$\sin^2 \theta$ and observed intensities for the room temperature and high temperature photographs. The high temperature picture was indexed on the basis of a rhombohedral centered hexagonal unit cell, $a = 2.96$ Å., $c = 15.77$ Å. It is isomorphous with lithium nickelate(III) ($a = 2.878$ Å., $c = 14.19$ Å.) and with sodium ferrate(III) ($a = 3.01$ Å., $c = 15.93$ Å.). One extra line of weak intensity was observed on the high temperature picture. It corresponds with the strongest line (hkl = 111) of the room temperature monoclinic form.

Acknowledgment.—The authors are indebted to Dr. J. R. Johnson who took the Debye–Scherrer photographs of sodium nickelate(III), to Mr. S. D. Fulkerson who did the differential thermal analysis, and to Mr. J. H. Edgerton and co-workers who performed some of the chemical analyses.

OAK RIDGE, TENNESSEE

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

Studies on Aging and Coprecipitation. XLIV. Aging of Silver Bromide in the Colloidal State[1]

BY I. M. KOLTHOFF AND R. C. BOWERS

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Upon aging of freshly prepared colloidal supensions of silver bromide a marked decrease of the specific surface is found as measured by adsorption of wool violet and by electron microscopy. This decrease is a result of Ostwald ripening. After about one day at room temperature, no further change occurs by Ostwald ripening and a metastable period is attained when the concentration of ions in solution is below the rapid flocculation value. This may be followed by a period of slow flocculation. Effects of temperature, dialysis and potassium nitrate in various concentrations on Ostwald ripening and slow coagulation have been investigated. Cyanide and an excess of bromide promote Ostwald ripening. The rate of exchange between freshly prepared silver bromide particles in colloidal suspension and radioactive bromide in solution is extremely great, homogeneous distribution being attained within a few seconds. With a well-aged dialyzed colloid the rapid exchange is limited to a distance of 50 to 80 Å. beyond the surface of the particles. This very rapid exchange is attributed to Schottky defects which cause, even at room temperature and at 0°, a high silver and bromide mobility. Adsorbed wool violet limits the exchange to the surface layer only; adsorbed dye also prevents Ostwald ripening.

The aging of silver bromide in the flocculated state, either in contact with a solvent or as a dry powder has been studied by Kolthoff and O'Brien[2] who concluded that silver bromide is subject to thermal aging, which they attribute to the relatively high thermal mobility (even at room temperature) of the silver and bromide ions held at the surface of the precipitate. In measurements of the electrical conductivity of pellets of silver bromide, Shapiro and Kolthoff[3] substantiated this high mobility of the surface ions of silver bromide. No exact picture could be given of the nature of the thermal mobility. It was thought that the thermal mobility caused a cementing together and then a complete fusion of the primary particles in a floc of silver bromide.

In order to learn more of the nature of the thermal mobility of silver and bromide ions in silver bromide, it was decided to first study the aging of silver bromide in the colloidal state in which no fusion of particles can occur. In a subsequent paper the aging of silver bromide flocs prepared from colloidal solutions of varying age will be described. It will be shown there that the aging of flocculated silver bromide is entirely thermal in nature, not only in the dry state, but also in dilute aqueous bromide solution.

As long as the particles are in the colloidal state the main type of aging to be anticipated is so-called Ostwald ripening, *i.e.*, small particles with a larger solubility go into solution and larger particles grow at the cost of the small ones. As is shown in the present paper the Ostwald ripening is found to be surprisingly rapid and gives rise to a very considerable decrease of the number of particles upon aging of the colloidal solution. This could be followed by measurements of the specific surface by means of wool violet[4] and by taking electron micrographs. Further insight into the thermal mobility of silver and bromide ions in colloidal particles of silver bromide was obtained by measuring the rate of exchange between inactive particles and radioactive bromide dissolved in the medium. In freshly prepared colloids complete homogeneous exchange between solid and liquid was observed within a few seconds. When sols were dialyzed and permitted to age no complete exchange between all the bromide in the particles and that in solution was found, but the very rapid exchange was several times greater than would correspond to surface exchange only.

