{[Ci^{-3}]^2[H^+]^4 N_{Th}}{[ThCi_2^{-2}] N^4_H}$$
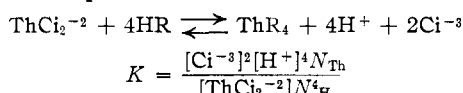
and $pK = 4 \log N_H + \log X - \log N_{Th} - 4 \log [H^+] - 2 \log T$ $pK = 21.59$ for the complex $ThCi_2^{-2}$.

The pK value for other assumed complexes was determined similarly. This series of calculations was repeated for all the equilibrium studies with titanium and zirconium as well as thorium.

Many of the assumed complexes gave a very large variation in pK, and were obviously not correct. Table III gives the most constant pK values obtained for titanium and thorium and the corresponding complexes. Included also in the case of titanium and thorium are the two next best assumed complexes and their pK values.

TABLE III
pK VALUES FOR ASSUMED COMPLEXES

The assumed complexes $TiCi^+$, $TiHCi^{+2}$, $Ti(HCi)^0_2$, $Ti(HCi)_3^{-2}$, $Ti(HCi)_4^{-4}$, TiH_2Ci^{+3}, $Ti(H_2Ci)_2^{+2}$, $Ti(H_2Ci)_3^+$, $Ti(H_2Ci)_4^0$ all gave pK values with greater variance than those listed below. The assumed complexes $ThCi_4^{-8}$, $ThHCi^{+2}$, $Th(HCi)_2^0$, $Th(HCi)_3^{-2}$, $Th(HCi)_4^{-4}$, ThH_2Ci^{+3}, $Th(H_2Ci)_2^{+2}$, $Th(H_2Ci)_3^+$, $Th(H_2Ci)_4^0$ all gave pK values with greater variance than those listed below.

| | Titanium | | | | Thorium | | |
pH	$TiCi_2^{-2}$	$TiCi_3^{-5}$	$TiCi_4^{-8}$	pH	$ThCi^+$	$ThCi_2^{-2}$	$ThCi_3^{-5}$
1.73	22.12	31.24	40.46	2.10	17.73	23.08	28.43
1.85	22.41	32.18	40.95	2.31	12.53	19.90	27.27
2.05	22.83	31.15	39.37	2.55	13.37	20.07	26.77
2.42	23.52	30.73	37.94	2.73	14.79	21.02	27.25
Range:	1.40	1.45	3.01	2.85	15.65	21.59	27.53
				3.47	14.86	19.35	23.84
				Range:	5.20	3.73	4.59

The calculated pK values in the case of zirconium were not such that any one complex could be chosen as being better than another. For that pH range where the plot of the zirconium C values (Fig. 1)

parallels the titanium and thorium plots, good agreement was obtained for several assumed complexes. This may be the result of the existence of more than one zirconium complex in the equilibrium solutions whereas the calculations were made for a single complex. The calculated pK values for the higher pH range show a larger variation. All the calculations for zirconium which gave reasonable agreement are listed in Table IV.

TABLE IV

pK VALUES OF ASSUMED COMPLEXES

pH	Zr-Cl₂⁻²	Zr-OCl⁻	Zr-OCl₂⁻⁴	Zr-OCl₃⁻⁷	ZrO-HCl⁰	ZrO-(HCl)₂⁻²	ZrO-(HCl)₃⁻⁴
	Zr-Cl$_2^{-2}$	Zr-OCl$^-$	Zr-OCl$_2^{-4}$	Zr-OCl$_3^{-7}$	ZrO-HCl^0	ZrO-(HCl)$_2^{-2}$	ZrO-(HCl)$_3^{-4}$
Region where Zr C values parallel Ti and Th C values							
1.59	23.96	12.03	21.27	30.72	8.30	14.01	19.71
1.73	24.24	12.30	21.25	30.19	8.81	14.25	19.70
1.83	23.89	12.05	20.70	29.35	8.66	13.91	19.16
1.88	24.11	12.11	20.71	29.21	8.86	14.02	19.18
1.86	24.31	12.48	21.04	29.60	9.11	14.31	19.51
1.95	24.16	12.42	20.72	29.02	9.14	14.17	19.19
Range:	0.42	0.45	0.57	1.70	0.84	0.40	0.55
Region of non-parallel C values							
2.28	23.53	12.08	19.43	26.78	9.13	13.54	17.94
2.84	23.02	11.98	17.81	23.64	9.59	13.03	16.47
4.08	22.73	11.90	15.02	18.15	10.75	12.73	14.71
5.39	25.21	13.21	14.88	16.55	13.38	15.22	17.05
Range:	2.48	1.31	4.45	10.23	4.25	2.49	3.23

From these data it seems that within the pH range studied, the predominant complexes are $TiCl_2^{-2}$ and $ThCl_2^{-2}$. The data for zirconium are less readily interpreted, but $ZrO(HCl)_2^{-2}$ seems to predominate at the lower pH values and $ZrOCl^-$ at the higher.

