[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Structural Changes Taking Place During the Aging of Precipitates. IX. The Mechanism of the Adsorption of Lead on Aged Barium Sulfate

BY I. M. KOLTHOFF AND W. M. MACNEVIN

Extensive investigations on the kinetics of the adsorption of thorium B and radioactive lead on aged barium sulfate and lead salts have been carried out by Imre.[1]

He postulated a mechanism of the adsorption which is quite involved and not entirely clear. In agreement with Imre's experimental work, it was found by the present authors that the adsorption of thorium B and active lead on well aged products of barium sulfate increases with the time of shaking.

Without subjecting Imre's interpretation to a detailed discussion, it may be stated that his conclusions are based upon incorrect assumptions. Especially in his last paper, Imre[1d] emphasizes that during the first stage of the "adsorption" of lead (nitrate) on lead salts, the surface of the latter is being covered with a layer of adsorbed lead nitrate (Anlagerungsadsorption). Actually it has been shown in this Laboratory[2] that lead nitrate is not measurably adsorbed by aged lead sulfate, and that the measured "adsorption" of thorium B or active lead is a result of an exchange between lead ions in the surface of the crystals and in the solution.[3] In the case of barium sulfate and lead nitrate solution again Imre assumes that he is dealing with a true adsorption of lead nitrate on the solid phase. In a subsequent paper it will be shown that aged barium sulfate does not adsorb lead nitrate measurably from an aqueous solution, but that we are dealing with an exchange between barium ions in the surface of the adsorbent and lead ions

$$\underset{\text{Surface}}{BaSO_4} + \underset{\text{solution}}{Pb^{++}} \longrightarrow \underset{\text{Surface}}{PbSO_4} + \underset{\text{solution}}{Ba^{++}}$$

virtually no nitrate ions being adsorbed. This exchange is closely comparable to the exchange between lead ions in a solution and those in the surface of a lead salt, the difference being that in the latter case the distribution coefficient of lead between solution and surface is equal to one, and in the former case to K

$$\frac{\text{Pb surface}}{\text{Pb solution}} = K \frac{\text{Ba surface}}{\text{Ba solution}} \qquad (1)$$

The value of this distribution coefficient K has been determined, and the results will be reported in a following paper. After exchange equilibrium has been reached, more lead is removed from solution upon continued shaking with barium sulfate. This is attributed by Imre to other phases of the "adsorption" and he assumes that a final state of equilibrium is reached after a certain period of shaking. This was not confirmed by our work since no final state of equilibrium was reached. It will be shown in this paper that the continuous removal of thorium B or active lead from the solution is to be attributed to a slow but continuous recrystallization of the aged barium sulfate, the lead sulfate being incorporated as mixed crystals in the recrystallizate.

Experimental

Preparation of Fine and Coarse Products of Barium Sulfate

A. "Fine" Product.—One thousand grams of Merck "Analytical Reagent" barium chloride dihydrate dissolved in three liters of water was poured quickly with vigorous mechanical stirring into three liters of a sodium sulfate solution containing about 3% in excess of the equivalent amount (600 g. of anhydrous salt, twice recrystallized as decahydrate and ignited). The suspension was diluted to approximately 10 liters and agitated violently for twelve hours by shaking in a 20-liter bottle. After allowing the suspension to settle overnight, the mother liquor was decanted. Ten liters of distilled water was now added and the agitation continued for twelve hours more. The mother liquor was again decanted after allowing the suspension to settle and the washing process repeated daily for two months. After one month no chloride was detectable in the decanted washings. The precipitate was air-dried by filtering the suspension on a sintered glass Gooch funnel, washed with water and finally several times with alcohol. Air was then drawn through the funnel for a period of two days and the precipitate stored over sulfuric acid.

The use of air-dried barium sulfate involves two distinct advantages. In the first place, a definite amount of the solid can be weighed out instead of using a measured volume of the suspension. In the second place, the air-dried barium sulfate when kept in a dry atmosphere does not age on standing, whereas in suspension the precipitate is subject to a slow, continuous aging process.[4]

---

(1) L. Imre (a) *Z. physik. Chem.*, **A153**, 262 (1931); (b) *Z. Elektrochem.*, **38**, 539 (1932); (c) *Z. physik. Chem.*, **A164**, 327, 343, 364 (1933); (d) **171**, 239 (1934).

