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

Structural Changes Taking Place During the Aging of Freshly Formed Precipitates. VII. The Kinetics of the Distribution of Thorium B through Fresh Lead Sulfate

BY I. M. KOLTHOFF AND CHARLES ROSENBLUM

The speed with which thorium B is removed from solutions when fresh lead sulfate preparations are shaken with radioactive lead nitrate solutions has been used as an indication of the progress of the aging and perfection of these precipitates.[1] From the expression $\frac{\text{ThB}_{\text{removed}}}{\text{ThB}_{\text{solution}}} = \frac{\text{Pb}_{\text{exchanged}}}{\text{Pb}_{\text{solution}}}$ the amount of lead in the solid which had taken part in the kinetic exchange ($\text{Pb}_{\text{exchanged}}$) was calculated. When $\text{Pb}_{\text{exchanged}}$ was found to be equal to the total amount of lead in the precipitate (=683 mg. per 1 g. lead sulfate), it was concluded that all of the lead ions in the precipitate had taken part in the kinetic exchange. In other words, the precipitate was considered to have experienced a complete recrystallization and the thorium B was considered to be distributed homogeneously through the precipitate. A closer examination shows that this conclusion is not entirely justified. Previous investigations[1] (I, III, IV) show rather conclusively that the aging, and also the accompanying distribution of the active lead throughout the precipitate, could be attributed to a recrystallization of the latter. Elementary considerations, however, lead one to expect that, at least during the early stages of this recrystallization process, an enrichment of the active lead in the crystals must result.

Let us consider a precipitate which contains 960 mg. of inactive lead suspended in a solution containing 40 mg. of active lead, a relation comparable to our standard conditions. When distribution equilibrium is attained, 96% of the radioactive lead will be found in the precipitate and 4% is left in the solution. We shall assume arbitrarily that the recrystallization of the lead sulfate occurs in successive portions of 40 mg. of lead each, and that the recrystallized portions are not subjected to further recrystallizations. A simple calculation then indicates that the first 40 mg. of recrystallized lead (as sulfate) contains 20 mg. of the radioactive lead; the second fraction 10 mg.; the third, 5 mg.; the fourth, 2.5 mg.; the fifth, 1.25 mg. In other words, after 200 mg. of the lead or about 20% of the precipitate has recrystallized, 97% of the total amount of lead will be found in the recrystallizate, or slightly more active lead is found in 20% of the recrystallizate than corresponds to homogeneous distribution of the active lead throughout the precipitate. If in the above example, we had made the assumption that the recrystallization involved successive portions of 4 mg., a 96% removal of the thorium B would have been found after recrystallization of about 12% of the precipitate. Finally, if the amount of lead taking part in each successive recrystallization were equal to the amount of lead in the external surface of the precipitate, a removal of thorium B corresponding to a complete distribution would be found after recrystallization of a relatively small fraction of the entire precipitate. With the assumption that the portion of lead sulfate once recrystallized is no longer subject to further recrystallizations and the amount of lead taking part in each successive recrystallization is equal to the amount of lead in the external surface, the following expression was derived giving the relation between the amount of thorium B removed on the one hand and the amount of lead in the surface and of lead in solution on the other hand.

$$\frac{\text{ThB removed}}{\text{ThB left}} = R = \frac{a}{b}\sum_{n=1}^{n}\left(\frac{a+b}{b}\right)^{n-1} = \left(\frac{a+b}{b}\right)^{n} - 1$$

In this expression a is the quantity of lead in the surface upon which each successive layer deposits during the recrystallization and is equal to the specific surface of the preparation divided by the amount of lead sulfate in grams; b is the amount of lead in solution = total active lead in the solution, whereas n is the number of layers recrystallized. Thus it is found that $\text{Pb}_{\text{exchanged}} = R\ (b/d)$, d being the weight of the sample. The expression leads us to expect that Pb exchanged values measured in a given time of shaking should decrease with decreasing specific surface and also with decreasing weight of sample used, and increasing amounts of lead solution. This actually has been shown to be true.