Experimental

Preparation and Aging of Colloidal Silver Bromide Suspensions. Stock Solutions.—0.1000 M silver nitrate solutions were prepared from Mallinckrodt A.R. silver nitrate which had been powdered and dried at 150°.

0.03214 M and 0.1000 M potassium bromide solutions were made from potassium bromide prepared by thermal decomposition of Mallinckrodt A.R. potassium bromate.

Method I. Non-dialyzed Colloid.—Forty-five-ml. samples of colloid were prepared by adding with a pipet having a drainage time of 13 seconds, 10 ml. of 0.1000 M silver nitrate to 35 ml. of 0.03214 M potassium bromide contained in a 100-ml. bottle. All of the non-dialyzed samples of colloid were prepared in this manner with the exception of a few where the effect of the concentration of potassium nitrate or the concentration of excess bromide was to be studied. In general the colloidal suspensions were 0.0222 M in solid

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[1] This investigation was supported by a research grant from the Office of Ordnance Research.

[2] (a) I. M. Kolthoff and A. S. O'Brien, THIS JOURNAL, **61**, 3414 (1939); (b) *J. Chem. Phys.*, **7**, 401 (1939).

[3] I. Shapiro and I. M. Kolthoff, *J. Phys. Colloid Chem.*, **52**, 1319 (1948).

[4] I. M. Kolthoff and A. S. O'Brien, THIS JOURNAL, **61**, 3409 (1939).

silver bromide, 0.0222 *M* in potassium nitrate and 0.00278 *M* in potassium bromide.

Method II. Dialyzed Colloid.—Nine hundred ml. of silver bromide colloid was prepared by adding 200 ml. of 0.100 *M* silver nitrate to 700 ml. of 0.0321 *M* potassium bromide while the solution was being stirred. The colloid was then poured into cellulose dialysis tubing and these tubes placed in a large glass cylinder, through which distilled water was allowed to flow continually. Dialysis was carried out for 40–42 hours at 25°, and after this period of time the dialyzed colloid was diluted to one liter in a volumetric flask. The amount of silver bromide was determined by flocculating and weighing the precipitate obtained from a given volume of the colloidal suspension. The excess bromide present in the colloidal suspension was determined by an amperometric titration of 25 ml. of the colloid with 0.0100 *M* silver nitrate. Prior to the titration, the colloidal silver bromide was flocculated with 2 ml. of 1 *M* calcium nitrate and aged until the supernatant liquid was clear. Eight drops of 0.5% gelatin were then added and the titration carried out at zero applied volt *vs.* the S.C.E. The concentration of nitrate ion in the supernatant liquid of a flocculated colloidal suspension was determined polarographically following the procedure recommended by Kolthoff, Harris and Matsuyama.[5]

In all the dialyzed colloidal suspensions the concentration of soluble bromide ion was between 5.6×10^{-5} and 3.0×10^{-4} *M*. This corresponds to from 88 to 98% removal of the dissolved bromide originally present. The concentrations of nitrate ion dropped to values between 2.9×10^{-5} and 8.6×10^{-5} *M*, which corresponds to 99.5 to 99.8% removal of the nitrate.

In some of the experiments a larger concentration of excess potassium bromide was desired than would remain after dialysis. The necessary concentration of excess bromide was obtained by adding a known volume of 0.1000 *M* potassium bromide to the dialyzed colloid before diluting to the mark in the volumetric flask. The exact concentration was determined after dilution by means of the amperometric titration mentioned above.

Method III. Electrodialyzed Colloid.—In a few of the experiments electrodialyzed silver bromide colloid was used. This was prepared by placing about 200 ml. of silver bromide colloid in the center compartment of an electrodialyzer and distilled water in the two outer ones. Not more than 0.5 ampere was then passed through the colloid solution by utilizing a 110 v. d.c. source of power and adjusting the current by means of a variable resistance in series with the electrodialyzer. In approximately 2 hours the current began to drop because of the decreased conductance of the colloidal suspension. The electrodialysis was terminated when the current fell to about 0.01 ampere with no external resistance in the circuit. After electrodialysis, excess potassium bromide was added and the concentration of silver bromide and bromide ion determined as outlined above.