(2) **Elution Experiments.**—The fact that both pH and temperature have a significant effect on the ion-exchange equilibrium is illustrated by the elution experiments. Without the temperature control jacket on the ion-exchange column, erratic shifts in the peaks of the elution curves were observed. The large pH effect is shown by the lack of separation of titanium and zirconium in a short resin bed at pH 2.0, while at pH 1.5 the titanium is held by the resin so strongly as to interfere with an efficient separation.

The elution with radioactive titanium as shown in Fig. 3 may be interpreted as follows. The titanium which appeared early in the elution is probably due to a colloidal form of titanium which passed through the resin bed without being held by the resin. The fact that the radioactivity was concentrated in the later part of the elution indicates that the peculiar shape of the elution curve is probably due to the partial separation of the isotopes of titanium. This is in agreement with the observation of Brewer[16] who reported a preferential desorption of the light isotope of potassium when a column of potassium-containing zeolitic greensand was eluted with a sodium chloride solution. Taylor and Urey[17] have also shown that in the exchange of potassium and ammonium in zeolites the heavier isotope is taken up more readily and is more difficult to replace.

(16) A. K. Brewer, THIS JOURNAL, **61**, 1597 (1939).

(17) T. I. Taylor and H. C. Urey, J. Chem. Phys., **6**, 429 (1938).

Recoil Reactions with High Intensity Slow Neutron Sources. II. The Retention of Radiobromine by Crystalline KBrO₃[1]

BY J. W. COBBLE AND G. E. BOYD

Retention of radiobromine as bromate, during bombardment of crystalline KBrO₃ in the Oak Ridge graphite pile, increased from an apparent zero-time value of 9 ± 1% to a limit of 32 ± 1% after 16 hr. irradiation. With the temperature at $-195°$ during irradiation, the retention was 13 ± 1% beyond five minutes. Heating the irradiated KBrO₃ above 80° or exposing it to an energetic gamma ray source (Co^{60}) returned the radiobromine to bromate at a rate dependent on the temperature or source intensity, respectively. No simple rate law could describe the thermal back-reaction; the radiation-induced reaction obeyed a first order velocity equation and showed an activation energy of $ca.$ 8 kcal./mole. Theoretical estimates were made of the retention from "cage" effects and from the chance cancellation of γ-ray recoils. The constant retention observed in long-time neutron bombardments was attributed to a steady state between the rate of production of separable Br^{82} and the rate of its recombination to bromate by pile γ-rays and fast neutrons.

Introduction

In our earlier study[2] of the enrichment of 35.9 h Br^{82} activity by recoil following neutron capture in KBrO₃ some evidence was obtained of the presence of thermal and of radiation-induced effects acting to return the radiobromine atoms to bromate. This paper is concerned with a detailed study of these novel and interesting solid state reactions.

Experimental Procedures

The quantity measured was the radiochemical separation, or recovery factor, ϕ_t, defined as the fraction of the total induced bromine activity chemically separable from neutron irradiated KBrO₃. The recovery factor so defined is a convenient index of the radiobromine behavior since its value is independent of radioactive decay. It is also perhaps more sensitive than other possible functions to changes in the distribution of activity between bromine and bromate.

The radiochemical separation procedure, radioactivity detection equipment, etc., have been described.[2] Briefly, when neutron irradiated potassium bromate is dissolved in water and bromine is added a large fraction of the radiobromine can be extracted into carbon tetrachloride. Since only bromide, bromine, hypobromite and bromate may co-exist in aqueous solutions, and since the first three of these exchange with one another rapidly and completely, the organic extraction separates all the radiobromine in stable valence forms lower than bromate. A precision of 0.5% was obtained in the estimation of the recovery factor upon the extraction of successive aliquots from a given sample of KBrO₃. However, values of ϕ_t were reproducible to only 2% in successive bombardments of the same duration. The majority of the recovery determinations utilized

(1) Presented before the Division of Physical and Inorganic Chemistry, 119th Meeting, American Chemical Society, April 16-19, 1951, Cleveland, Ohio.

(2) G. E. Boyd, J. W. Cobble and Sol Wexler, THIS JOURNAL, **74**, 237 (1952).