JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 60 MARCH 8, 1938 NUMBER 3

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

Studies on Aging of Fresh Precipitates. XIX. Aging of Freshly Precipitated Barium Sulfate in Dilute Barium and Sulfate Solutions[1]

BY I. M. KOLTHOFF AND G. E. NOPONEN

In previous investigations carried out in this Laboratory it was shown[2] that freshly precipitated lead sulfate when aged in the mother liquor was subject to a drastic perfection as a result of repeated recrystallizations of the primary imperfect crystals. Although no conclusive evidence was obtained, it was inferred that the classical type of aging, the so-called Ostwald ripening, was of subordinate significance and that the recrystallizations occur mainly in a liquid film around the particles and not *via* the bulk of the solution. In the present study carried out with freshly precipitated barium sulfate more conclusive evidence was obtained that under certain conditions of aging the Ostwald ripening did not play a part, whereas a pronounced perfection of the particles—as a result of recrystallization—occurred.

In previous studies it was shown[3] that chromate ion when added to a barium sulfate suspension in a solution containing an excess of sulfate ion is incorporated in the solid in the form of mixed crystals of barium sulfate and barium chromate. In the present study the speed of formation of these mixed crystals under specified conditions was used as an indicator of the degree of perfection (or the progress of the aging) of the barium sulfate. In a similar manner the speed of formation of mixed crystals between barium sulfate and lead sulfate[4] when the former is shaken with a solution containing barium and lead nitrate is used as an indicator of the aging of the barium sulfate. Moreover, the change of the total surface of the barium sulfate precipitate after various periods of aging has been determined by measuring the amount of wool violet[5] adsorbed on the saturated surface under specified conditions.

Experimental

Aging of Barium Sulfate in Solutions Containing an Excess of Barium as Determined by the Speed of Formation of Mixed Crystals with Lead.—In all of the following experiments the barium sulfate was prepared from about 0.1 *M* barium nitrate and 0.1 *M* sodium sulfate. To 25 ml. of 0.11 *M* barium nitrate in a 110-ml. bottle was added at 26 ± 1° 25 ml. of 0.10 *M* sodium sulfate; if there were no coprecipitation the mother liquor would be 0.005 *M* in barium. The bottle was stoppered with a paraffined cork and shaken for various periods of time at 26 ± 1° on a mechanical shaker which gave the bottle a vertical throw of about 10 cm. at a speed of 150 phases per minute. After a certain time of aging the bottle was opened and 10 ml. of 0.100 *M* lead nitrate was added. The suspension was put on the mechanical shaker for different periods of time and then centrifuged until the supernatant liquid was clear.

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[1] From a thesis submitted by G. E. Noponen to the Graduate School of the University of Minnesota in partial fulfilment of the requirements of the degree of Doctor of Philosophy, June, 1936.

[2] I. M. Kolthoff and Ch. Rosenblum, THIS JOURNAL, 56, 1264, 1658 (1934); 57, 597, 607, 2573, 2577 (1935); 58, 116, 121 (1936).

[3] Kolthoff and Noponen, *J. Phys. Chem.*, 42, 237 (1938).

[4] I. M. Kolthoff and G. E. Noponen, THIS JOURNAL, 60, 197 (1938).

[5] I. M. Kolthoff and Wm. M. MacNevin, *ibid.*, 59, 1639 (1937).

Twenty-five ml. samples of the latter were analyzed for lead by precipitation as lead chromate in the presence of perchloric acid[4] and iodimetric determination of the precipitate. The results are given in Table I and plotted in Fig. 1.

Table I

Speed of Penetration of Lead into Barium Sulfate after Aging in 0.005 *M* Barium Solution

Time of shaking with lead solution	Percentage of added lead in precipitate Age of precipitate Fresh	5 min.	1 hour	24 hours	1 week
5 minutes	9.4	14.0	4.4	..	...
1 hour	16.7	14.5	9.5	3.3	1.7
24 hours	20.5	19.7	16.7	7.2	3.3
1 week	16.2	16.3	16.3	10.4	5.6
1 month	14.4	..	..	11.0	6.5
2 months	14.1	..	..	10.9	7.7