Experimental Methods. (a) Determination of Specific Surface with Wool Violet.—A known volume of standard wool violet was added to the colloidal suspensions of silver bromide, which always contained an excess of bromide. The suspensions were shaken for one hour and the colloid then flocculated by making the suspension 0.04 *M* in calcium nitrate. After centrifugation a portion of the supernatant liquid was drawn off and diluted to an appropriate volume in order to determine the optical density at 550 mμ with a Beckman Model B spectrophotometer. It was shown that, at 550 mμ, a plot of optical density *vs.* concentration of wool violet gave a straight line between concentration limits of 0.001 and 0.008 mg./ml., and that calcium did not affect the optical density of the wool violet solutions.

O'Brien[6] found that adsorption equilibrium of wool violet on silver bromide was attained very rapidly and that surface saturation was complete when the equilibrium concentration of wool violet was above 30 mg./ml. We found no appreciable difference between the amount of wool violet adsorbed at equilibrium concentrations between 40 and 216 mg./ml. Equilibrium was found to be established in less than one-half hour of shaking with wool violet.

(b) Exchange with Radioactive Bromide.—Radioactive Br^{82} which has a half-life of 34 hours was obtained on allocation from Oak Ridge National Laboratories as irradiated potassium bromide. Standard counting plates were prepared from each stock solution of the r.a. bromide and their decay followed over the entire period during which the stock solution was used. The counting plates were prepared by precipitation of the r. a. bromide as silver bromide from known volumes of stock solution or of the supernatant liquid of the exchange systems. Sufficient inactive potassium bromide was added to give 100 mg. of silver bromide upon precipitation. The precipitate of silver bromide was filtered onto a disk of filter paper[7] which was then placed in a shallow aluminum disk.

For the determination of the amount of exchange between r.a. bromide in solution and silver bromide a known quantity of r.a. bromide stock solution was added in a few seconds, from a calibrated syringe to a sample bottle containing colloidal silver bromide. After shaking for various periods of time, the colloid was flocculated by making the suspension either 0.04 *M* in calcium nitrate or 0.001 *M* in lanthanum nitrate and a small portion of the supernatant liquid rapidly filtered by suction through a sintered glass filter. When the exchange between r.a. bromide and wool violet coated particles was determined, the sample bottles were centrifuged after flocculation with calcium nitrate.

A Geiger-Mueller Model TGC-21B84 thin mica window tube counter was used for counting. Sufficient time was allowed in counting each plate so that the total number of counts would be 10^4 or more. Correction for decay was made by comparison with standard plates.

(c) Electron Micrographs.—The electron microscope offers an excellent method for studying the actual dimensions and habit of colloidal particles which are from about 0.01 μ to several μ in diameter. It was realized that a direct observation of the silver halides would not be possible under the electron microscope because of decomposition upon exposure to the electron beam. It was found that sufficient exposure to sunlight would completely reduce the silver in the colloidal silver bromide particles to the metal, the residual silver having the same shape as the original particle.

Observations of various preparations of silver bromide colloid were made under the electron microscope. Before mounting the colloidal particles on the grid, they were diluted to give a colloidal suspension of from 0.004 to 0.008% by weight in silver bromide. The dilution was made with a solution of wool violet of sufficient strength to ensure the complete saturation of the surface of the silver bromide particles with the dye. Immediately after dilution, a very small drop was placed on a nickel grid which had previously been coated with a thin layer of formvar. After about a minute the excess liquid on the grid was withdrawn with a piece of filter paper. The grid was then exposed to direct sunlight for one-half hour to one hour before placing it in the microscope.

