of lead sulfate. All conclusions drawn from these abbreviated data have been substantiated by experiments with each independently prepared batch.

Summary

Fresh lead sulfate appears to undergo three distinct types of thermal aging.

1. *Microscopic aging by a sintering of the particles.* A pronounced sintering has been found at temperatures of 400°, and a very slow sintering at 300°.

2. *Internal thermal aging* at temperatures far below that of sintering. This aging is attributed to the high speed of evaporation of lattice ions on the active surface (Taylor and Langmuir). After a sufficiently long heating period the "age" approaches a final state which is characteristic for each temperature.

3. *Thermal aging promoted by adsorbed and occluded water.* This aging occurs at temperatures below the point where internal aging begins. It proceeds continuously with the time of heating. It accounts for the much more pronounced perfection after heating for twenty hours at 250° than after the same time of heating at 305 and 400°.

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

Structural Changes Taking Place During the Aging of Freshly Formed Precipitates. VI. The Perfection and Aging of Lead Sulfate Precipitated under Various Conditions

BY I. M. KOLTHOFF AND CHARLES ROSENBLUM

In previous studies the aging of fresh lead sulfate obtained by mixing 0.1 *M* solutions of lead nitrate and potassium sulfate has been reported. In the present study, the effect of varying conditions of precipitation upon the perfection and the speed of aging of lead sulfate has been investigated.

Designation of the Various Precipitates of Lead Sulfate

1. Lead Sulfate from 0.025 M Solutions.—To 103.6 cc. of 0.025 *M* lead nitrate, 98.6 cc. of 0.025 *M* potassium sulfate was added in about five or six minutes. Four such precipitations were performed and the four portions of solid combined. The precipitate formed slowly, about half a minute being required before it appeared. One minute after the addition of the sulfate, the precipitate was filtered on a Büchner funnel, and treated further as sample 2. The "fresh" precipitate was thirteen to fourteen minutes old after washing with alcohol. Another sample was prepared by gently rotating the precipitate in the supernatant liquid for an hour before filtration.

2. Lead sulfate from 0.1 M solutions was prepared as described in a previous paper.[1]

3. Lead Sulfate from 0.4 M Solution.—To 53 cc. of 0.4 *M* lead nitrate was added 50 cc. of 0.4 *M* potassium sulfate while stirring. After the precipitation was complete, half of the suspension was decanted and placed in a rotatory shaker for one hour. The remainder was filtered immediately, washed with four 20-cc. portions of water, then with alcohol and finally air-dried. The fraction of the precipitate which had been shaken for one hour was treated in a similar way. Both the filtration and the washing process were rather slow, because the fine precipitate tended to cake on the filter and clog it. The "fresh" precipitate after the washing with water was twenty-four to twenty-five minutes old.

4. Lead Sulfate from Extremely Dilute Solutions.[2]—To 25 cc. of conductivity water were added simultaneously and dropwise from two dropping pipets 50 cc. of 0.1 *M* lead nitrate and 50 cc. of 0.1 *M* potassium sulfate, the suspension being stirred continuously during the precipitation. The precipitate which settled readily was filtered, washed and air-dried. The "fresh" precipitate was twelve minutes old.

5. Lead Sulfate from 0.1 M Solutions at Boiling Temperature.—To 103.6 cc. of 0.1 *M* lead nitrate heated to boiling was added in about five to six minutes 98.6 cc. of 0.1 *M* potassium sulfate solution at a temperature of about 95–100°. After precipitation, half of the suspension was decanted and placed on a rotatory shaker for

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[1] THIS JOURNAL, **56**, 1264 (1934) [Procedure A 1].

[2] F. Hahn, *Z. anorg. allgem. Chem.*, **126**, 257 (1923).

TABLE I

DISTRIBUTION OF THORIUM B THROUGH, AND ADSORPTION OF WOOL VIOLET BY LEAD SULFATE PRECIPITATED UNDER VARIOUS CONDITIONS

Sample of lead sulfate	Age of lead sulfate	Amount of PbSO shaken with Th B, g.	Mg. of Pb exchanged per 1 g. $PbSO_4$ after shaking in Th B for 5 min.	15 min.	1 hr.	3 hrs.	Wool Violet adsorbed in mg. per 1 g. $PbSO_4$
I 0.025 *M* Sol; R. T.	Fresh (14 min.)	0.300		0.75		5.3	0.43
	74 min.	.300		.57		4.2	.43
II 0.1 *M* Sol; R. T.	Fresh (9 min.)	.300	50		500	700	1.8
	50 min.	.300	20	30	80	350	
III 0.4 *M* Sol; R. T.	Fresh (24 min.)	.300		95		460	2.8
	84 min.	.300		31		180	2.6
IV Hahn; R. T.	Fresh (12 min.)	.300		4.0	7.8	11.4	.6
V 0.1 *M* Sol; hot	Fresh (14 min.)	.300	10	16		85	1.2
	74 min.	.300	2.4	2.5		3.4	.95

one hour, the suspension slowly cooling in the air. The remainder was filtered two minutes after addition of lead nitrate, washed and made air-dry. After washing with the water, the "fresh" precipitate was fourteen to fifteen minutes old.

Experimental Procedures

Adsorption of Wool Violet.—The relation between the magnitudes of the external surfaces of the various precipitates was found from the amounts of wool violet adsorbed in the saturated state.[3] Weighed portions of the air-dried precipitates were shaken for thirty to forty minutes with 20 cc. of a wool violet solution containing 0.25 g. of dye per liter. After shaking, the suspension was centrifuged and the dye concentration determined colorimetrically. The sample of dye used was different from that in previous experiments.[1,3]

Distribution of Thorium B.—Weighed portions of the air-dried precipitates were shaken violently (400 phases p. m.) at room temperature for various periods of time with 23.53 cc. of a radioactive lead nitrate solution which was 0.00162 molar in lead nitrate and 0.065 molar in potassium nitrate. The amounts of thorium B taken up by the precipitates were measured as usual.[1] The results obtained are reported in a condensed form in Table I.