(2) I. M. Kolthoff and Ch. Rosenblum, THIS JOURNAL, **55**, 2656 (1933).

(3) F. Paneth and W. Vorwerk, *Z. physik. Chem.*, **101**, 445 (1922).

(4) *Cf.* I. M. Kolthoff and Ch. Rosenblum, THIS JOURNAL, **57**, 607 (1935).

In the adsorption experiments, a weighed amount of the barium sulfate was added to a solution containing the various constituents. In this way, more reproducible results were obtained than when the constituents of the solution were added individually to the adsorbent. The samples of barium sulfate were weighed and exposed to the air. No changes in weight were noticed at varying humidities of the air. Exposure to laboratory air for two weeks did not affect the adsorption.

B. "Coarse" Product.—A coarsely crystalline product was prepared according to the method of Hahn and Otto:[5] 48.8 g. of barium chloride dihydrate was dissolved in one liter of distilled water. An equivalent amount of anhydrous sodium sulfate was also dissolved in one liter of water and both solutions were placed in dropping funnels suspended above a 4-liter beaker. One liter of 2 *N* hydrochloric acid was now placed in the beaker, heated to boiling, and vigorous mechanical stirring was begun. To maintain the barium ions in excess during the precipitation, about 10 cc. of the barium chloride solution was run in dropwise before the addition of sulfate was begun at the same rate. One and one-half hours were required for the addition of the reagents.

After completion of the precipitation, the suspension was allowed to settle (five minutes required) and the mother liquor decanted. In order to obtain a sufficient quantity of barium sulfate, the above operation was repeated seven times. The precipitates were combined in a 20-liter bottle, the volume made up to about 10 liters and the whole shaken for twelve hours. After settling and decanting, washing was continued daily as with the fine precipitate. No chloride was detectable in the washings after fourteen days. Washing was continued for one month and the precipitate filtered, air-dried and stored over concentrated sulfuric acid.

Adsorption of Thorium B on Glass and Radio-Colloid Effect.—In the following work, the solutions as a rule did not contain inactive lead. Therefore, the possibility of losing some thorium B by adsorption on the walls of the containers or on dust particles (radio colloid effect) was much greater than in the case of lead salts as adsorbents. For this reason experiments were made in ordinary soft glass tubing in order to study the adsorption of thorium B under various conditions. Upon shaking for six hours at 25°, no adsorption was found at a nitric acid concentration equal to or greater than 10^{-2} *N;* 7.5% being adsorbed at an acid concentration of 10^{-3} *N*, 21% at 10^{-4} *N*, 47% at 10^{-5} *N*. Small amounts of inactive lead and barium decrease the thorium B adsorption. From a solution 10^{-4} *N* in nitric acid and 10^{-7} *M* in lead the adsorption was 7.5%, and 0% when the lead concentration was 10^{-6} *M*. Similar experiments were made at 95°. Keeping the nitric acid concentration equal to 10^{-3} *N*, 16.7% thorium B was adsorbed after six hours of shaking, no thorium B being adsorbed when the lead or barium concentrations were equal to or greater than 10^{-6} molar.

The experiments at room temperature described in the following were carried out in paraffin lined glass containers.

In the experiments with barium sulfate some thorium B might be lost by a radio-colloid effect (adsorption on dust, etc.). From a great number of experiments described in the thesis of the junior author, it was concluded that this effect was eliminated at nitric acid concentrations of 10^{-3} *N* or greater.

General Technique of Adsorption Measurements.—Weighed amounts of the adsorbent were added to the solution containing thorium B from which the removal of the radioactive lead was studied. The mixtures were shaken in a high speed shaker (400 oscillations per minute), centrifuged after a given time and samples of the supernatant liquid taken for the radioactive measurements. The technique of the radioactive measurements was the same as recorded in previous papers from this Laboratory.[6]

Effect of Period of Shaking.—The results of experiments reported in Table I and plotted in Fig. 1 show that equilibrium with regard to disappearance of thorium B from solution was not reached with either the fine product (A) or the coarse one (B) even after long periods of shaking. This behavior was generally encountered with all precipitates used.