An RCA Model EMU-2 electron microscope, equipped with a biased gun and intermediate lens, was used. Magnification calibration had been carried out by means of a shadowed formvar replica of an original diffraction grating which measured 14,438 lines/inch. Before being photographed in the microscope, the average spacing of the pre-shrunk replica had been determined in a spectrometer. Supplementary meters, which read objective and projector lens currents more accurately than is possible with the control panel test meter, eliminated the necessity of exact duplication of specimen distance for each specimen studied (for further details of the calibration procedure used for this particular microscope (see Hartmann).[8]

Experimental Results

A. **Wool Violet Adsorption.** (1) **Aging** of Non-dialyzed **Colloidal Silver Bromide.**—In this series of experiments, samples of silver bromide colloid were prepared by method I and aged for various periods of time before the addition of wool violet. Aging was carried out by: (1) allowing the bottles to stand undisturbed at room temperature (in the dark); (2) shaking the bottles at room temperature; (3) allowing the bottles to stand undisturbed in an oven kept at 90 ± 2°.

It was observed that upon standing overnight a considerable portion of the silver bromide had settled, leaving a

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[5] I. M. Kolthoff, W. F. Harris and G. Matsuyama, THIS JOURNAL, **66**, 1782 (1944).

[6] A. S. O'Brien, Ph.D. Thesis, University of Minnesota (1938).

[7] F. C. Henriques, Jr., G. B. Kistiakowsky, C. Margnetti and W. G. Schneider, *Ind. Eng. Chem., Anal. Ed.*, **18**, 349 (1946).

[8] J. F. Hartmann, *J. Comp. Neur.*, **99**, 201 (1953).

small layer of relatively clear supernatant liquid above the colloid. After several days standing (or a few hours at 90°), a very compact ring of silver bromide adhered to the bottom of the vessel and the supernatant liquid was entirely clear. This ring of silver bromide was quite difficult to dislodge from the bottom of the vessel even with shaking.

The results are plotted in Fig. 1, x/m being the number of mg. of wool violet adsorbed per gram of silver bromide. All of the colloidal suspensions were 0.0222 M in silver bromide and 0.00278 M with respect to potassium bromide during the aging period. The concentration of potassium nitrate was varied from 0.0222 to 0.12 M in the colloidal suspension allowed to age by standing.

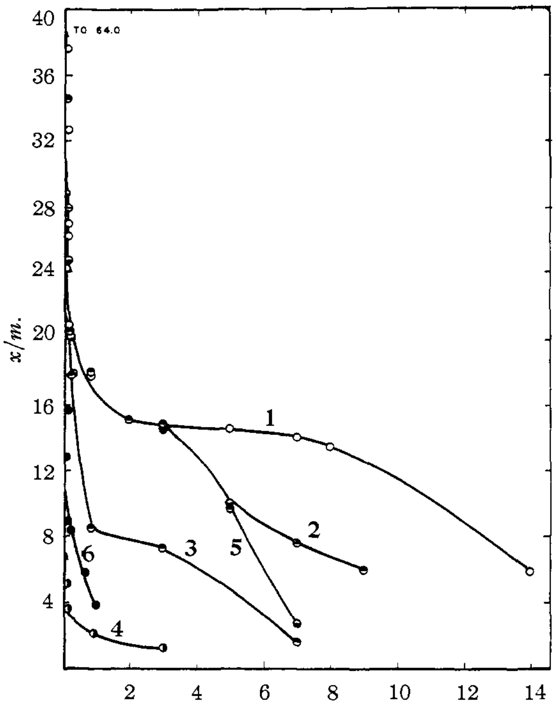

Fig. 1.—Adsorption of wool violet on colloidal silver bromide: 1, 0.0222 M in KNO_3; 2, 0.045 M in KNO_3; 3, 0.070 M in KNO_3; 4, 0.12 M in KNO_3; 1-4 all standing at 25°; 5, 0.0222 M in KNO_3, shaken at 25°; 6, 0.0222 M in KNO_3, standing at 90°.

(2) **Aging in the First Few Minutes after the Addition of Potassium Nitrate.**—In order to study the effect of electrolyte concentration on the rate of aging of silver bromide colloids in the first few minutes after the addition of electrolyte, samples prepared by method I were aged for one minute. Then 10 ml. of 0.45 M, 0.55 M or 1.67 M potassium nitrate was injected with a hypodermic syringe. After the desired period of aging with stirring, wool violet solution was added, also by means of a hypodermic syringe; and the amount of wool violet adsorbed determined.