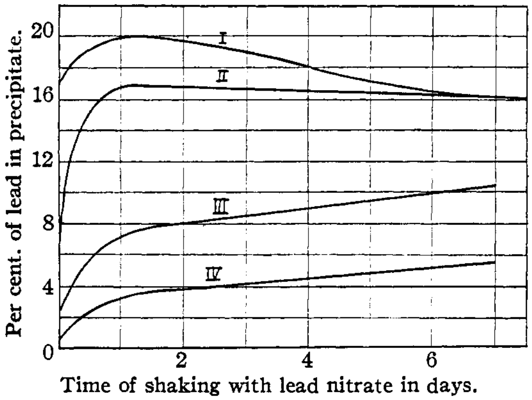

Fig. 1.—Speed of penetration of lead into $BaSO_4$. Ordinate of 16.2 indicates homogeneous distribution of lead through solid phase. I, Fresh; II, 1 hour old; III, 24 hours; IV, 1 week.

The curves for the fresh, five-minutes old and one-hour old precipitates show a maximum in the amount of lead in the solid phase. The occurrence of this maximum disappears with increasing age of the precipitate. In order to explain this maximum we have to distinguish between two types of recrystallizations: (1) recrystallization of the barium sulfate only (unidirectional recrystallization); (2) repeated recrystallizations of the mixed crystals formed as a result of (1). Both processes occur simultaneously. It can be shown easily that the unidirectional recrystallization yields heterogeneous mixed crystals the average lead content of which is greater than that of homogeneous mixed crystals in equilibrium with the mother liquor. Moreover, the barium concentration of the solution increases continuously with increasing incorporation of lead in the solid, while the concentration of lead decreases continuously as a result of the exchange.

$$BaSO_4 + Pb^{++} \longrightarrow PbSO_4 + Ba^{++}$$

During the early stages of shaking fresh (zero to one-hour old) precipitates of barium sulfate, the unidirectional recrystallization (1) is more pronounced, thus explaining the maximum in the amount of lead taken up by the solid as a result of the formation of heterogeneous mixed crystals. The decrease of the lead content after reaching the maximum is due to the repeated recrystallizations which tend to establish equilibrium between the mixed crystals and the solution. After shaking of the fresh suspension for one to two months with the lead solution a homogeneous distribution of the lead throughout the solid phase is found. The occurrence of the maximum depends upon the relative velocities of the two types of recrystallizations; when dealing with a relatively fresh precipitate, type (1) is initially faster than type (2) and a maximum occurs; when dealing with a twenty-four-hour old precipitate the respective velocities become more comparable and no maximum occurs.

From the curves in Fig. 1 it is evident that freshly prepared barium sulfate when aged at room temperature in 0.005 *M* barium solution perfects itself relatively slowly; even in a week-old precipitate the lead distributes itself with a measurable speed.

In the above experiments the sulfate solution was added to the barium solution. Precipitations have been made also in the reverse way by adding 25 ml. of 0.11 *M* barium nitrate to 25 ml. of 0.10 *M* sodium sulfate. From a few of the results given in Table II it is seen that such precipitates behave in a way comparable to those obtained by adding the sulfate to the excess of barium (Table I).

Table II

Speed of Penetration of Lead into Barium Sulfate. Reverse Precipitation

Time of shaking, with Pb solution	1 hour	6 hours	24 hours	1 week	1 month
Lead in ppt. in %, fresh	11.8	16.2	17.4	15.4	13.8
Lead in ppt. in %, 1 hr. old	7.7	12.3	14.5	14.4	13.0

Aging of Barium Sulfate in Solutions Containing an Excess of Sulfate as Determined by the Speed of Formation of Mixed Crystals with Chromate.—To 25 ml. of 0.11 *M* sodium sulfate was added 25 ml. of 0.10 *M* barium nitrate. The suspension was shaken for various periods of time at 26 ± 1°. After a certain time of aging the bottle was opened and 25 ml. of 0.01 *M* sodium chromate was added. The mixture was put back on the shaker and after different periods of time samples were centrifuged and analyzed for chromate iodimetrically. The results are given in Table III and shown graphically in Fig. 2.

TABLE III

SPEED OF PENETRATION OF CHROMATE INTO BARIUM SULFATE AFTER AGING IN 0.005 *M* SULFATE SOLUTION

Time of shaking with chromate soln.	Percentage of added chromate in precipitate Age of precipitate Fresh	1 hour	24 hours
0.5 hour	89.5	..	...
1 hour	92.2	34.6	2.9
2 hours	90.6	..	...
24 hours	82.7[a]	82.7[a]	4.9
1 week	82.7	82.6	6.5

[a] Homogeneous distribution of chromate throughout precipitate.