TABLE I

EFFECT OF TIME OF SHAKING UPON AMOUNT OF THORIUM B REMOVED

Fine Product. 0.2 g. of product A with 49.5 cc. solution containing Th B, barium nitrate (2×10^{-4} *M*), nitric acid (2×10^{-3} *M*) (25°) (Curve 1a in Fig. 1).

Coarse Product. 1 g. of product B with 48.5 cc. of solution containing Th B, barium nitrate (4.1×10^{-5} *M*) and nitric acid (2×10^{-3} *M*) (25°) (Curve 1b in Fig. 1).

Time of shaking, hours	Thorium B removed, %	Time of shaking, hours	Thorium B removed, %
0.08	17.3	0.5	7.9
.33	21.7	1	11.6
.50	23.1	2	16.7
1.0	26.1	6	25.4
8	33.9	9	32.2
24	44.2	18	39.8
48	49.9		

Effect of Temperature on the Speed of Removal of Thorium B

The effect of temperature upon the speed of removal of thorium B was investigated with the fine and coarse products of barium sulfate. 0.2 g. of the fine product (A) was shaken for the periods indicated, at temperatures of 25 and 45°, respectively, with 49.5 cc. of a solution, 2×10^{-4} molar in barium nitrate and 2×10^{-3} *N* in nitric acid. In the experiments with the coarse product (B), 1 g. of the barium sulfate was shaken with 49.5 cc. of a solution, 4.1×10^{-5} molar in barium nitrate and 2×10^{-3} *N* in nitric acid. The results are reported in Table II and plotted in Fig. 2. It is seen that the slope of the more linear parts of the curves are, both for the fine and the coarse product, much steeper at 45 than at 25°. During the earlier stages of shaking, the temperature effect is

---

[5] F. L. Hahn and R. Otto, *Z. anorg. allgem. Chem.*, **126**, 257 (1923).

[6] Kolthoff and Rosenblum, THIS JOURNAL, **55**, 2656 (1933); **56**, 1264 (1934).

TABLE II

EFFECT OF TEMPERATURE UPON SPEED OF REMOVAL OF Th B

Time of shaking, hours	% Thorium B removed at 25°	45°
	Fine Product[a]	
0.08	17.3	24.4
.33	21.7	30.2
.50	23.1	31.8
1.0	26.1	34.4
2.0	..	39.9
8.0	33.9	57.8
	Coarse Product[a]	
0.30	..	10.3
.50	9.5	..
1.0	13.5	16.9
3.0	..	28.2
4.0	21.0	..

[a] Both products were recovered from other experiments. Therefore, they are not exactly identical with the products A and B used throughout this work.

less pronounced, since under these conditions we are dealing mainly with the exchange adsorption. Upon longer times of shaking, part of the thorium B is taken up in the form of mixed crystals by the recrystallized portion of the barium sulfate, the speed of recrystallization increasing with increasing temperature.

Effect of the Barium-Ion Concentration upon the Amount of Thorium B Removed.—If the adsorption of thorium B is to be attributed to an exchange governed quantitatively by equation (1), the amount of thorium B adsorbed should decrease with increasing barium concentration in the solution. In the following experiments this was shown to be the case: 1.02 g. of the fine barium sulfate (A) was shaken for one hour with 49.73 cc. of a solution 0.002 N in nitric acid and containing a concentration of barium nitrate indicated in Table III.