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[1] I, THIS JOURNAL, **56**, 1264 (1934); II, **56**, 1658 (1934); III, **57**, 597 (1935); IV, **57**, 706 (1935); V, **57**, 2573 (1935); VI, **57**, 2577 (1935).

The validity of the above expression was tested experimentally by determining the speed of removal of thorium B under various conditions and comparing computed values of n required to give a certain percentage removal or Pb exchanged.

A systematic study was made of the speed of disappearance of thorium B from solutions containing varying amounts of suspended fresh lead sulfate, keeping the concentration of lead in solution, the temperature and the speed of shaking constant. Similar experiments were performed with constant amounts of lead sulfate at constant temperature and speed of shaking, but with varying lead concentrations in the solution. The results obtained were exactly in accord with the requirements of the above expression. However, this agreement between experimental results and the expression derived is by no means conclusive proof of the postulates upon which the expression was based. In the first place it was assumed that the speed of perfection, *i. e.*, of recrystallization of the lead sulfate, was the same in different media, whereas it was to be expected, and will be shown below, that this speed decreases with increasing lead concentration in the solution. Therefore, the results obtained in experiments with constant amounts of lead sulfate and varying lead concentrations in the solutions are not directly comparable. Furthermore, it could be shown that part of the lead sulfate which had recrystallized once could participate in further recrystallizations. In other words, we are not dealing solely with an unidirectional recrystallization, but with a succession of recrystallizations.

From the experimental data presented in this paper, it could be concluded that during the initial stages of the aging of fresh lead sulfate the recrystallization is mainly unidirectional and that an enrichment of the thorium B in the recrystallizate occurs, but that on prolonged shaking, successive recrystallizations occur, ultimately leading to a homogeneous distribution of the radioactive lead. The above discussion indicates the possibility of finding an apparent Pb exchanged which, as a result of the enrichment of active lead during the unidirectional recrystallization, is greater than the total amount of lead in the precipitate (683 mg. per 1 g. lead sulfate. Since the individual speeds of the respective processes are unknown, it was not possible to derive an expression describing the kinetics of the entire process.

Experimental

For the method of preparation of larger samples of fresh, air-dried lead sulfate and for experimental details regarding the radioactive measurements, reference is made to previous communications.[1]

Effect of Amount of Lead Sulfate upon Speed of Distribution of Thorium B.—0.3000-g. and 0.0401-g. samples of fresh lead sulfate were shaken for various periods of time at room temperature with 23.53 cc. of a radioactive lead nitrate solution which was 0.00162 molar in lead nitrate and 0.065 M in potassium nitrate. Several representative results are given in Table I. The apparent number of lead ions which has taken part in the exchange process has been calculated in the ordinary way and is expressed in mg. of lead exchanged per 1 g. of lead sulfate.

TABLE I

EFFECT OF AMOUNT OF LEAD SULFATE UPON SPEED OF DISTRIBUTION OF ThB

$Pb_{solution}$ = 8.39 mg.

Amount of $PbSO_4$, g.		0.3000	0.0401
% ThB adsorbed after shaking for	15 min....	61.4	6.5
	3 hours....	96.9	16.9
$Pb_{exchanged}$, mg. per 1 g. $PbSO_4$ after shaking	15 min....	43	14
	3 hours....	865	42

The results in Table I show conclusively that the amount of lead taking part in the recrystallization (perfection) process is a function of the available surface of precipitate. With the small amount of lead sulfate the distribution is far from complete even after three hours of shaking. This supports the assumption that the recrystallization is mainly unidirectional during the early stages of the aging.

In Table II are reported results dealing with the speed of removal of thorium B when 0.3000 g. of lead sulfate is shaken with 23.53 cc. of radioactive lead solutions which contain varying amounts of inactive lead nitrate and which are 0.065 molar in potassium nitrate. The total amount of lead ion in solution was determined analytically in identical solutions, saturated with lead sulfate, by precipitation as lead chromate and iodometric titration of the latter. The batch of lead sulfate used in these measurements differed from the sample involved in Table I.