Only the curve obtained with the fresh precipitate shows a maximum, discussed in the previous section. Apparently the precipitate ages much faster in 0.005 *M* sulfate solution than in 0.005 *M* barium. A similar conclusion is arrived at by comparing the curves in Figs. 1 and 2. This inference, however, is not conclusive, as different indicator ions were used in the two different cases and the speeds of mixed crystal formations of the lead in an excess of barium and of chromate in an excess of sulfate are not quite comparable. In order to get conclusive evidence that the precipitate ages much faster in an excess of sulfate than in an excess of barium the following experiment was performed. To 25 ml. of 0.11 *M* barium nitrate was added 25 ml. of 0.10 *M* sodium sulfate, and the suspension was shaken for twenty-four hours. It was centrifuged, washed once with water and centrifuged again. To the wet precipitate were added 25 ml. of water, 25 ml. of 0.01 *M* sodium sulfate and 25 ml. of 0.01 *M* sodium chromate, this mixture having the same composition as the supernatant liquid in the experiments of Table III, and the suspension was placed in the shaker again. The results are given in Table IV and plotted in Curve D in Fig. 2. Comparison of Curves C and D reveals that the barium sulfate ages much more drastically in 0.005 *M* sulfate than in 0.005 *M* barium solution. A precipitate aged for twenty-four hours in 0.005 *M* barium behaved in about the same way as a precipitate aged for only one hour in 0.005 *M* sulfate solution (Curve B in Fig. 2).

TABLE IV

SPEED OF PENETRATION OF CHROMATE INTO SULFATE AFTER AGING FOR 24 HOURS IN 0.005 *M* BARIUM SOLUTION

Time of shaking with chromate	1 hour	24 hours	1 week
Chromate in precipitate, %	20.9	88.4	86.6

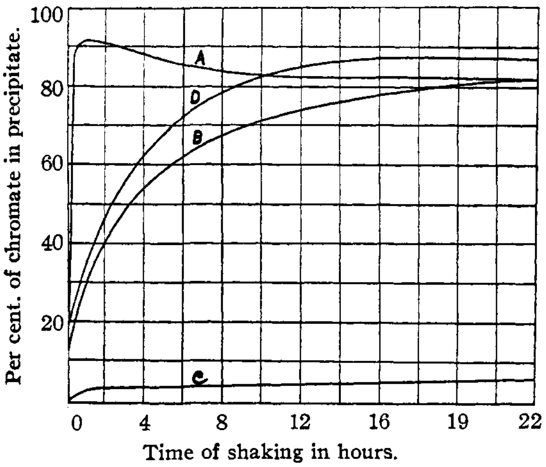

Fig. 2.—Speed of penetration of chromate into barium sulfate: A, fresh precipitate; B, 1-hour old precipitate aged in excess of sulfate; C, 24-hour old precipitate aged in excess of sulfate; D, 24-hour old precipitate aged in excess of barium.

Aging of Barium Sulfate as an Equivalent Body.—Equivalent amounts of 0.1 *M* sulfate and 0.1 *M* barium were added together and the precipitate obtained considered as an "equivalent body." This is not exactly true since the supernatant liquid may not contain equivalent amounts of sulfate and barium as a result of coprecipitation and also because the isoelectric point of barium sulfate may be located asymmetrically. However, for the present purpose the approach to an equivalent body is close enough to justify the conclusions drawn. In order to get comparable results the following experiments were performed. In one series (aging as equivalent body) 10 ml. of 0.1 *M* barium nitrate was added to 10 ml. of 0.1 *M* sodium sulfate. The suspension was aged for various periods of time on the shaker and then 10 ml. of 0.1 *M* sodium sulfate, 50 ml. of water and 10 ml. of 0.1 *M* sodium chromate were added. This mixture was placed on the shaker again and after various periods of time centrifuged samples were analyzed for chromate. In the other series (aging in 0.033 *M* sodium sulfate) 10 ml. of 0.1 *M* barium nitrate was added to 20 ml. of 0.1 *M* sodium sulfate. The suspension was aged for various periods of time on the shaker and then 50 ml. of water and 10 ml. of 0.1 *M* sodium chromate were added. The mixture was shaken for various periods of time and the centrifugate analyzed for chromate. The results are given in Table V and represented graphically in Fig. 3.