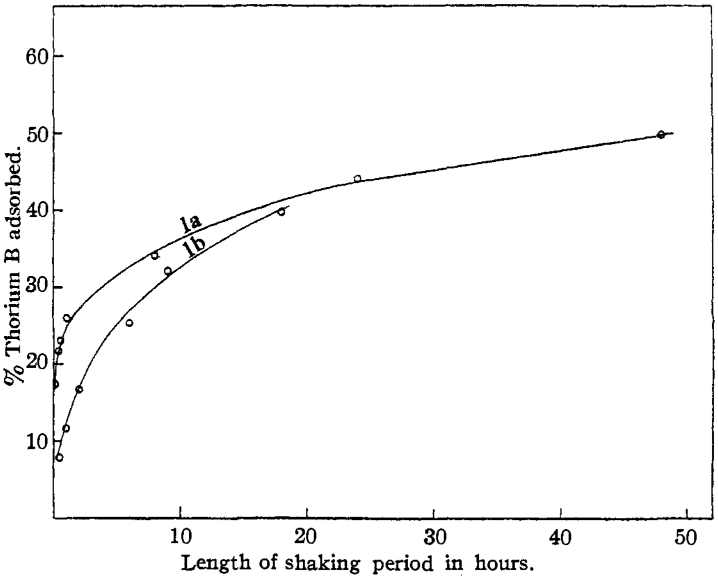

Fig. 1.

TABLE III

EFFECT OF CONCENTRATION OF BARIUM NITRATE UPON ADSORPTION OF Th B

Concn. $Ba(NO_3)_2$, molar	10^{-5}	10^{-4}	10^{-3}	10^{-2}
Th B adsorbed in %	99.0	96.2	28.9	10.8

Effect of Inactive Lead Ion in Micro-concentrations upon the Amount of Thorium B Removed.—In the early experiments thorium B was the only source of lead present in the experiments, its concentration being of the order of 10^{-12} molar. According to expression (1) as long as the amount of barium ions in the surface remains practically unchanged after the exchange has taken place the distribution of the lead between solution and barium sulfate should be independent of the amount of lead. The results in Table IV show that under the experimental conditions given, identical results were obtained at lead concentrations between 10^{-12} and 10^{-7} molar. At lead concentrations of 10^{-5} N and greater, less lead is removed since (Ba surface) decreases as a result of the exchange.

TABLE IV

EFFECT OF MICRO QUANTITIES OF LEAD

1.000 g. $BaSO_4$ (B); c $Ba(NO_3)_2 = 4 \times 10^{-5}$ m.; c $HNO_3 = 2 \times 10^{-3}$ m. Volume = 49.7 cc.

Period of shaking, hours	Th B removed in % at lead concns., M 10^{-12}	2×10^{-7}	2×10^{-5}	2×10^{-3}
0.5	9.0	8.0	..	...
1	11.5	11.5	5.0	0
2	16.9	16.7	..	...
4	21.0	23.0	10.4	1.4
6	25.4	24.5	..	...

Effect of Ethanol upon the Speed of Removal of Thorium B.—If the slow removal of Th B upon longer periods of shaking is to be attributed to a continuous recrystallization of barium sulfate, it is to be expected that the slope of the more linear part of the time–adsorption curve will be much less in a medium in which the solubility is less than in water. The solubility of barium sulfate in a mixture of water and ethanol is much less than in aqueous medium, and consequently, the speed of recrystallization should decrease with increasing ethanol concentration of the medium.[7]

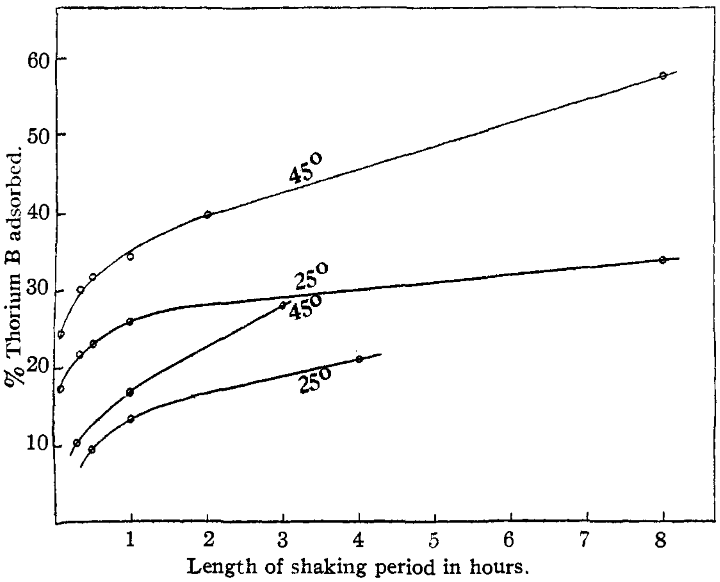

Fig. 2.—Effect of temperature: upper curves, fine product; lower curves, coarse product.

