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

Studies on Aging of Fresh Precipitates. XIV. The Aging of Silver Chloride as Indicated by the Speed of Penetration of Bromide Ions into the Solid

BY I. M. KOLTHOFF AND HENRY C. YUTZY[1]

In a previous paper[2] has been reported a study of the aging of freshly precipitated silver chloride as indicated by differences in the amount of a dye, wool violet, adsorbed by preparations of various ages. It was assumed that the magnitude of the dye adsorption was proportional to the external surface presented by the precipitate. In order to gain an insight into other possible phases of the aging process the rate of penetration of bromide ions into the solid was also investigated. In analogy to other aging studies on fresh crystalline precipitates, such as lead sulfate[3] and barium sulfate,[4] it was expected that this mode of attack should reveal considerable information about the speed of perfection and recrystallization of the solid silver chloride. In the other work referred to, it was found that the speed of mixed crystal formation upon shaking of lead sulfate with aqueous thorium B[3] solution and of barium sulfate with solutions of lead or chromate[4] was determined by the speed of recrystallization of the precipitate. From such investigations it was predicted that, qualitatively, similar results would be obtained when the rate of distribution of bromide ions between solid silver chloride and aqueous chloride–bromide solutions was studied. Thus, the anticipated behavior when a standard solution of soluble bromide and chloride was shaken with silver chloride was a more or less rapid initial displacement of chloride in the solid by the bromide to form heterogeneous mixed crystals, followed by a slower continued entrance of bromide until equilibrium was attained. The initial rate of entrance, especially, and the rate of attainment of equilibrium, were expected to vary considerably with the age and degree of perfection of the particular solid in question. Conditions were selected such that there could be no mass precipitation of silver bromide as a second phase. The data obtained in these experiments as described below, do not agree with such expectations and indicate that the explanation of the exchange of bromide with solid silver chloride must be based upon some additional mechanism besides an ordinary recrystallization process.

Experimental

The Speed of Penetration of Bromide into a Nineteen-Hour-old Precipitate.—The precipitates investigated were prepared by adding 25 ml. of 0.2791 *M* silver nitrate with stirring[5] to a mixture of 25 ml. of water and 25 ml. of 0.2791 *M* sodium chloride. After two minutes of stirring the bottles were stoppered and shaken for nineteen hours. After this period 50 ml. of water, 50 ml. of 2 *M* sodium chloride and 50 ml. of 0.01 *M* potassium bromide were added and the shaking continued. After various periods of time the bottles were centrifuged and the supernatant liquids analyzed for bromide by the modified van der Meulen–d'Ans–Höfer[6] method. The final bromide concentrations in the solution are given in Table I. As an indication of the speed of penetration of bromide into the precipitates the values of K' in the expression

$$\frac{[\mathrm{Cl}^-]_{\text{solution}}}{[\mathrm{Cl}^-]_{\text{crystal}}} = K' \frac{[\mathrm{Br}^-]_{\text{solution}}}{[\mathrm{Br}^-]_{\text{crystal}}}$$

are reported in Table I. The values of K' vary with the time of shaking and become equal to the distribution coefficient[7] K when distribution equilibrium has been attained. The values of K' are given in parentheses as they indicate the progress of distribution but do not correspond to equilibrium conditions. For comparison the data obtained with a fresh precipitate are also given in Table I.

TABLE I

SPEED OF PENETRATION OF BROMIDE INTO A 19-HOUR-OLD PRECIPITATE

Time of shaking with bromide solution, hours	19-hour-old precipitate		Fresh precipitate	
	Bromide concn. in soln., $M \times 10^4$	K'	Bromide concn. in soln., $M \times 10^4$	K'
0	22.2		22.2	
1	2.96	(100)	1.90	(160)
3	2.11	(146)	1.50	(200)
11	1.69	(185)		
25	1.63	(193)	1.22	(265)
71	1.30	248[a]		
144	1.29	250[a]	1.28	252[a]

[a] Equilibrium value of K.

Apparently, the bromide enters the precipitate faster when the latter is fresh than when it is nineteen hours old. How-

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(1) From a thesis submitted by H. C. Yutzy to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

(2) I. M. Kolthoff and H. C. Yutzy, THIS JOURNAL, **59**, 1215 (1937).

