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Structural Changes Taking Place During the Aging of Freshly Formed Precipitates. II. The Free Mobility of Lead Ions in Amicroscopic Crystals of Lead Sulfate

BY I. M. KOLTHOFF AND CHARLES ROSENBLUM

In a previous study[1] it was found that lead sulfate, freshly precipitated at room temperature from 0.1 *M* lead nitrate and 0.1 *M* potassium sulfate solutions, consists of distinct microscopic needles. These crystals are entirely porous, all of the lead ions within the fresh precipitate behaving as though present at the surface. The microscopic crystals consist of amicroscopic primary crystals; on standing a rapid aging occurs, resulting in a perfection of the primary crystals in the interior of the microscopic crystals. These inferences were made from studies of the adsorption of thorium B by precipitates of lead sulfate of various ages, the internal specific surface being approximated from the adsorption of thorium B after one minute of shaking. It appeared of interest to study the distribution of thorium B between solution and the crystals upon longer times of shaking at various ages of the precipitates. In addition it was desirable to study the reverse process by preparing radioactive precipitates and determining the distribution of the thorium B between the radioactive crystals of varying age and the inactive mother liquor. The results of these studies are described in the present paper. Experimental details are found in previous communications.[1]

Experiments with Inactive Lead Sulfate.—In the first paper of this series[1] it was mentioned that the "specific surface" of fresh precipitates of lead sulfate, as computed from the distribution of thorium B between the radioactive solution and the inactive precipitate and from the amount of lead in the solution, does not yield the actual amount of lead ions in the surface at a particular moment. The term "specific surface" is unsatisfactory because part of the thorium B is incorporated in the aging crystals. For this reason we prefer to use the expression "exchanged lead"[2] instead of "specific surface." From the relation

$$\frac{\text{Thorium B adsorbed}}{\text{Thorium B solution}} = \frac{\text{Pb exchanged}}{\text{Pb solution}}$$

the total amount of lead in the precipitate which has taken part in the kinetic exchange (Pb exchanged) is easily found.

In the following experiments 9.81 cc. of 0.1 *M* potassium sulfate was added to 10.29 cc. of 0.1 *M* lead nitrate in a paraffined bottle. The bottle was closed with a paraffined stopper and gently shaken for a given time (=age of precipitate). Then 9.96 cc. of a thorium B solution which was 20% saturated in lead sulfate and of known activity was added from a paraffined pipet and the whole violently shaken (400 phases p. m.) for a given length of time as specified in the tables. The determination of the amount of thorium B adsorbed was carried out in the same way as previously described.[1]

The results are given in Table I.

TABLE I

LEAD EXCHANGED ON SHAKING LEAD SULFATE OF DIFFERENT AGES FOR VARIOUS TIMES WITH RADIOACTIVE LEAD NITRATE

Lead in precipitate = 0.2032 g.; lead in solution = 10.2 mg.; t = 26°

Age of precipitate	Time of shaking with thorium B	Thorium B adsorbed in %	Pb exchanged in mg. per 1 g. $PbSO_4$	$\frac{\text{Pb exchanged}}{\text{Total Pb in ppt.}} \times 100$
9 minutes	1 minute	56	43.7	6.4
9 minutes	3 minutes	75.4	105	15.4
9 minutes	5 minutes	86.0	211	30.9
9 minutes	15 minutes	94.4	580	84.6
9 minutes	1 hour	95.9	800	100
9 minutes	3 hours	95.6	750	100
50 minutes	1 minute	14.5	5.8	0.9
50 minutes	5 minutes	37.3	20.4	3.0
50 minutes	15 minutes	47.0	30.9	4.5
50 minutes	1 hour	72.1	88.6	13.0
50 minutes	3 hours	91.8	385	56
50 minutes	17 hours	96	820	100
3 hours	1 minute	7.0	2.6	0.4
3 hours	5 minutes	12.2	4.8	0.7
3 hours	15 minutes	24.4	11.1	1.6
3 hours	1 hour	49.5	33.8	5.0
3 hours	17 hours	89.7	299	44

The last column Pb exchanged/Total Pb in ppt. × 100 gives the percentage of the lead in the precipitate which has taken part in the kinetic exchange.