TABLE V

SPEED OF PENETRATION OF CHROMATE INTO BARIUM SULFATE AFTER AGING AS EQUIVALENT BODY AND IN 0.033 *M* SULFATE

Time of shaking with chromate soln.	Percentage of added chromate in precipitate Age of precipitate (equivalent body) 1 hour	24 hours	Age of precipitate in 0.033 *M* sulfate Fresh	1 hour	24 hours
1 hour	2.5	0.35	17.4	5.84	0.6
24 hours	10.8	.6	34.5[a]	20.7	1.9
9 days	17.7	.8	35.3[a]	26.3	3.4
3 weeks		1.4			4.3

[a] Equilibrium value.

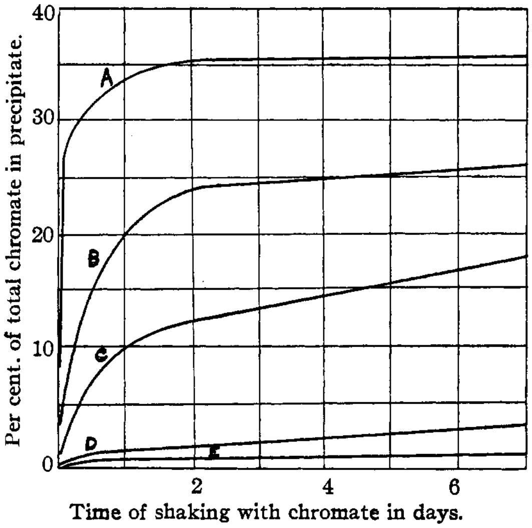

Fig. 3.—A, fresh precipitate; B, 1-hour old precipitate aged in 0.033 *M* sulfate; C, 1-hour old precipitate aged as equivalent body; D, 24-hour old precipitate aged in 0.033 *M* sulfate; E, 24-hour old precipitate aged as equivalent body.

The results show that barium sulfate ages faster as an equivalent body than in a 0.033 *M* sulfate solution. Comparison of Figs. 2 and 3 and of Tables III and V reveals that barium sulfate ages faster in 0.005 *M* sulfate than in 0.033 *M* sulfate solution, whereas in the latter case the aging is much more pronounced than in 0.005 *M* barium solution (Table IV).

Effect of Shaking on Aging.—The experiments described in Table V were repeated with the difference that the precipitate was allowed to age in the supernatant liquid without shaking before addition of chromate, etc. After addition of chromate, etc., the suspensions were shaken as before. For the sake of brevity only a few of the results obtained on aging in 0.033 *M* sulfate solution are reported in Table VI.

TABLE VI

EFFECT OF SHAKING UPON SPEED OF AGING OF BARIUM SULFATE

Time of shaking with chromate solution	Percentage of added chromate in precipitate Age of precipitate 1 hour Not shaken	Shaken	24 hours Not shaken	Shaken
1 hour	6.55	5.85	0.35	0.6
24 hours	21.8	20.7	2.1	1.9
9 days	27.4	26.3	4.0	3.4
3 weeks	..	..	5.2	4.3

These results show that shaking has hardly any effect upon the speed of aging of barium sulfate. Apparently, after the longer periods of aging, the precipitate has perfected itself slightly more when the suspension is shaken than when it is allowed to stand quietly.

Aging of Barium Sulfate Studied by the Adsorption of Wool Violet.—A microscopic measurement of the particle size of fresh barium sulfate precipitated at room temperature by rapid mixing of 0.1 *M* solutions is impossible because of the minuteness of the particles. It has been found[5] that the amount of wool violet adsorbed on the saturated surface of barium sulfate is proportional to the magnitude of the surface of the product. An application thereof has been made in the determination of the change of the magnitude of the external surface of barium sulfate upon aging under various conditions. In the following experiments the original concentration of the dye in the suspension was 500 mg. per liter and never less than 300 mg. per liter after the adsorption had taken place. This has been shown[5] to be a sufficient concentration of dye to give a saturated surface on aged products of barium sulfate. In the first place it was ascertained that adsorption equilibrium was established after a short time of shaking and that the adsorbed dye prevented further change in the extent of surface. The latter result is in agreement with those obtained with lead sulfate[2] and with silver chloride.[6]

To 25 ml. of 0.11 *M* barium nitrate was added 25 ml. of 0.1 *M* sodium sulfate followed immediately by 50 ml. of wool violet solution containing 1 g. of dye per liter. The suspension was put on the shaker. After various periods of shaking samples were taken and centrifuged for five minutes, and 10 ml. of the clear supernatant liquids analyzed for dye by the volumetric method.