(3) I. M. Kolthoff and C. Rosenblum, *ibid.*, **56**, 1264, 1658 (1934); **57**, 597, 607, 2573, 2577 (1935); **58**, 116, 121 (1936).

(4) G. E. Noponen, Thesis, University of Minnesota, June, 1936.

(5) For exact conditions, *cf.* ref. 2.

(6) I. M. Kolthoff and H. C. Yutzy, *Ind. Eng. Chem., Anal. Ed.*, **9**, 75 (1937).

(7) H. C. Yutzy and I. M. Kolthoff, THIS JOURNAL, **59**, 916 (1937).

TABLE II

SPEED OF PENETRATION OF BROMIDE INTO PRECIPITATES AGED FOR THIRTY-FIVE DAYS IN VARIOUS MEDIA

Aging medium	Bromide concentration ($M \times 10^5$) in solution after shaking for 2 hrs.	6 hrs.	24 hrs.	7 days	31 days	K' after 31 days
1 M ammonia	11.55	9.37	8.25	6.60	5.68	(112)
2 M NaCl	15.35	9.99	8.22	6.07	4.22	(168)
Water	12.4	9.90	7.60	5.40	4.06[a]	(174[b])
0.001 M $AgNO_3$ in water	11.1		5.27	3.54	3.70	(195)
0.001 M NaCl in water	13.6		7.26	4.92	4.06	(174)
Ethanol	9.64	7.25	5.37	3.86	3.56	(204)
0.5 M LiCl in ethanol	8.64	7.34	6.75	4.38	4.14	(170)
0.001 M $AgNO_3$ in ethanol	7.87	6.30	4.89	4.04	3.54	(205)
Fresh, not filtered	5.59		3.19	3.01[c]	3.08	243
Fresh, but filtered	8.02	5.51	4.27	3.05	3.06	241

[a] After 55 days 3.36. [b] After 55 days 223. [c] After five days instead of after seven days.

ever, the difference in behavior between the two precipitates is very slight, and the proposed method is not suitable for a study of the changes occurring during the early stages of aging.

Effect of the Medium upon Precipitates Aged for Thirty-five Days.—A number of precipitates were prepared in as nearly the same way as possible. To 210 ml. of 0.2791 M sodium chloride were added 210 ml. of water and with constant stirring 210 ml. of 0.3355 M silver nitrate. Five minutes after precipitation, the precipitate was washed several times by decantation, filtered on sintered glass and washed again with water and then several times with the solution in which aging was to take place. Not less than ten nor more than fifteen minutes after precipitation, the silver chloride was removed from the filter and suspended in 100 ml. of the aging medium and rapidly shaken for thirty-five days. After this time, it was filtered on a sintered glass crucible, washed with water, then with ethanol and made air dry by sucking air through for three hours. In the distribution experiments 0.080-g. portions of the precipitates were shaken with a mixture of 100 ml. of 0.2 M sodium chloride, 50 ml. of 0.001 M potassium bromide and 75 ml. of water (initial bromide concentration $2.2 \times 10^{-4}M$). After various periods of shaking the supernatant liquids were analyzed for bromide as described above. The results of duplicate experiments (referring to the aging of silver chloride) agreed within the experimental error. The aging media and the results are given in Table II and some of the data are plotted in Fig. 1. It is readily seen from curves 5 and 6 in Fig. 1 that the speed of penetration of bromide into the fresh silver chloride is reduced materially during the early periods of shaking with bromide if the precipitate is filtered and air-dried before shaking it in the chloride–bromide mixture. It is evident that these precipitates, which are extremely well aged, particularly Nos. 1 and 2, are taking up bromide much more rapidly during the early stages of shaking than would be expected to occur as a result of recrystallization of the solid phase.

Effect of Wool Violet on the Speed of Penetration of Bromide.—In the aging studies of fresh lead sulfate[3] it was found that wool violet adsorbed on the precipitate prevented the recrystallization of the latter and its aging, although it allowed a kinetic exchange to take place between lead ions in solution and on the surface of the precipitate. Thus, it was possible to determine the specific surface of freshly precipitated lead sulfate by Paneth's method with radioactive lead in the presence of wool violet. It was expected that the dye would have a similar effect upon the aging of silver chloride. In a previous paper[2] it was shown conclusively that the specific surface of fresh silver chloride did not change with time of shaking when the surface of the particles was saturated with dye.