In the experiments with radioactive precipitates of lead sulfate described below, it was desirable to study the distribution of thorium B between the crystals and a solution containing about the same amount of lead as the precipitate. Since the speed of kinetic exchange and the extent of aging during shaking may be different from those in which the supernatant liquid contained only a small amount of dissolved lead (conditions prevailing in Table I), it was decided to run parallel experiments with inactive precipitates in order to get results comparable with the active precipitates. The experiments reported in Table II were therefore made in the following way. To 10.29

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[1] Kolthoff and Rosenblum, THIS JOURNAL, **56**, 1264 (1934).

[2] F. Paneth, *Physik. Z.*, **15**, 924 (1914).

cc. of 0.1 *M* lead nitrate solution was added 9.81 cc. of 0.1 *M* potassium sulfate and the mixture gently shaken for a noted time (=age of precipitate). Then 9.94 cc. of a 0.0936 *M* radioactive lead nitrate solution of known activity was added and the whole violently shaken for a given period. With the precipitate fifty minutes of age the adsorption of thorium B after one hour of shaking was so small that the amount of exchanged lead could not be calculated with any degree of accuracy.

TABLE II

LEAD EXCHANGED ON SHAKING LEAD SULFATE OF DIFFERENT AGES FOR VARIOUS TIMES WITH RADIOACTIVE LEAD NITRATE SOLUTION

Pb in precipitate = 0.2033 g.; Pb^{++} in solution = 0.2030 g.; t = 24–26°

Age of precipitate	Time of shaking with thorium B	Thorium B adsorbed in %	Pb exchanged in mg. per 1 g. of $PbSO_4$	$\frac{\text{Pb exchanged}}{\text{Total Pb in ppt.}} \times 100$
8–8.5 minutes	15 minutes	6.5 (±2)	47.5	7
8–8.5 minutes	1 hour	10.8 15.9 } 13.4	105.6	15
50 minutes	1 hour	0	...	..
50 minutes	3 hours	5.9 9.1 } 7.5	55	8
50 minutes	12 hours	14.2 16.4 } 15.3	123	18

Experiments with Radioactive Lead Sulfate Shaken with Inactive Lead Nitrate.—To 25.10 cc. of 0.0996 *M* potassium sulfate in a paraffined bottle was added 24.90 cc. of 0.1000 *M* radioactive lead nitrate of known activity. Immediately thereafter 0.925 cc. of 0.1 *M* inactive lead nitrate was added to precipitate the excess of sulfate, the whole operation to this point requiring about two and one-half minutes. The bottles were then violently shaken for various lengths of time and centrifuged for four to five minutes. Three 9.96-cc. portions of the clear centrifugate were evaporated and the activity of the residues compared with that of suitable standards, containing the same amounts of lead and potassium nitrate as the unknowns. In these experiments the weight of the radioactive precipitates amounted to 0.755 g. or to 0.516 g. of lead, the weight of the inactive lead sulfate being 0.0030 g. The excess of lead nitrate in the supernatant liquid corresponded to a 1.62×10^{-3} molar solution. From previous work it was derived that the solubility of the lead sulfate in the supernatant liquid was equal to 0.15×10^{-3} molar, therefore the total lead concentration in the solution was 1.77×10^{-3} molar, corresponding to 18.7 mg. of lead in 50.93 cc. of solution. If the thorium B, originally present in the precipitate, could distribute itself homogeneously throughout the entire system, $(18.7/(516 + 18.7)) \times 100 = 3.5\%$ of the radioactive lead or 18.1 mg. would be found in the solution.