TABLE II

EFFECT OF LEAD CONCENTRATION IN SOLUTION UPON SPEED OF DISTRIBUTION OF ThB

0.3000 g. $PbSO_4$

Lead nitrate concn. in soln., molar	Lead in soln., mg.	$Pb_{exchanged}$, mg. per 1 g. $PbSO_4$ after shaking for 15 min.	1 hr.	3 hrs.	4 hrs.	10 hrs.
4.935×10^{-4}	3.71	202	685	680		
1.62×10^{-3}	8.39	80	500	760		
5.07×10^{-3}	24.7	49	194		450	
1.62×10^{-2}	79.0		38	130		230

The data in Table II show that the speed of distribution of active lead decreases with increasing lead concentration in the solution. This is partly to be attributed to the fact that after recrystallization of the same fraction of the precipitate, less ThB is removed from the more concentrated solutions. In addition, however, it could be shown that the actual speed of recrystallization and, therefore, also of perfection, decreases with increasing lead concentration in the solution. This is to be expected, since the solubility of the lead sulfate decreases with increasing lead concentration in the solution.

The experiments reported in Table III show that a much more pronounced aging occurs when the fresh lead sulfate is kept in dilute lead nitrate than in more concentrated solutions. Samples of the same batch of lead sulfate were shaken for forty-five minutes on a rotatory shaker at room temperature in 0.016 and 0.0016 molar lead nitrate solutions, respectively, both solutions being 0.065 molar in potassium nitrate. After so aging, the samples were filtered by suction, washed quickly with five 10-cc. portions of water, then with absolute alcohol and made air-dry. 0.3000-g. portions of both samples were shaken with 23.53-cc. solutions of radioactive lead sulfate which was 0.00162 *M* in lead nitrate and 0.065 *M* in potassium nitrate.

TABLE III

EFFECT OF LEAD CONCENTRATION IN SOLUTION UPON SPEED OF AGING OF LEAD SULFATE

Aging medium, *M*	$Pb(NO_3)_2$	0.016	0.0016
	KNO_3	.065	.065
Pb$_{\text{exchanged}}$, mg. per 1 g. $PbSO_4$ after shaking with standard active lead solution for	15 min.	10.8	2.9
	1 hour	115	3.6
	3 hours	768	4.8

Evidence of Successive Recrystallization.—From Table I and from experiments reported later in this paper it can be concluded that a heterogeneous distribution of the thorium B through the precipitate takes place upon shaking of fresh inactive lead sulfate with active lead solutions for short periods of time. Were it true that the active lead sulfate once recrystallized, no longer participated in succeeding recrystallizations, a continuous extraction of the thorium B from the solution would result from the continuous recrystallization of the inactive portions of the lead sulfate. Thus under proper condition, amounts of Pb$_{\text{exchanged}}$, much greater than would correspond to the total amount of lead in the precipitate, should be found after sufficiently long periods of shaking. On the other hand, when thermodynamic equilibrium between the solid and solution is established, the amount of Pb$_{\text{exchanged}}$ should be equal to the amount of lead in the precipitate. Neither in our previous work[1] nor in the present study has definite evidence been obtained that the amount of Pb$_{\text{exchanged}}$ ever exceeds the value which corresponds to thermodynamic equilibrium. It is true that in working with radioactive lead solutions dilute in lead (0.0005 to 0.0016 molar) amounts of Pb$_{\text{exchanged}}$ were found occasionally greater than the equilibrium value (see, *e. g.*, Tables I and II). However, under these conditions the percentage of thorium B left in the solution upon attainment of homogeneous distribution is so small (1.8% in the least concentrated solution) that an error of a few tenths per cent. in the measurements of the active deposits could change the value of Pb$_{\text{exchanged}}$ from 683 (homogeneous distribution) to say, 865 (see Table I).