Discussion

From the results it appears that the concentrations of the reacting lead nitrate and potassium sulfate solutions are important factors in determining the size and the perfection of the precipitated lead sulfate crystals. The surface of a precipitate obtained from 0.025 molar solutions is about four times smaller than that from 0.1 *M* solutions, whereas that of the latter is about half as great as the surface of the lead sulfate from 0.4 *M* solutions. These conclusions follow from the amounts of wool violet adsorbed by the various precipitates.

The degree of perfection of a fresh precipitate obtained from 0.025 *M* solutions is relatively great; consequently the speed of its further perfection is relatively small. By carrying out the thorium B distribution experiments at a smaller lead-ion concentration in the solution, the progress of the perfection on aging of this precipitate could be shown more conclusively than by the data reported in Table 1. To 10.30 cc. of 0.025 *M* lead nitrate in paraffined containers was added 9.82 cc. of 0.025 *M* potassium sulfate. After aging for one minute and one hour, respectively, after precipitation, 9.94 cc. of a stock thorium B solution in 2.5×10^{-5} molar lead sulfate was added and the whole shaken for various periods of time. The results obtained are given in Table II.

TABLE II

PROGRESS OF AGING OF LEAD SULFATE PRECIPITATED FROM 0.025 *M* SOLUTIONS AT ROOM TEMPERATURE

Amount of lead sulfate 0.0745 g.; lead concentration in solution 5.5×10^{-4} *M*.

Age of precipitate	Mg. of Pb exchanged per 1 g. of $PbSO_4$ after shaking with Th B for 5 min.	15 min.	1 hour	3 hours
1 minute	34	70	175	320
1 hour	7	10	26	60

The results of the experiments reported in Table I regarding the perfection and the speed of aging of precipitates obtained from 0.4 *M* solutions are not entirely conclusive. It is to be expected that the crystals obtained from 0.4 *M* solutions would be much less perfect than those formed on mixing of 0.1 *M* solutions. The results in the table seem to indicate just the opposite. It is possible that the speed of distribution of the thorium B, which is a direct function of the speed

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[3] I. M. Kolthoff, W. von Fischer and C. Rosenblum, THIS JOURNAL, **56**, 832 (1934).

of recrystallization, is greater with a precipitate obtained from 0.1 *M* solutions than from 0.4 *M* solutions. Thus, it has been shown by Roller[4] that the dissolution factor of calcium sulfate crystals reaches a maximum at a size of 2.8 microns, and decreases with increasing and decreasing size of the particles. However, it should be realized that the results are but qualitative in nature since the precipitate obtained from 0.4 *M* solutions is hard to filter and wash and has a tendency to cake together in the air-dried state after washing with alcohol. Therefore, during the filtration and washing, it might have been subjected to a drastic aging process, and the specific surface might have been greater in the unfiltered than in the filtered and air-dried state. Moreover, it should be mentioned that the "fresh" precipitate was twenty-four minutes old and was compared with a nine-minute old precipitate obtained from 0.1 *M* solutions. If the latter had been twenty-four minutes old the speed of distribution of thorium B would have been found of the same order as that found with precipitate III.

It has been ascertained that the unexpected results are not due to an excessive coprecipitation of lead nitrate by precipitate III. Such a contamination would increase $\mathrm{Pb}_{\mathrm{soln.}}$ so that the true $\mathrm{Pb}_{\mathrm{exch'ged}}$ value might actually exceed values obtained with precipitate II. "Fresh" precipitates obtained from 0.1 and 0.4 *M* solutions were filtered, washed and air-dried in the usual manner. Three-tenth-gram portions were shaken with the "standard" solution, which is 0.00162 molar in lead nitrate and 0.065 molar in potassium nitrate, and the supernatant liquids analyzed for lead. In all cases the total lead concentration was found to be $1.72\ (\pm\ 0.02) \times 10^{-3}\ M$. Subsequent work, designed to study in greater detail the degree of perfection of a precipitate obtained from 0.4 *M* solutions, is planned.

A precipitate obtained by F. Hahn's extreme dilution method is fairly coarse but still highly imperfect. As a matter of fact, it appears that the precipitate obtained at room temperature from 0.025 *M* solutions is more perfect than a precipitate formed according to Hahn from 0.1 *M* solutions.

It is of great interest to notice that the effect of concentration of the reacting solutions exerts a greater influence upon the degree of perfection of the separated lead sulfate than does the temperature. A precipitate rapidly formed at higher temperatures from 0.1 molar solutions is much less coarse and much less perfect than when obtained from 0.025 *M* solutions at room temperature. The former, when aged in the slowly cooling liquid, is subjected to a rapid perfection process. This is to be expected since the speed of recrystallization rapidly increases with the temperature.

Summary

A preliminary study was made of the degree of perfection and the speed of aging of lead sulfate as a function of the concentrations of lead nitrate and potassium sulfate and of the temperature during the precipitation. A precipitate obtained from 0.025 *M* solutions is much more perfect and coarser than a precipitate obtained from 0.1 *M* solutions. A precipitate obtained from 0.1 *M* solutions at boiling temperature in the fresh state is much less perfect and has a smaller size than a precipitate obtained from 0.025 *M* solutions at room temperature.

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[4] P. S. Roller, *J. Phys. Chem.*, **35**, 1133 (1931).