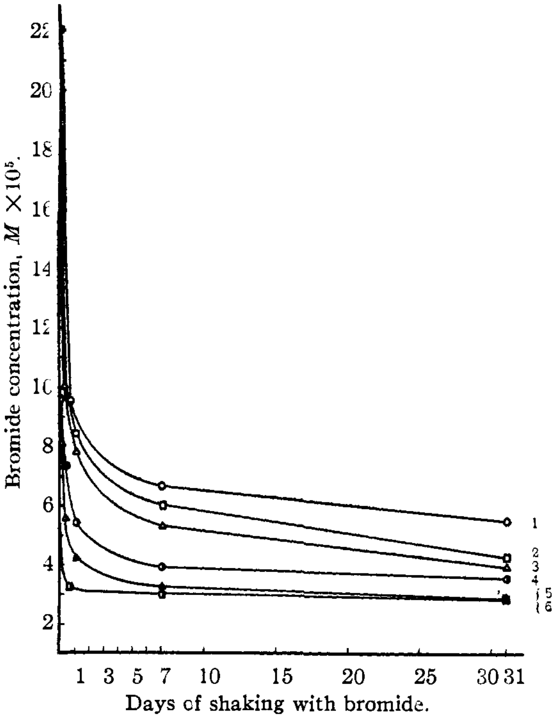

Fig. 1.—Speed of penetration of bromide into aged silver chloride: ○ curve 1, 1 M NH_3; □ curve 2, 2 M NaCl; △ curve 3, water; ◑ curve 4, ethanol; ▲ curve 5, fresh, filtered; ◧ curve 6, fresh, unfiltered.

If the adsorbed dye would allow a kinetic exchange between surface chloride and bromide ions in the solution but prevent a further penetration of the bromide into the solid, it should be possible to determine the specific surface of a precipitate of silver chloride of any age, making use of the known distribution coefficient of bromide between silver chloride and solution. Actually, it was found that adsorbed wool violet allowed the kinetic exchange to take place on the surface of silver chloride and that it retarded the entrance of bromide into the solid considerably, but did not prevent it. Thus, if silver chloride is saturated with wool violet and the suspension shaken with a solution containing chloride and bromide, the concentration of the latter in the solution not only decreases relatively rapidly until kinetic exchange equilibrium between surface and solution is attained, but continues to decrease slowly due to penetration of the bromide into the solid. The following experiment illustrates this behavior.

TABLE III

SPEED OF PENETRATION OF BROMIDE INTO FRESH PRECIPITATE (2.79 MILLIMOLES OF AgCl) IN THE PRESENCE OF WOOL VIOLET

Time of shaking with bromide	Concn. bromide, *M*/1.	Bromide in soln., moles	Chloride in soln., moles	Bromide in ppt., moles
2 hrs.	16.9×10^{-5}	3.89×10^{-5}	0.02	1.10×10^{-5}
24 hrs.	16.6×10^{-5}	3.82×10^{-5}	.02	1.17×10^{-5}
4 days	16.9×10^{-5}	3.89×10^{-5}	.02	1.11×10^{-5}

TABLE IV

SPEED OF PENETRATION OF BROMIDE INTO FRESH PRECIPITATE IN THE PRESENCE OF WOOL VIOLET

Time of shaking with bromide, days	Concn. bromide, *M*/1.	Bromide in soln., moles	Chloride in soln., moles	Bromide in ppt. moles	Average	Surface, %
1	21.3×10^{-4}	4.90×10^{-4}	0.200	1.00×10^{-5}	1.1×10^{-5}	0.92
4	21.2×10^{-4}	4.88×10^{-4}	.200	1.23×10^{-5}		
1	8.78×10^{-5}	2.02×10^{-5}	.020	0.49×10^{-5}	0.52×10^{-5}	.81
4	8.43×10^{-5}	1.94×10^{-5}	.020	0.56×10^{-5}		
(5)	(11.7×10^{-5})	(2.7×10^{-5})	(.010)	(2.31×10^{-5})		(1.8)