In working with more concentrated lead solutions, no indication was ever obtained that more thorium B than corresponded to homogeneous distribution was removed from solution, even after longer periods of shaking. In the experiments reported in Table II, the maximum Pb$_{\text{exchanged}}$ in the two more concentrated lead nitrate solutions was not reached in the shaking periods employed. Since it has been shown that the excess of lead in the solution decreases the speed of recrystallization, it was decided to repeat the experiments with larger amounts of lead in solution at a higher speed of recrystallization. The latter was accomplished either by working at higher temperatures or at room temperature in the presence of nitric acid.[1]

Experiments in the Presence of Nitric Acid.—0.3-g. samples of fresh lead sulfate were shaken at room temperature with an active lead nitrate solution which was 0.0162 molar in lead nitrate, 0.24 molar in nitric acid and 0.0652 molar in lead nitrate. The residual activity of the solutions was determined by first evaporating in watch glasses to remove acid, washing the residue into standard copper dishes[1] and again evaporating. Electroscopic tests showed that the only activity left on the glass dishes was due to thorium C and that thorium B was transferred quantitatively to the copper dishes. The results are given in Table IV.

TABLE IV

EFFECT OF NITRIC ACID AND OF TEMPERATURE UPON THE SPEED OF DISTRIBUTION OF THORIUM B

Conditions during shaking		Nitric acid, Room temp.	Neutral 90°
Pb$_{\text{exchanged}}$, mg. per 1 g. $PbSO_4$ after shaking for	15 min.	84	...
	31 min.	118	117
	1 hour	220	187
	2 hours	266	235

Comparison of these figures with those in Table II at the same lead concentration shows the enhancing effect of nitric acid upon the speed of recrystallization. However, no indication is obtained that the amount of thorium B removed will pass through a maximum upon prolonged periods of shaking. If this were the case, the rate of thorium B removed should be extremely rapid and approach the hump in the curve in the early stages of the process.

Experiments at 90°.—These experiments were carried out with a product of lead sulfate which was slightly more aged than the samples used in previous experiments. To 0.3-g. samples of lead sulfate in unparaffined bottles was added 23.53 cc. of an active lead solution, 0.0162 *M* in lead nitrate and 0.065 *M* in potassium nitrate. The mixture was heated for five minutes in a boiling water-bath, the bottle stoppered with a collodion-coated cork and placed on a relatively slow rotatory shaker in an oven at 90°. After the indicated time of shaking, the precipitates were allowed to settle in the oven and samples of the supernatant liquid pipetted off while the solution remained at the elevated temperature. Blanks were run under the same conditions. Reproducible results were obtained in this manner. Irregular results were obtained when the bottles were allowed to cool and the mixtures centrifuged at room temperature.

The results are reported in Table IV and are comparable with those obtained at room temperature in the presence of nitric acid. The close agreement between the two sets of figures is rather accidental, since the product used at room temperature in nitric acid was fresher than that treated at 90°.

Conclusive Evidence of Successive Recrystallization.—Although the above experiments indicated that during aging in liquid medium fresh lead sulfate is subjected to successive recrystallizations, it was thought desirable to present more conclusive evidence. For this reason the following experiments were carried out. 0.3-g. samples of fresh lead sulfate were shaken for fifteen minutes with 23.53 cc. of an active lead nitrate solution which was 4.93×10^{-4} molar in lead nitrate and 0.065 molar in potassium nitrate. This treatment was found to leave only 5.8% of the thorium B in solution. After the above time of shaking 70.6 mg. of solid inactive lead nitrate was added, thus raising the lead nitrate concentration from 4.93×10^{-4} to 9.55×10^{-3} *M*. Continuing the shaking for one hour, 10.5% of the original amount of thorium B was found back in the solution; and after three hours of shaking, 17.3%. If in the presence of the large amount of lead, a homogeneous distribution of the active lead throughout the system had taken place, 18.5% of thorium B should have been found in the solution. An unidirectional recrystallization of the lead sulfate, however, would require that the thorium B removal from solution continue in spite of the addition of the larger amount of lead nitrate. Actually the *thorium B was extracted from the precipitate* and returned to solution so as to approach a homogeneous distribution in the presence of excess of lead. This experiment shows conclusively the occurrence of successive recrystallizations during the perfection of fresh lead sulfate.