Figure 2 indicates that there is a limiting concentration of potassium ion above which a further increase in its concentration does not affect the rate of decrease in specific surface. This fact was made use of in determining the "flocculation value" of potassium nitrate with respect to fresh silver bromide colloid.

Samples of fresh colloid were prepared by method I. After one minute they were made from 0.097 to 0.324 M with respect to potassium nitrate. Ten seconds after the injection of the potassium nitrate solution, a solution of standard wool violet was introduced by means of a hypodermic syringe and the wool violet adsorption determined. From Fig. 3 we obtain a flocculation value of 0.108 M for potassium nitrate for fresh silver bromide colloid.

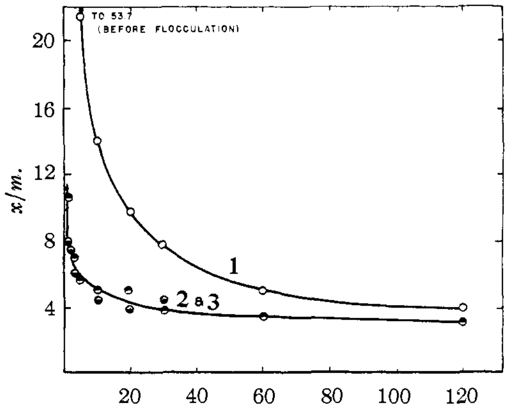

Fig. 2.—Decrease in specific surface of fresh colloid in the first two minutes after the addition of KNO_3: 1, ○, 0.102 M in KNO_3; 2, ◓, 0.120 M in KNO_3; 3, ◒, 0.324 M in KNO_3.

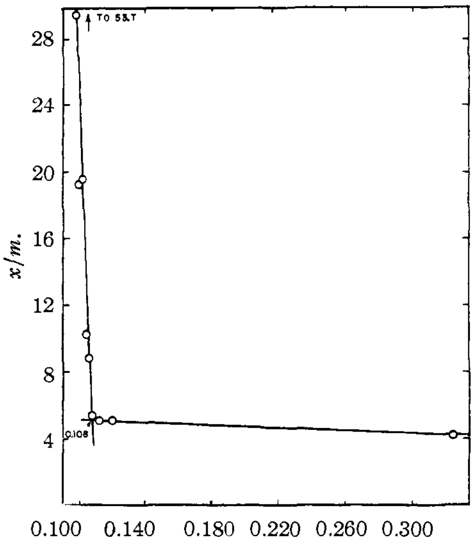

Fig. 3.—Wool violet adsorption as a function of KNO_3 concentration on flocculated fresh silver bromide, ten seconds after addition of electrolyte.

(3) **Aging of Dialyzed Colloidal Silver Bromide.**—Dialyzed colloids prepared by method II were aged by allowing the colloids to stand at room temperature, and at 90°, and by shaking at room temperature. In Fig. 4, the time of aging refers to the time elapsed following the termination of dialysis, which was 42 hours after the formation of the colloid.

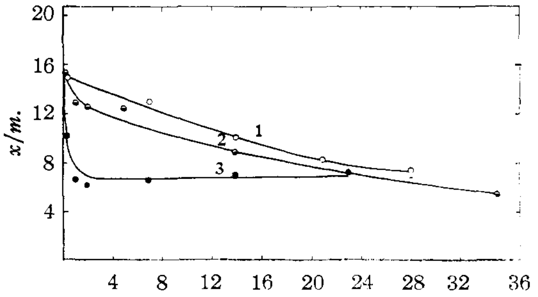

Fig. 4.—Decrease in wool violet adsorption upon further aging of dialyzed colloid 0.02 M in silver bromide: 1, 0.0025 M in KBr, standing at 25°; 2, 0.0028 M in KBr, shaken at 25°; 3, 0.0028 M in KBr, standing at 90°.