Actually it was found that after one minute shaking of the two to two and one-half minutes old precipitate, 11.9 mg. of radioactive lead or 66% of the maximum amount had gone into solution, after fifteen minutes of shaking 19.0 mg. or 104% of the maximum amount and after one hour and twenty minutes shaking, 19.5 mg. or 107% of the maximum amount. Considering the fact that after complete partition of the thorium B only 3.5% of the latter goes into the solution, it may be safely concluded that the experimental figures found, 3.7 and 3.8% respectively, represent homogeneous distribution throughout the two phases. These experiments with the radioactive lead sulfate substantiate the conclusion arrived at in the first paper of this series[1] that after a relatively short time of shaking of the fresh precipitate with the supernatant liquid, all of the lead in the former behaves as if it were present at the surface.

The conditions in the above experiments were very unfavorable for a study of the speed of distribution of the thorium B between radioactive precipitates of varying age and the supernatant liquid, since at most 3.5% of the radioactive lead could go into solution. In order to get a larger enrichment in the solution it was necessary to increase the inactive lead concentration of the latter. The experiments were performed in the following way. To 9.96 cc. of 0.1 *M* radioactive lead nitrate solution of known activity in a paraffined bottle was added 10.00 cc. of 0.1 *M* potassium sulfate. After a given length of time (=age of precipitate) 9.96 cc. of 0.1 *M* inactive lead nitrate was added and the whole shaken for various times. After centrifuging, three 4.96-cc. samples of the clear centrifugate were evaporated and the thorium B content of the residues determined. From the activities found, the percentage of the radioactive lead which had gone into the inactive lead solution from the radioactive precipitate could be calculated. The corresponding figures are found in column 3 of Table III. In all of the experiments the amount of radioactive lead in the precipitate was equal to 0.2064 g. and that of inactive lead to 0.0008 g. Originally the supernatant liquid contained 0.2055 g. of inactive lead. If the thorium B were to distribute itself homogeneously throughout the entire system, $(0.2055/(0.2072 + 0.2055)) \times 100 = 49.8\%$ of the radioactive lead would be found in the solution. This figure corresponds to the maximum amount of thorium B which could be found in the solution. In column 4 of Table III is reported the percentage of the maximum amount of thorium B which was found in the solution.

From the results obtained it was also possible to calculate the number of lead ions in the precipitate which had acted like surface lead during the shaking process or, in other words, the amount of Pb exchanged. Had x mg. of the radioactive lead in the precipitate had an opportunity to act like surface (*i. e.*, to take part in the exchange process) then $x(205.5/(205.5 + x))$ mg. of radioactive lead would be found in the solution. The amount of radioactive lead which had gone into the solution was easily calculated from the figures in column 3 in Table III, and x computed from the simple equation. In column 5 the values of x expressed in mg. of lead exchanged per 1 g. of lead sulfate are reported and in the last column the percentage of all of the lead in the precipitate which had taken part in the exchange. These figures are analogous to those reported in Tables I and II of inactive precipitates.

Discussion of the Results

1. Comparison of the data in Tables II and III shows that the distribution of thorium B between an active lead nitrate solution and an aging precipitate of inactive lead sulfate is strictly com-

TABLE III

LEAD EXCHANGED ON SHAKING RADIOACTIVE LEAD SULFATE OF DIFFERENT AGES FOR VARIOUS TIMES WITH INACTIVE LEAD NITRATE SOLUTION