A fresh precipitate was prepared by placing 10 ml. of 0.2791 *M* sodium chloride and 10 ml. of water in a weighed bottle and adding, with stirring, 10 ml. of silver nitrate (0.2791 *M*). After five minutes of additional stirring, 50 ml. of wool violet containing 1 g. of dye per liter and 100 ml. of 0.2 *M* sodium chloride were added and the whole shaken for half an hour to allow attainment of adsorption equilibrium. Then 50 ml. of 0.001 *M* potassium bromide was added and shaking continued for various periods of time before analysis. The analytical procedure used was as follows: after shaking, the bottle was strongly centrifuged and as much as possible of the supernatant liquor removed by suction. Then the bottle and residue were weighed and the volume of the residual solution calculated from the weight difference. The precipitate and residual solution were digested with 10 g. of sodium chloride before analyzing for bromide by the D'Ans–Höfer method.[6] From these data the amount of bromide in the precipitate can be calculated easily. In these cases it was necessary to analyze the solid phase for bromide as the amount of this constituent removed from the solution was too small to determine accurately by analysis of the liquid phase before and after shaking. Some of the results are given in Table III.

The amount of bromide taken up by the precipitate in this case is apparently constant. If this is assumed to be present in the surface of the precipitate as a mixed crystal, the amount of chloride originally present in the surface may be calculated, assuming the distribution coefficient to be approximately 300, from the relation

$$[\mathrm{Cl}]_{\text{Surface originally}} = [\mathrm{Br}]_{\text{Surf.}}\left(1 + \left(\frac{\mathrm{Cl}}{\mathrm{Br}}\right)_{\text{Soln.}} \times \frac{1}{300}\right)$$

$$= 1.15 \times 10^{-5}\left(1 + \frac{0.02}{3.85 \times 10^{-5}} \times \frac{1}{300}\right)$$

$$= 3.15 \times 10^{-5} \text{ mole}$$

This represents a mole fraction of bromide of 1.15/3.15 = 0.36 which corresponds roughly to a *K* of 300.[7] This calculation would show the fresh precipitate to have a surface of approximately $(3.15 \times 10^{-5})/(2.79 \times 10^{-3}) \times 100 = 1.1\%$. Similar experiments were carried out, varying only the amount of excess chloride and soluble bromide added. They are reported below, together with the apparent ratio of surface to solid as calculated above.

In the above experiments a continued entrance of bromide is observed upon longer periods of shaking, but this entrance is very slow. In the absence of dye a twenty-five hour period of shaking is sufficient for the attainment of homogeneous distribution through the solid phase, corresponding to a calculated "surface" of 100% instead of 1% as is found in the presence of dye.

It is gratifying to note that the amounts of surface calculated from the experiments reported in Tables III and IV agree so well, even though the amounts of chloride and bromide in the solutions varied within wide limits. This indicates that the method may be useful for the determination of the amount of surface of fresh precipitates of silver chloride.

Similar experiments were carried out with 0.5 g. (= 3.49

TABLE V

SPEED OF PENETRATION OF BROMIDE INTO 3.49 MILLIMOLES OF ONE-YEAR OLD PRECIPITATE IN THE PRESENCE OF WOOL VIOLET

Time of shaking with bromide, weeks	Br(soln.) moles $\times 10^5$	Br(ppt.) moles $\times 10^6$	Cl(soln.) moles	Cl(surface calcd.) moles $\times 10^6$	Surface, %
1	4.16	0.83	0.04	3.49	1.0
3	3.66	1.33	.04		
1	3.06	1.92	.01	4.0	1.2
3	2.36	2.61	.01		
1	1.75	0.75	.02	3.6	1.0
3	1.45	.98	.02		
1	8.30	1.79	.02	3.2	0.9
3	6.07	4.13	.02		
1	48.8	1.09	.2	2.6	.7
3	48.6	1.33	.2		
1	24.2	0.84	.2	3.2	.9
3	24.0	.95	.2		

$\times 10^{-3}$ mole) of a precipitate which had been aged for a year in water. In this case the period of shaking was extended to one week and three weeks, respectively.