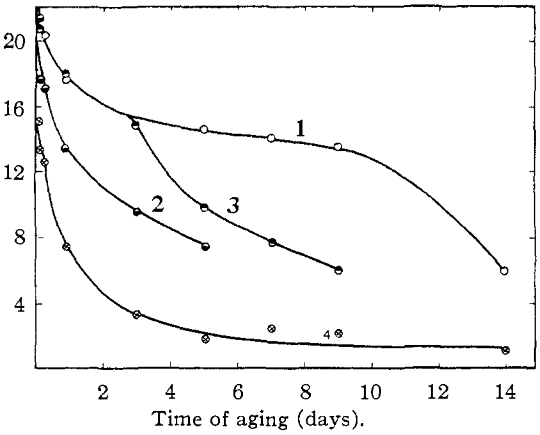

Fig. 5.—Effect of KCN and concentration of KBr on rate of aging of non-dialyzed colloid: 1, 0.0222 *M* in KNO_3, 0.00278 *M* in KBr; 2, 0.0222 *M* in KNO_3, 0.00278 *M* in KBr, 1.0×10^{-4} *M* in KCN; 3, 0.045 *M* in KNO_3, 0.0025 *M* in KBr; 4, 0.020 *M* in KNO_3, 0.0275 *M* in KBr, all aged by standing.

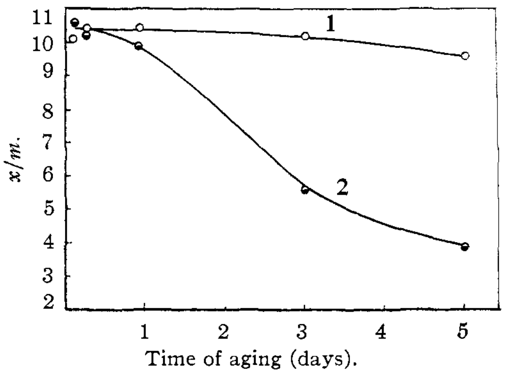

Fig. 6a.—Effect of KCN on rate of aging of 2 week old dialyzed colloid: 1, 0.0025 *M* in KBr; 2, 0.0025 *M* in KBr, 1.0×10^{-4} in KCN.

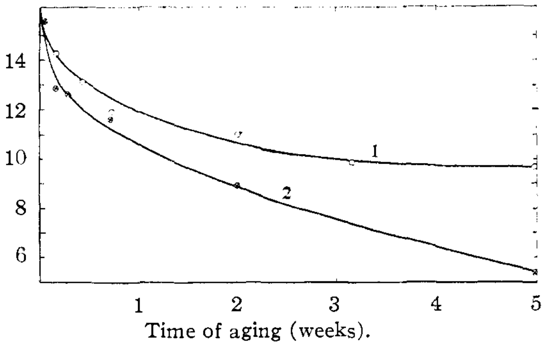

Fig. 6b.—Effect of KBr concentration on aging of 2-day old dialyzed colloid: 1, 0.00029 *M* in KBr, 0.0025 *M* in KNO_3; 2, 0.0028 *M* in KBr.

A clear supernatant liquid was observed after several days of standing at room temperature. The settled colloid appeared to have a very small volume of sedimentation and would not readily break up upon shaking.

(4) **Effect of Increasing the Bromide Ion Concentration and of a Small Amount of Cyanide Ion on the Aging of Silver Bromide Colloids.**—Increasing the bromide concentration and the presence of ammonia have been found to increase the rate of aging of flocculated silver bromide.[2a] Experiments were carried out on the effect of bromide and of cyanide concentration on the aging of both non-dialyzed colloids and dialyzed colloids. The desired concentrations of potassium bromide, nitrate and cyanide were obtained by adding solutions of these salts to the fresh colloid or to the dialyzed colloid after dialysis. The concentration of potassium ion in these colloidal suspensions was kept constant by varying the concentration of potassium nitrate.

Aging of the non-dialyzed colloids was carried out by letting the colloids stand undisturbed at room temperature in the dark, whereas the aging of the dialyzed colloids was allowed to proceed with shaking at 25°.