The curves in Fig. 3 show that the slope of the curve is much less in 50% ethanol than in aqueous medium. In the experiments in aqueous medium 0.2 g. of barium sulfate "A" was shaken with 49.5 cc. of a solution 2×10^{-4} molar in barium nitrate and 0.002 N in nitric acid. The experiments in 50% ethanol were carried out in a similar way, except that the solution contained 50% ethanol and was 1.4×10^{-4} molar in barium nitrate. The results are reported in Table V.

From the data listed in Table V, it may be inferred that exchange equilibrium between barium and thorium B ions in a medium containing 50% ethanol is established after a shaking period of about one-half to one hour. Therefore, in the experiments to show that the distribution of thorium B between the surface of barium sulfate and the solution is determined by the expression

$$\frac{\text{Th B surface}}{\text{Th B solution}} = R = K\frac{\text{Ba surface}}{\text{Ba solution}} \qquad (2)$$

a shaking time of one hour was chosen. By determining R with varying amounts of barium sulfate (Ba surface) or barium nitrate in the solution it was possible to prove experimentally that the above equation holds. In the following experiments barium sulfate (A) was shaken for one hour in a medium of 50% ethanol containing the constituents indicated below. After centrifuging, the amount of thorium B left in the solution was determined. The experiments reported in Table VI were carried out with varying amounts of barium sulfate. It was found that in a medium of 50% ethanol, a marked adsorption of barium nitrate occurred whereas in aqueous medium under the same conditions, such an adsorption is hardly noticeable. In a subsequent paper we will deal with this interesting phenomenon in greater detail. Suffice it to say that in all experiments carried out in 50% ethanol, the final concentration of barium nitrate was determined experimentally. From equation (2) it follows that R (Ba solution) is proportional to the amount of barium sulfate taken.

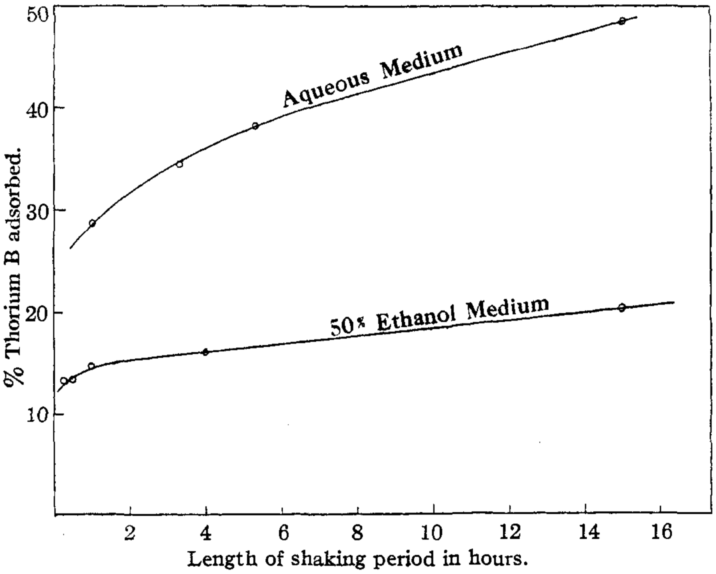

Fig. 3.

Similar experiments were carried out in which the amount of adsorbent was kept constant but the concentration of barium nitrate changed. Again the final concentration of barium was determined analytically. From the results in Table VII it is seen that with constant (Ba sur-

---

[7] *Cf.* Kolthoff and Rosenblum, THIS JOURNAL, **57**, 597 (1935).

face) the expression R (Ba solution) is found to be constant.