Again, a slow entrance of bromide is observed, although the precipitate used was one year old. For this reason, the value of the amount of surface calculated after one week of shaking (0.7–1.2%) is much too high. The one-year old precipitate adsorbed only about 0.2 mg. of dye per gram, as compared to 3 mg. per gram by the fresh silver chloride.

The surface of this year old precipitate was estimated using the radioactive method.[8] Radioactive chloride was prepared by radiation of 6 molar sodium chlorate, containing a known amount of sodium chloride, with radon-beryllium, extraction of the radio chloride with silver nitrate and conversion to soluble chloride via a sulfide treatment. Further details are given in the thesis of the junior author[1] and in the literature.[9] The "indicated" chloride solution of known activity was shaken for various periods of time with 5 g. of the aged precipitate before measuring the activity of the supernatant liquid. The amount of radio-chloride entering the solid was found to be constant after five minutes within the experimental error (10%) and indicated a surface of 0.05 to 0.06%. This substantiates the above conclusion that the surface calculated from the results given in Table V is much too high.

Effect of Gelatin on Speed of Penetration of Bromide and on Aging.—Since gelatin is often used as a protective colloid in nephelometric determinations, and since it plays a predominant part in photographic emulsions, a few experiments were made to study the effect of gelatin on the aging of silver chloride and upon the speed of penetration of bromide into the precipitate. From the work described in the literature one would expect that gelatin would exert an effect similar to that of adsorbed dye.

In the analyses of the supernatant liquid for bromide the gelatin was removed by evaporation to dryness and fusion with sodium peroxide in a nickel crucible. The residue was taken up in water, filtered, neutralized, evaporated to a smaller volume and analyzed for bromide by the method mentioned previously.

In the distribution experiments fresh precipitates (0.08 g.) were prepared by adding 2.00 ml. of 0.2791 *M* silver nitrate to a mixture of 2.00 ml. of water and 2.00 ml. of 0.2791 *M* sodium chloride. Two minutes after precipitation 20 ml. of water, 50 ml. of 1.12% gelatin solution (Nelson's Photographic No. 1) and 100 ml. of 0.2 *M* sodium chloride were added and the mixture shaken for three hours. Then 50 ml. of 0.001 *M* potassium bromide was added, the suspensions shaken for various periods of time and the supernatant liquids analyzed for bromide. A similar set of experiments was run in which the precipitates were aged for fifty hours in the chloride-gelatin solution before the addition of bromide.

In order to study the effect of gelatin upon the aging of the precipitate a set was run in which the precipitates were aged in the chloride solutions for fifty hours before adding the gelatin and the bromide. Finally two sets of experiments were run with a precipitate aged for a year in water, determining in one set the rate of distribution of bromide in the absence of gelatin and in the other in the presence of gelatin.

TABLE VI

DISTRIBUTION AND AGING IN GELATIN

Aging conditions	Condition of distribution	Bromide concn. in soln. $\times 10^4$ after time shaking 0	2 hrs.	22 hrs.	1 week
Five minutes old	No gelatin	2.22	0.55	0.32	(0.30)
Three hours in NaCl–gelatin	In gelatin	2.21	1.99	1.73	1.05
50 hours in NaCl	In gelatin	2.21	2.15		1.97
50 hours in NaCl–gelatin	In gelatin	2.21	2.12		1.97
1 year old in H_2O	No gelatin	2.21	1.13	0.65	0.48
1 year old in H_2O	In gelatin	2.22	2.17	2.16	2.11

Discussion

1. From a comparison of the speed of entrance of bromide into a fresh and a nineteen-hour old precipitate (Table I), one might infer that the latter precipitate had aged very slightly only. In the introduction of this paper it was stated, however, that the speed of penetration of the bromide into the precipitate is not determined solely by the speed of recrystallization of the particles, but under the experimental conditions also by another mechanism. That the precipitate ages considerably when kept in the mother liquor could be shown in two ways. In the first place the speed of entrance of chloride was determined when the precipitate was shaken with a radioactive chloride solution. This speed is determined by the rate of recrystallization of the precipitate as is the speed of penetration of thorium B into lead sulfate by the rate of recrystallization of the latter.[3] The experiments were carried out with the aid of Dr. Donald Hull[8] and will not be reported in detail. Due to the rapid decay of the radioactive chlorine the results are of a qualitative nature only. They showed conclusively, however, that the rate of entrance of the radioactive chloride decreased rapidly with increasing age of the silver chloride. Qualitatively the behavior resembled that of thorium B with lead sulfate.[3] In the second place, the experiments carried out in the presence of gelatin (Table VI) showed conclusively that a rapid aging of the silver chloride occurred in dilute chloride solutions. After the precipitate, which had been aged for three hours in the presence of gelatin, had been shaken for one week with bromide (in the presence of gelatin) more than 50% of the bromide had been removed from solution. When the precipitate was aged for fifty hours in dilute sodium chloride only 11%