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(6) I. M. Kolthoff and H. C. Yutzy, This Journal, **59**, 1215 (1937).

TABLE VII

CHANGE OF SPECIFIC SURFACE OF BARIUM SULFATE AGED IN 0.005 *M* BARIUM SOLUTION

Time of aging before addition of dye	5 min.	1 hr.	5 hrs.	16 hrs.	24 hrs.	41 hrs.	1 wk.	2 wks.
Wool violet adsorbed, mg./1 g. of $BaSO_4$	31.0 31.2	34.4 34.8	38.1	40.6	41.0 41.1	36.7	30.8	26.1

After ten minutes of shaking, 29.9 mg. of dye was found to be adsorbed per gram of barium sulfate, after twenty minutes 31.0 mg., after thirty minutes 31.0 and after one hour 31.0 mg. Hence, adsorption equilibrium is attained quickly. In these and some of the following experiments the barium concentration of the dye-containing suspension was 0.0025 *M*. Since there was a possibility of the precipitation of the barium salt of the dye, a blank was run by mixing 10 ml. of 0.01 *M* barium nitrate, 10 ml. of water and 20 ml. of dye solution (1 g./l.) and shaking the mixture for twenty-one hours. It was found that 1.7 mg. of wool violet had disappeared, which is a negligible amount in these experiments.

Change of Surface of Barium Sulfate Aged in 0.005 *M* Barium Solution and 0.005 *M* Sulfate Solution, Respectively.—To 25 ml. of 0.11 *M* barium nitrate was added 25 ml. of 0.1 *M* sodium sulfate, the suspension was aged with shaking for various periods of time, and then 50 ml. of dye solution was added. The mixture was put on the shaker for one hour, centrifuged and the supernatant liquid analyzed for dye. The results are given in Table VII.

Some figures in Table VII show that the reproducibility of the experiments is very good. The slight increase of the dye adsorption during the first twenty-four hours of aging may be attributed to an increase of the barium concentration in the supernatant liquid.[5] It has been shown (Table I) that upon aging, the barium sulfate perfects itself. This perfection is accompanied by a purification process during which coprecipitated barium salt disappears from the precipitate into the solution. The results of Table VII indicate that the specific surface of barium sulfate decreases very slightly only upon aging of the fresh precipitate in 0.005 *M* barium solution. This is substantiated by the fact that the filterability of the suspension does not improve upon longer periods of aging. In some experiments described below it was necessary to centrifuge the suspensions before addition of dye and other agents to the barium sulfate. Since there was a possibility that centrifuging might pack the particles together and promote aggregation, some of the experiments in Table VII were repeated in such a way that after the aging the suspension was subjected to high speed centrifuging for five minutes; then dye was added as before. With the one-hour old precipitate 33.8 mg. of dye was found to be adsorbed per gram of barium sulfate (without centrifuging 34.6), with the two-weeks old precipitate 25.0 mg. (without centrifuging 26.1). Hence the centrifuging before the addition of the dye has hardly any effect upon the results.

In the following experiments the barium sulfate was aged in 0.005 *M* sulfate before the adsorption of dye was determined. To 25 ml. of 0.11 *M* sodium sulfate was added 25 ml. of 0.1 *M* barium nitrate. The suspension was shaken for various lengths of time, then 50 ml. of dye solution was added, the mixture was shaken for 1 hour and further treated as described above. The results are reported in Table VIII.

TABLE VIII

CHANGE OF SPECIFIC SURFACE OF BARIUM SULFATE AGED IN 0.005 *M* SULFATE SOLUTION

Time of aging before addition of dye	5 min.	1 hr.	24 hrs.	1 week
Wool violet adsorbed; mg./1 g. of $BaSO_4$	25.6	19.4	6.0	5.3

It is found that the surface of the barium sulfate decreases more than 4 times upon aging for twenty-four hours in 0.005 *M* sulfate solution. The results of Tables VII and VIII are not strictly comparable, as in the former case the dye adsorption was determined in an excess of barium and in the latter case in an excess of sulfate. In order to get comparable results the experiments of Tables VII and VIII were repeated. After aging of the precipitates the suspensions were centrifuged, the mother liquor was discarded, and 25 ml. of water, 25 ml. of 0.01 *M* barium nitrate and 50 ml. of dye solution were added. After shaking for one hour the dye concentration was determined in the centrifugate.