Pb in precipitate is 207.2 mg.; Pb in solution is 205.5 mg.; *t* = 24–26°

Age of precipitate	Time of shaking with inactive lead nitrate	Radioactive lead found in solution in %	Percentage of maximum amount of radioactive lead in solution	Pb exchanged in mg. per 1 g. of $PbSO_4$	$\frac{\text{Pb exchanged}}{\text{Pb precipitate}} \times 100$
1–1.5 minutes	1 minute	9.1 and 7.7 = 8.4	17	62	9.1
1–1.5 minutes	5 minutes	14.2	28.5	113	16.5
1–1.5 minutes	15.5 minutes	27	54	251	37
1–1.5 minutes	1 hour	39.3 and 40.0 = 39.7	80	447	65.5
1–1.5 minutes	16 hours	42.6	86	506	74
1–1.5 minutes	35 hours	42.2	85	500	73
7.5–9 minutes	1 minute	3.5 and 3.1 = 3.3	7	23	3.4
7.5–9 minutes	5 minutes	4.48 and 4.77 = 4.6	9	33	4.8
7.5–9 minutes	15 minutes	8.25 and 8.10 = 8.2	16	61	8.9
7.5–9 minutes	1 hour	18.3 and 19.0 = 18.7	38	156	23
7.5–9 minutes	3 hours	26.4	53	244	36
7.5–9 minutes	16.5 hours	35.4	71	372	55
7.5–9 minutes	35 hours	34.0 and 38.0 = 36	72.5	382	56
50 minutes	1 minute	2.04 and 2.05 = 2.04	4.1	14	2.1
50 minutes	10 minutes	2.64 and 1.72 = 2.2	4.4	14.7	2.2
50 minutes	1 hour	7.40 and 8.65 = 8.0	16	59	8.7
50 minutes	3 hours	10.2	20.5	77	11.3
50 minutes	7 hours	15.5 and 17.4 = 16.5	33	134	20
50 minutes	18 hours	27.7	56	260	38
50 minutes	35 hours	34.8 and 31.1 = 33.0	66	335	49

parable to the distribution between an active precipitate and an inactive solution. The exchange phenomena observed therefore are strictly reversible. From the figures in Tables I and II it follows that a large excess of lead nitrate in the supernatant liquid diminishes the complete distribution of thorium B between a lead solution and an aging precipitate of lead sulfate.

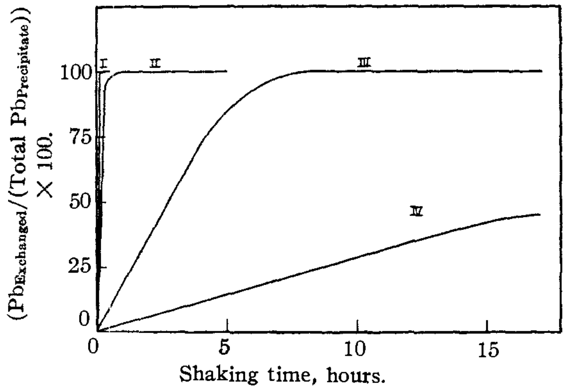

Fig. 1.—Curve I, precipitate 50 seconds old; Curve II, precipitate 8.5–9 minutes old; Curve III, precipitate 50–51 minutes old; Curve IV, precipitate 3 hours old.

2. The results reported in Table I of a previous paper[1] showed that when fresh precipitates of lead sulfate were shaken for three to five minutes with a radioactive lead solution, the active lead distributed itself homogeneously throughout the entire system. Comparison of the previous results with those given in Table I of the present paper reveals that the speed of exchange rapidly decreases with increasing age of the lead sulfate. Thus, after three minutes of shaking of a one-minute old precipitate with thorium B solution, all of the lead in the precipitate had acted as if it were present at the surface; for a nine-minute old precipitate only 15% of all the lead acted as surface, while with a fifty-minute old precipitate only 2% behaved like surface. The most striking result of this study is that even with a fifty-minute old precipitate a homogeneous distribution of all of the lead was found when shaken for less than seventeen hours with the precipitate. The behavior of precipitates of varying ages is clearly shown in Fig. 1, in which the percentage of all the lead in the precipitate which had taken part in the exchange is plotted against the time of shaking with thorium B.