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[8] At this place we wish to express our sincere appreciation to Dr. D. Hull for his valuable aid in the performance of the experiments.

[9] S. C. Lind, D. Hull, and C. Shiflett, THIS JOURNAL, **58**, 535 (1936).

of the bromide was removed after the same period of shaking. Apparently, the addition of gelatin before the bromide allows a much closer differentiation between the progress of aging of silver chloride, particularly during the early stages of the aging, than when the gelatin is absent. From a practical viewpoint it is unfortunate that the analyses became so time-consuming in the presence of gelatin.

2. From the results obtained with precipitates kept for thirty-five days in various media, it is evident that all of them had aged drastically. Even after shaking for thirty-one days with a chloride–bromide solution, distribution equilibrium had not been reached with any of the precipitates. The effect of the nature of the aging medium is pronounced, particularly when the parts of the curves are compared when the latter have flattened out (Fig. 1). The speed of aging was found to decrease in the following order: 1 M ammonia > 2 M sodium chloride > water > ethanol. This is the same order in which the solubility of silver chloride decreases, the solubility being 0.06 M in 1 M ammonia, 4×10^{-4} M in 2 M sodium chloride, 1.3×10^{-5} M in water, and 1×10^{-7} M in ethanol. Hence, the aging is favored by increasing solubility, a result in agreement with that obtained in the aging studies of lead sulfate.[3] The presence of a slight excess of lattice ions in a particular medium was not found to be very pronounced. Still, from the results in Table II it is seen that the precipitate aged less rapidly in 0.001 M silver nitrate than in pure water, whereas the precipitate aged in 0.001 M chloride behaved in about the same way as that aged in water. By means of the wool violet method[2] a much more rapid aging was found in 0.001 M chloride than in water. However, in the latter case the effects were studied during the first twenty hours of aging only, and the results are not strictly comparable to those in which the aging period was extended over a period of thirty-five days.

3. Adsorbed wool violet was found to decrease greatly the speed of penetration of bromide into the silver chloride. Indication was obtained that upon relatively short periods of shaking of the chloride–bromide solution with the precipitate the exchange is limited to the surface layer only. Making use of this fact it was estimated that about 1% of a fresh precipitate, obtained under conditions as described in this paper, consists of surface. It may be expected that the method should be applicable to the determination of the surface of aged products if the proper time of shaking for the attainment of surface equilibrium is established.

4. From a comparison of the speed of entrance of bromide into a fresh precipitate in the presence and absence of gelatin (Table V) it is evident that the gelatin greatly lowers the speed of penetration but does not prevent it. Undoubtedly, gelatin retards the kinetic exchange between solution and surface, as the latter is covered more or less with adsorbed protein. The adsorbed protein is strongly hydrated, which may account for the unexpected fact that the speed of aging of silver chloride, as indicated by the rate of entrance of bromide, was found to be the same in the absence as in the presence of gelatin (fifty-hour old precipitates, Table VI). This result indicates that the Ostwald ripening was insignificant as compared with other types of aging, as the gelatin certainly inhibits the speed of recrystallization in the bulk of the solution considerably.

A more extensive study of the aging of silver bromide is being carried out in which use is made of the speed of distribution of radioactive bromide as an indicator of the speed of perfection of the particles. Since the mechanism of the distribution of bromide through silver chloride and solution is not entirely understood a detailed interpretation of the results described in this paper is reserved until the study with silver bromide is concluded.

Summary

1. The speed of penetration of bromide into silver chloride upon shaking of a solution containing chloride and bromide with the precipitate is not determined solely by the rate of recrystallization.