From the results in Table IX it is evident that the specific surface hardly changes upon aging in 0.005 *M* barium for twenty-four hours whereas there is a pronounced decrease in 0.005 *M* sulfate.

TABLE IX

CHANGE OF SPECIFIC SURFACE OF BARIUM SULFATE UPON AGING IN 0.005 M BARIUM AND 0.005 M SULFATE, RESPECTIVELY

Time of aging before addition of dye	5 minutes	1 hour	24 hours
Aged in 0.005 M Ba; dye adsorbed mg./1 g. $BaSO_4$	37.2	37.2	42.2
Aged in 0.005 M SO_4; dye adsorbed mg./1 g. $BaSO_4$	37.4	28.5	13.2

It may be inferred that under the experimental conditions the specific surface of the fresh precipitate is practically independent of the order of mixing the barium nitrate and sodium sulfate solution.

Discussion

The present study yields a deeper insight into the mechanism of the aging than has been obtained so far.[2] Moreover, all phenomena observed may be interpreted on the basis of certain views, the correctness of which can be tested experimentally. In the first place it is evident that the classical type of aging, namely, the Ostwald ripening, is of subordinate significance. The Ostwald ripening involves the growth of large particles at the expense of smaller ones, it assumes the irreversible transfer of lattice material from the small particles to the large ones *via* the bulk of the solution (recrystallization by way of the solution). From the facts that the specific surface of barium sulfate aged for longer periods of time in 0.005 N barium solution hardly changes (Tables VII and IX) and that the precipitate is subject to a pronounced perfection upon aging under these conditions (Table I), it follows conclusively that virtually no Ostwald ripening occurs upon aging of fresh barium sulfate in 0.005 M barium solution at room temperature. The results described in this paper and particularly those to be reported in subsequent papers show that the perfection of the particles is to be attributed to a recrystallization process.[2] Since it has been shown that under some conditions the specific surface hardly changes (0.005 M Ba) whereas repeated recrystallizations occur (homogeneous distribution of the lead throughout the solid phases) we are led to the conclusion that these recrystallizations occur in a liquid film around the highly imperfect particles. Lattice ions at highly active spots rapidly enter into the liquid film which becomes supersaturated with regard to more normal surface. Hence, the ions deposit again on the more normal surface, and we get, so to speak, a self-perfection or self-digestion of the particles. The speed of this perfection is extremely great immediately after the formation of the highly imperfect particles and decreases with increasing age in the mother liquor. All factors increasing the solubility of the lattice material in the *liquid film* promote the self-perfection.

It has been shown that the fresh barium sulfate decreases its surface markedly when aged in 0.005 M sulfate. This might be attributed to an Ostwald ripening with the simultaneous occurrence of the self-perfection (Table III). However, the decrease of the specific surface is not necessarily a consequence of the Ostwald ripening and may be attributed to a drastic change of the surface as a result of the perfection or to a cementing together of the particles, or to both. The particles, immediately after their formation, may share their liquid films and form loose agglomerates. During the perfection, lattice material may deposit in the liquid film between the particles in one agglomerate, forming solid bridges. Upon further aging the cementing process may become more complete by the entire elimination of the liquid film by lattice material between the particles in one agglomerate, thus giving rise to the formation of larger crystals with a mosaic structure. This picture explains the decrease of the specific surface obtained on aging in 0.005 M sulfate solution. That the Ostwald ripening does not account for the decrease of the surface may be inferred from the fact that shaking of the suspension is without influence upon the progress of the aging, whereas it would promote the aging materially if recrystallization would occur *via* the bulk of the solution.

The most pronounced perfection has been found upon aging of the "equivalent body." This was to be expected since the solubility of barium sulfate is greatest in a solution containing equivalent amounts of barium and sulfate. Excess of either of these ions represses the solubility and hence the speed of aging. The speed of aging in the mother liquor has been found to decrease in the following order

$$Ba^{++} = SO_4^{=} > 0.005\ M\ SO_4^{=} > 0.033\ M\ SO_4^{=} > 0.005\ M\ Ba^{++}$$

That the speed of aging is less in 0.033 M sulfate than in 0.005 M solution is easily explained by the solubility effect. It was not anticipated that the precipitate would age so much more slowly in 0.005 M barium than in 0.005 M sulfate and even in 0.033 M sulfate.