The Heterogeneous and Homogeneous Distribution of Thorium B through the Precipitate.—Since during the early stages of shaking of fresh lead sulfate with a radioactive lead solution an enrichment of thorium B in—and therefore, a heterogeneous distribution of active lead through—the precipitate must occur, it was attempted to show experimentally the heterogeneous distribution after short periods of shaking and the homogeneous distribution after long periods of shaking under proper conditions.

To 10.30 cc. of 0.1000 *M* lead nitrate was added 9.82 cc. of 0.1000 *M* potassium sulfate, the addition requiring fifty-five seconds. After the indicated time of aging (one minute or forty minutes) 9.94 cc. of a thorium B solution containing 10 mg. of lead sulfate per liter was added, and the whole shaken violently for the noted time. The precipitate was filtered rapidly by suction, and washed several times with 3-cc. portions of conductivity water (taking about one minute). The precipitate was then washed with 25 cc. of 0.0454 *M* ammonium acetate solution added in ten to thirteen smaller portions of 1–3 cc. This portion of washings was collected directly in a large test-tube within the suction flask, then transferred to paraffined containers for storage until analyzed. This portion of ammonium acetate is designated as I in Table V. The precipitate was then washed with a 100-cc. portion of ammonium acetate, the filtrate being discarded. The next 25 cc. of ammonium acetate washing was collected and is designated as II. Again the precipitate was washed with 100 cc. of ammonium acetate, the filtrate being discarded, and the following 25-cc. portion (designated as III) again collected for analysis.

In 10-cc. samples of portions I, II and III, the lead content was determined by precipitation as chromate and iodometric titration of the latter (mg. Pb per 10 cc. solution). In 4.96-cc. samples of portions I, II and III, the thorium B content was determined by evaporating to dryness in standard copper dishes and comparing the residues with those from standard solutions which were 0.0454 *M* in ammonium acetate and had been obtained by diluting the stock thorium B solution. In Table V the activity is recalculated on the basis of 10-cc. samples and is expressed arbitrarily in divisions for second (ThB act. per 10 cc.). The column ThB/Pb gives the ratio of thorium B activity to total lead per 10 cc. of each ammonium acetate portion analyzed.

The solubility of lead sulfate in 0.05 *M* ammonium acetate is about 10 mg. per 25 cc. Therefore, portion I roughly contains the outermost 10 mg. of the precipitate (approx. 0.28 g.). The next 100 cc. of wash liquid dissolves approximately 40 mg. and portion II again 10 mg. (approx. 0.23 g. left). Portion III contains approximately 10 mg. of lead sulfate after about 35% of the precipitate has been dissolved (approx. 0.18 g. left). If the thorium B were distributed homogeneously throughout the precipitate the ratio ThB/Pb should be found constant in portions I, II and III. Actually it is seen that the ratio found in a one-minute old precipitate shaken for five minutes with active lead solution increases in the order I, II, III, showing the heterogeneous distribution of thorium B and its enrichment in the recrystallizate (interior of the precipitate). Even after shaking for fifteen minutes the distribution is heterogeneous, although from the determination of the amounts of $\mathrm{Pb}_{\mathrm{exchanged}}$ (see ref. 1, I, II and III) it was concluded that with a similar precipitate after five and fifteen minutes of shaking a homogeneous distribution had taken place. From the results in Table V it is seen that after about two hours of shaking with active lead solution, a constant ratio and therefore homogeneous distribution is approached. For a precipitate which had been aged for forty minutes before addition of active lead solution, homogeneous distribution was approached or attained after about three hours of shaking.