A possible explanation of this free diffusion of lead ions throughout the entire precipitate could be found if the freshly formed precipitate, consisting of crystalline particles of the order of 0.5 to 1 micron in width and 1 to 2 microns in length, were a metastable modification and quickly transformed into the stable form. This would cause a complete destruction of the primary crystals in the fresh precipitate and create an opportunity for all of the lead to act as though it were on the surface during the transformation. x-Ray pictures, made at our request by Dr. E. J. W. Verwey[3] at the University of Groningen (Holland), revealed that a precipitate less than fifteen minutes old gave the same pattern as a well aged lead sulfate. The lines in the fresh precipitate, however, were very diffuse and it was roughly estimated that the amicroscopic particles within the microscopic crystals contained at least 1000 to 10,000 molecules.

From the above it is evident that the freshly formed microscopic crystals of lead sulfate have a spongy structure. They consist of primary particles separated by fine capillaries with a diameter of the order of molecular dimensions, which allow a diffusion of thorium B (lead) ions to the internal surface. On aging, a perfection process occurs in the interior of the crystals, resulting in a growth of the primary particles and a decrease of the internal surface. At present it is impossible to approximate these changes of the internal surface with any degree of accuracy, since it may be expected that the capillaries will be filled up with lattice material during the perfection process. It is planned to make an extensive study of the changes of the x-ray pattern during the aging, in order to approximate the magnitude of the internal surface at various stages of the process.

The most important conclusion which may be drawn from the present study is that *lead ions can move freely through the primary amicroscopic crystals and cause a homogeneous distribution of thorium B throughout the entire system.*

The lead ions in the primary particles are not bound to a definite position but have a free mobility, thus allowing all of them to reach the surface at various times and take part in the kinetic exchange process. The present studies are being continued and we hope to be able to throw more light upon the nature of the internal structural changes taking place on aging of freshly prepared lead sulfate.

Summary

1. The exchange phenomena between aging inactive lead sulfate and a radioactive lead solution are identical with those between radioactive lead sulfate and an inactive lead solution.

2. A large excess of lead nitrate in the supernatant liquid diminishes the speed of exchange between the precipitate and the solution.

3. The lead ions in the primary amicroscopic crystals of lead sulfate, even in a precipitate fifty minutes old, can move freely, thus explaining the homogeneous distribution of thorium B throughout the entire system.

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[3] At this place we wish to thank Dr. Verwey for his kind assistance.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Activity of Sodium and Potassium Dissolved in Gallium

BY E. S. GILFILLAN, JR., AND H. E. BENT

A great many organic reactions of alkali metals or alkali metal amalgams have been studied. One of us has been interested for some time in the addition of alkali metals to organic free radicals.[1] A quantitative thermodynamic treatment of these reactions is possible providing the activity of the alkali metal has been determined in the amalgam used in the investigation. The use of sodium amalgams puts certain limitations on such experiments due to the fact that over most of the concentration range sodium amalgams are solid at temperatures suitable for organic reactions. In the hope of discovering alloys which would have quite different activities of sodium and which would be liquid at room temperature the following investigation was carried out on gallium.

Materials Used

The methods of preparing the various materials have been described elsewhere, with the exception of the gallium.[2] This was purchased from Charles Hardy, 415 Lexington Ave., New York City, at four dollars a gram. The best method of handling the material seemed to be to melt it under a solution of one molar sulfuric acid, then to supercool the vessel with ice water and while still liquid to cut the viscous metal with a glass rod. The pellets were then seeded with solid gallium. Solution of the metal in the acid is very slow. The pellets so prepared were clean and bright and

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[1] Bent, THIS JOURNAL, **52**, 1498 (1930); **53**, 1786 (1931); Bent and Dorfman, *ibid.*, **54**, 1393 (1932); Bent, Dorfman and Bruce, *ibid.*, **54**, 3250 (1932).

[2] Bent and Gilfillan, *ibid.*, **55**, 24, 3989 (1933).