In order to explain this behavior we have to recall that the speed of perfection does not depend upon the solubility of the barium sulfate in the *bulk of the solution but in the liquid film around the particles.* The fact that barium ions are more effective in inhibiting the aging than sulfate ions may be explained by the fact that barium ions are more strongly attracted by the barium sulfate lattice than are the sulfate ions. The adsorption of barium nitrate is greater than that of sodium sulfate from solutions of the same concentration.[7] Consequently, the concentration of the barium ions in the liquid film may be much greater than that of sulfate ions, although both are present in the same concentration in the bulk of the solution. Barium ions, therefore, inhibit the aging more than sulfate ions. An effect of the charge of the particles may also have to be considered.

Summary

1. Barium sulfate precipitated at room temperature from 0.1 M barium nitrate and 0.1 M sodium sulfate is highly imperfect. Its speed of perfection decreases in the following order with the composition of the mother liquor: $Ba^{++} = SO_4^{=} > 0.005\ M\ SO_4^{=} > 0.033\ M\ SO_4^{=} > 0.005\ M\ Ba^{++}$.

2. The specific surface of fresh barium sulfate increases slightly upon aging for a day in 0.005 M barium solution, showing conclusively that Ostwald ripening does not play a part. The decrease of the specific surface upon aging in 0.005 M sulfate solution is explained by an agglomeration with a subsequent cementing together of the particles as a result of the recrystallizations occurring in the liquid film around the particles.

3. It is postulated that the speed of perfection depends upon the solubility of the lattice material in the liquid film around the particles. In connection herewith an explanation is offered of the fact that barium sulfate perfects itself much more rapidly in 0.005 M sulfate than in 0.005 M barium solutions.

4. The properties of the fresh barium sulfate have been found to be independent of the way of mixing the 0.1 M precipitating agents.

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(7) *Cf.* S. Mattson, *J. Phys. Chem.*, **32**, 1546 (1928).

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

Studies on Aging of Fresh Precipitates. XX. Aging of Freshly Precipitated Barium Sulfate[1]

BY I. M. KOLTHOFF AND G. E. NOPONEN

In a previous paper[2] the mechanism of the aging in dilute barium and sulfate solutions of barium sulfate, precipitated at room temperature from 0.1 M solutions, has been discussed. In the present paper the effects of various factors affecting the speed of aging are discussed. Regarding the materials used and the methods of analysis the reader is referred to the previous paper.[2]

Aging in 50% Ethanol.—The solubility of barium sulfate is much less in mixtures of water and ethanol than in pure water. Therefore it may be expected that the speed of aging will be reduced considerably when the barium sulfate is allowed to age in a medium of 50% ethanol instead of in water. A similar effect of alcohol has been found on the speed of aging of freshly prepared lead sulfate.[3]

To 25 ml. of 0.11 M barium nitrate was added 25 ml. of 0.1 M sodium sulfate followed immediately by the addition of 50 ml. of absolute ethanol. The resulting suspensions containing an excess of barium were shaken for twenty-four hours at 26 ± 1°, centrifuged and the alcoholic mother liquor poured off. To the barium sulfate left were added 25 ml. of water, 25 ml. of 0.01 M sodium sulfate and 25 ml. of 0.01 M sodium chromate and the suspension shaken for one hour and twenty-four hours, respectively. After one hour of shaking 55.5% of the chromate had disappeared by going into the precipitate; after twenty-four hours, 92.0%. When the barium sulfate was aged for twenty-four hours without the addition of 50 ml. of ethanol and then treated as above 20.9 and 88.4% of chromate were found to be removed after one hour and twenty-four hours of shaking with the chromate–sulfate solution. Comparing the results with those in Table III of the previous paper[2] reveals that only very slight aging had occurred

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(1) From a thesis submitted by G. E. Noponen to the Graduate School of the University of Minnesota in partial fulfilment of the requirements of the degree of Doctor of Philosophy, June, 1936.

(2) I. M. Kolthoff and G. E. Noponen, THIS JOURNAL, **60**, 499 (1938).

(3) I. M. Kolthoff and Ch. Rosenblum, *ibid.*, **57**, 597 (1935).