We see from the above that, even if in exchange experiments the following relation is found to hold after a certain period of shaking: $\frac{\mathrm{ThB}_{\mathrm{removed}}}{\mathrm{ThB}_{\mathrm{solution}}} = \frac{\mathrm{Pb}_{\mathrm{in\ precipitate}}}{\mathrm{Pb}_{\mathrm{solution}}}$; it need not necessarily be true that the distribution of the active lead is homogeneous throughout the system.

The heterogeneous and homogeneous distribution, respectively, of the active lead in the experiment reported in Table V could also be demonstrated in another way. From the exchange experiments (ref. 1, I and II) it was known that after the periods of shaking indicated in the table, 95.5% of the thorium B added after the precipitation had been taken up by the precipitates. Since the original activity of the thorium B and the total amount of lead in the entire system were known, the total amount of lead corresponding to the experimentally determined activities of the ammonium acetate extracts could be calculated (designated as *r. a.* Pb = radioactive lead). For the sake of brevity the calculations will be omitted and the results are condensed in the last column of Table V under the heading *r. a.* Pb/Pb, giving the ratio of milligram of lead per 10 cc. found from the activity determinations to the amount of lead determined analytically. If the active lead were distributed homogeneously throughout the precipi-

TABLE V

HETEROGENEOUS AND HOMOGENEOUS DISTRIBUTION OF ThB THROUGH $PbSO_4$

Age of $PbSO_4$ before addition of ThB, min.	Time of shaking with radioactive lead solutions	Portion of ammonium acetate solution	Pb in 10 cc. solution, mg.	ThB activity in 10 cc. solution	$\frac{ThB}{Pb}$	*r. a.* Pb in 10 cc. soln.	*r. a.* Pb/Pb
1	5 minutes	I	1.68	0.244	0.145	1.37	0.815
1	5 minutes	III	1.12	.212	.188	1.19	1.05
1	5 minutes	I	1.77	.210	.108	1.18	0.67
1	5 minutes	II	1.29	.192	.148	1.08	.84
1	5 minutes	III	1.15	.196	.170	1.10	.96
1	15 minutes	I	1.80	.204	.113	1.33	.74
1	15 minutes	II	1.63	.238	.146	1.56	.97
1	15 minutes	I	1.99	.204	.102	1.33	.67
1	15 minutes	II	1.47	.179	.122	1.17	.80
1	2 hours	I	1.67	.234	.140	1.53	.92
1	2 hours	II	1.42	.204	.144	1.33	.94
1	2 hours	I	1.84	.236	.128	1.54	.94
1	2 hours	II	1.60	.208	.130	1.36	.95
40	3 hours	I	1.83	.308	.168	1.76	.96
40	3 hours	II	1.43	.244	.170	1.39	.97
40	3 hours	III	1.24	.202	.163	1.15	.93
40	3 hours	I	1.75	.290	.166	1.65	.95
40	3 hours	II	1.53	.249	.163	1.42	.93
40	3 hours	III	1.32	.220	.166	1.25	.94

tate, the ratio should be found equal to 1 and, in addition, constant in the portions I, II, III. The results again substantiate the conclusion that after short time of shaking there occurs an enrichment of the active lead in the first recrystallizate which is located in the interior of the precipitate.

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Summary

1. Experimentally it has been shown that when fresh lead sulfate is shaken with a radioactive lead nitrate solution, an enrichment of the thorium B in the recrystallizate occurs.

2. Upon short periods of shaking a heterogeneous distribution of the active lead through the precipitate occurs. Upon prolonged periods of shaking the distribution becomes homogeneous as a result of successive recrystallizations of the precipitate.

3. If upon shaking of fresh lead sulfate with radioactive lead solutions $Pb_{exchanged}$ calculated in the ordinary way is found to be equal to $Pb_{precipitate}$, the result does not necessarily indicate homogeneous distribution of the active lead throughout the system.

4. Comparable results in a study of the speed of distribution of thorium B through lead sulfate are obtained only if the same amounts of precipitate and of lead in solution are used in all experiments.

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