2. During the early stages of the aging of silver chloride the rate of entrance of bromide into the precipitate is a good indicator of the progress of the aging if gelatin is added to the system.

3. Increasing solubility in the aging medium increases the speed of aging.

4. Gelatin and particularly wool violet retard the penetration of bromide into silver chloride strongly but do not prevent it.

5. The speed of aging as indicated by the speed of entrance of bromide into the precipitate is the same when the aging is carried out in the presence

of gelatin as in the absence of gelatin. This result shows that Ostwald ripening is of no, or of subordinate, significance under the aging conditions described in the paper.

6. The magnitude of the surface of a year-old precipitate has been determined by Paneth's method using radioactive chloride as an indicator.

7. Indication has been obtained that the amount of bromide removed from the solution corresponds to exchange in the surface layer only, if the values obtained upon shaking of silver chloride in the presence of wool violet are extrapolated to a zero time of shaking.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA AND THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Determination of the Specific Surface of Barium Sulfate

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

In a previous publication[1] methods have been described for the determination of the distribution coefficient *K* of thorium B between the surface of barium sulfate and solutions in water or in 50% ethanol. Knowing the value of *K* the same methods can be applied to the determination of the specific surface of arbitrary samples of barium sulfate

$$Ba_{surface} = \frac{ThB_{surface}}{ThB_{solution}} \times \frac{Ba_{solution}}{K}$$

From the practical viewpoint the method involves certain disadvantages. In the first place it requires equipment for the radioactive measurements. In the determination of the distribution of thorium B between the surface and the solution, the fraction of the thorium B entering the lattice as a result of recrystallization has to be taken into account. This recrystallization complicates matters, particularly when dealing with fresh, imperfect precipitates. Finally the amount of barium in solution has to be known under equilibrium conditions. If the barium sulfate investigated is imperfect and impure, and contains coprecipitated barium or sulfate, as is often the case, the amount of barium added to the solution may change during the experiment and should be determined in the sample when analyzed for thorium B.

In a discussion of exchange adsorptions on the surface of barium sulfate[2] it was mentioned that the following reaction can be made use of in the determination of the specific surface

$$\underset{\text{Surface}}{Ba^{++}SO_4^{=}} + \underset{\text{Solution}}{CrO_4^{=}} \longrightarrow \underset{\text{Surface}}{Ba^{++}CrO_4^{=}} + SO_4^{=}$$

The following relation holds when equilibrium is attained in the surface

$$\frac{CrO_4^{=}{}_{surface}}{CrO_4^{=}{}_{solution}} = K\,\frac{SO_4^{=}{}_{surface}}{SO_4^{=}{}_{solution}}$$

K being equal to 1.1 at 25°.[2]

With imperfect products of barium sulfate the exchange upon shaking with solutions containing sulfate and chromate is not limited to the surface layer only, because there is recrystallization. Upon extrapolation of the "time–adsorption" curve to a time of shaking of zero, the amount of chromate exchanged in the surface is found when the product does not recrystallize too rapidly. The method has distinct advantages over the "radioactive" one, because it is easily carried out and slight impurities of sulfate or barium in the barium sulfate have hardly any effect upon the results. Moreover, a rapid and simple method has been developed, according to which the magnitude of the surface was found from the amount of wool violet adsorbed when the surface was saturated with the dye. The use of wool violet 4BN for the determination of the specific surface of lead sulfate has been described before.[3] In the latter case the same amounts of wool violet were found to be adsorbed from solutions containing either slight excess of sulfate or of lead. In the case of barium sulfate such a simple relation was not found to hold.

Preparations Used

Wool Violet 4BN.—Several samples were obtained from the National Aniline and Chemical Company and purified by methods described previously. The sodium content was found to be 4.04%, although in the earlier work the sodium content was found to be 5.85–6.0% (theoretical

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[1] I. M. Kolthoff and W. M. MacNevin, THIS JOURNAL, **58**, 725 (1936).

[2] I. M. Kolthoff and G. E. Noponen, *ibid.*, **59**, 1237 (1937).

[3] I. M. Kolthoff, W. von Fischer and Charles Rosenblum *ibid.*, **56**, 832 (1934).