TABLE V

EFFECT OF ALCOHOL UPON THE SLOPE OF THE TIME-ADSORPTION CURVE

Aqueous Medium		In 50% Ethanol	
Time of shaking, hours	Th B removed, %	Time of shaking, hours	Th B removed, %
1	28.8	0.25	13.3
4	34.4	.50	13.5
6	38.2	1.0	14.9
15	48.5	4	16.2
		15	20.3

TABLE VI

CHANGE OF R WITH VARYING AMOUNTS OF BARIUM SULFATE (A) IN 50% ETHANOL

Barium sulfate taken, g.	0.2	0.4	0.6
Final concn. $Ba(NO_3)_2$, $M \times 10^4$	1.70	1.59	1.42
Th B adsorbed, %	12.3	24.4	37.1
R	0.14	0.32	0.59
R(Ba solution) $\times 10^5$	2.4	5.1	8.3

TABLE VII

CHANGE OF R WITH VARYING (Ba SOLUTION) IN 50% ETHANOL

Barium sulfate taken, g.	0.6	0.6	0.6
Orig. $Ba(NO_3)_2$ concn., $M \times 10^4$	1	2	4
Final $Ba(NO_3)_2$ concn., $M \times 10^4$	0.72	1.42	3.20
Th B adsorbed, %	59.4	37.1	20.4
R(Ba solution) $\times 10^5$	8.0	8.3	8.1

Finally experiments were made with varying (Ba surface) and (Ba solution), but keeping the ratio of the two constant. Under these conditions the amount of thorium B adsorbed should be constant (Table VIII).

TABLE VIII

ADSORPTION OF Th B WITH VARYING (Ba SURFACE) AND (Ba SOLUTION) IN 50% ETHANOL

Barium nitrate, g.	0.6	1.2	2.4
Barium nitrate, $M \times 10^4$	4	8	16
Th B adsorbed, %	17.7	17.3	17.8

Reversibility of Adsorption of Thorium B.—The results described so far indicate that upon shaking of barium sulfate with an aqueous thorium B solution containing some barium nitrate, a rapid exchange (equation 1) occurs, whereas simultaneously some thorium B is removed as a result of recrystallization of barium sulfate. The latter process is going on continuously, whereas it is strongly inhibited by addition of a sufficient amount of ethanol. In connection with the determination of the distribution coefficient K (equation 1) it was desirable to have conclusive proof of the above mechanism. That part of the thorium B which is removed by exchange with barium ions on the external surface of barium sulfate should be adsorbed in a reversible way. It should be possible to remove virtually all of the Th B from the surface by adding an adequate amount of barium salt to the solution (see equations 1 and 2). On the other hand, that part of the thorium B which is incorporated in the lattice as a result of recrystallization cannot be removed by extraction with a large excess of barium if the speed of recrystallization is small. Thus, by application of this principle, it is possible to find how much of the total amount of the thorium B removed has participated in the exchange and how much has been incorporated in the lattice.

Reversibility in Aqueous Medium.—0.200-g. samples of the fine barium sulfate were shaken for the periods indicated with 49.5 cc. of an aqueous solution 2×10^{-4} molar in barium nitrate and 2×10^{-3} normal in nitric acid. The "adsorption" of thorium B was then determined. Duplicate experiments were done and an excess of barium nitrate was added after the same periods of shaking. This excess was sufficiently large that had it been present from the beginning, no adsorption would have occurred. The suspension containing the excess barium nitrate was now shaken for one minute and the Th B "adsorption" determined. Similar experiments were made but in which the shaking with excess of barium nitrate was carried on for 2, 5, 8, 10, 20, 30 minutes, 1 hour and 5 hours, respectively. In each experiment the reversibility reached a maximum after five minutes of shaking independent of the length of the shaking period previous to adding excess barium nitrate.

TABLE IX

REVERSIBILITY OF Th B REMOVAL FROM AQUEOUS MEDIUM

Period of shaking in minutes before adding excess of $Ba(NO_3)_2$	5	20	30	60	480
Total Th B removed, %	17.3	21.7	23.1	26.1	33.9
Th B removed irreversibly, %	0.0	3.0	6.1	10.3	17.5
Th B removed (exchange), %	17.3	18.7	17.0	15.9	16.4
Th B remaining in solution, %	82.7	78.3	76.9	73.9	66.1
R	0.21	0.25	0.22	0.215	0.25

The row "Th B removed (exchange)" in Table IX gives the percentage of thorium B which had taken part in the kinetic exchange with barium ions in the surface of barium sulfate. This value is not constant after varying initial periods of shaking, since part of the thorium B is removed simultaneously by recrystallization. However, the value $R = \frac{\text{Th B removed (exchange)}}{\text{Th B remaining in solution}}$ should yield a constant value (see equations 1 and 2).

The data given in the last row show this within the experimental error to be the case. From the figures in Table IX it may be concluded that exchange adsorption in aqueous medium is virtually complete after five minutes of shaking.

Similar experiments were carried out with a coarse product obtained by a drastic aging process (see Table XI; "Th B removed by B "175°"). Under the conditions described for the experiments reported in Table XI, 8.6, 9.2 and 10.7% Th B was removed after one-half, one and four hours of shaking, respectively. After addition of the excess of barium nitrate, maximum reversibility was reached after five minutes of shaking, 0.2, 0.5 and 1.9% of the thorium B being found irreversibly adsorbed after the original periods of shaking of one-half, one and four hours, respectively.

Reversibility in a Medium Containing 50% Ethanol.—The experiments were carried out in a similar way as described above. After the addition of the excess of barium nitrate, it was necessary to shake for twenty minutes in order to obtain maximum reversibility.

TABLE X

REVERSIBILITY OF Th B REMOVAL FROM 50% ETHANOL

Period of shaking in minutes before addition of excess of $Ba(NO_3)_2$	30	60	120
Total Th B removed, %	30.4	33.5	35.3
Th B removed irreversibly, %	0.2	0.0	0.3
Th B removed (exchange), %	30.4	33.5	35.0

Evidently the recrystallization of barium sulfate in a medium of 50% ethanol is insignificant even after two hours of shaking. In addition the figures show that attainment of exchange equilibrium in 50% ethanol is much slower than in aqueous medium. This is substantiated by the fact that in the former medium with an excess of barium a shaking time of twenty minutes was required in order to get maximum reversibility as compared with five minutes in aqueous medium.

Effect of Perfection of Barium Sulfate upon the Slope of the Time-Adsorption Curve.—The amount of thorium B removed by recrystallization of the barium sulfate should decrease with increasing perfection of the adsorbent. In order to prove this point, samples of the fine barium sulfate (A) were subjected to a drastic aging process. A portion was heated in 2 *N* hydrochloric acid in a sealed tube at 175° for four days. It was then washed until chloride free. One-gram samples were shaken in 4×10^{-5} *M* barium nitrate and 0.002 *N* nitric acid for one-half, four and eighteen hours. The amounts of thorium B removed in per cent. were 10.6, 13.1 and 15.1, respectively. 0.2-g. samples of the original product (A) were shaken in 2×10^{-4} *M* barium nitrate and 0.002 *N* nitric acid for one-half, four and fourteen hours. The amounts of thorium B removed were 26.8, 34.4 and 49.0%, respectively. Samples of the coarse product B were also subjected to a drastic aging process. One portion was treated at 175° exactly in the same way as described for product A. Another portion was digested in 2 *N* hydrochloric acid at 95° for four days. One-gram samples of the three products were shaken in 4×10^{-5} *M* barium nitrate and 0.002 *M* nitric acid for the periods of time indicated in Table XI.

TABLE XI

EFFECT OF DEGREE OF PERFECTION OF BARIUM SULFATE UPON SPEED OF RECRYSTALLIZATION

Period of shaking, hours	0.5	1	4
Th B removed by product "B," %	11.4	14.5	22.8
Th B removed by B, "95°"	10.3	11.4	14.0
Th B removed by B, "175°"	8.6	9.2	10.7

Evidently the speed of recrystallization decreases markedly with increasing perfection of the barium sulfate crystals, although the size of the particles had hardly changed.

Summary

1. It has been shown that upon shaking of barium sulfate with an aqueous solution containing thorium B, active lead is removed by two reactions; (a) by an exchange between lead and barium ions in the surface of barium sulfate, this process taking place very rapidly; (b) by an incorporation of the exchanged lead in the lattice of the barium sulfate as a result of recrystallization. The speed of this recrystallization depends upon the degree of perfection of the barium sulfate, the temperature and the composition of the solution.

2. The speed of recrystallization is inhibited very strongly in a medium of 50% ethanol.

3. The thorium B adsorbed as a result of kinetic exchange can be desorbed completely upon addition of a large excess of barium salt.

MINNEAPOLIS, MINN. RECEIVED DECEMBER 6, 1935