(5) **Aging of Silver Bromide in the Presence of Wool Violet.**—Several colloids were prepared by method I and allowed to age for 5 minutes. Five ml. of a solution of wool violet containing 2 g./l. of the dye was then added and the bottles shaken for one-half hour to ensure a complete saturation of the surface with wool violet. The colloidal suspensions were then aged without shaking for various periods of time and the amount of wool violet present in the supernatant liquid determined in the usual manner. Even after 4 weeks of standing no change in the specific surface was observed. Hence adsorbed wool violet prevents aging.

B. **Exchange between Radioactive Bromide Ions in Solution and Silver Bromide Colloids.**—The results of the measurements of the extent of r.a. bromide penetration into silver bromide precipitates are expressed in two different ways.

(1) Apparent % exchange: this quantity is defined as

$$\text{Apparent \% exchange} = \frac{\text{activity in solid} \times 100}{\text{activity in solid at 100\% exch.}} \qquad (1)$$

(2) Apparent mmoles of bromide exchanging per mmole of silver bromide: if the exchange is homogeneous then the following relationship is valid

$$\left(\frac{Br^-}{Br^{-*}}\right)_{Sol.} = \left(\frac{Br^-_{exch.}}{Br^{-*}_{exch.}}\right)_{Solid} \qquad (2)$$

If A_0 is designated as the initial activity of the supernatant liquid, A_t as the activity of the supernatant liquid at time *t*, M_p as the number of millimoles of silver bromide and M_s the number of millimoles of bromide ion in the solution, then equations 1 and 2 become, respectively

$$\text{Apparent \% exchange} = \frac{(A_0 - A_t) \times 100}{(A_0(M_p/M_s + M_p)} \qquad (3)$$

$$\frac{\text{Apparent mmoles Br}^- \text{ exch.}}{\text{mmole AgBr}} = \frac{M_s(A_0 - A_t)}{M_pA_t} \qquad (4)$$

(1) **Exchange between R.A. Bromide Ions in Solution and Non-dialyzed Silver Bromide Colloids of Various Ages.**—The rate of exchange of r.a. bromide ions with silver bromide colloids which were (1) fresh, (2) 9 days old and (3) 4 weeks old (flocculated) was determined both in the presence and absence of wool violet. The colloids were prepared by method I, and aged by standing at room temperature for the appropriate time before the addition of the r.a. bromide stock solutions.

With freshly prepared colloidal silver bromide suspensions and in the absence of wool violet the distribution of bromide was homogeneous (100 % exchange) within the time required to separate solid from liquid (about 15 seconds). In the experiments performed in the presence of wool violet, the colloidal suspensions were shaken for one-half hour with the dye before r.a. bromide was added. The exchange found after 30 minutes of shaking was practically the same as after three hours. With a fresh (1 min. old) silver bromide colloid the exchange corresponded to 0.150 mmole of bromide per mmole of silver bromide, with a 9-day old colloid to 0.06 and a four-week old suspension (flocculated) to 0.01. When the fresh colloid was aged for 4 weeks in the presence of wool violet the exchange was the same as found originally. Some typical results obtained with a 9-day old colloid are illustrated in Table I.

(2) **Exchange between R.A. Bromide and Dialyzed Colloids.**—Dialyzed colloids were prepared both by methods II and III. Those prepared by method II were aged for two weeks before the exchange was measured. Electrodialyzed colloids, prepared by method III, which were two weeks old were further aged for 4 and 24 hours, respectively, at 90° before exchange measurements were made. The results of these experiments are listed in Tables II and III.

TABLE I

EXCHANGE BETWEEN R. A. BROMIDE AND 9-DAY OLD COLLOIDAL SILVER BROMIDE

$M_p = 1.00$; $M_s = 0.136$; $x/m = 13.4$.

	No wool violet		Wool violet present	
Time of exch., min.	Apparent % exch.	Apparent mmoles Br^- exch./ mmole AgBr	Time of exch., min.	Apparent mmoles Br^- exch./ mmole AgBr
0.5	97.4	0.81	30	0.062
1	98.4	.87	60	.072
3	98.5	.89	120	.065
11	99.1	.92	180	.067
30	100	.99		
60	99.5	.94		

TABLE II

APPARENT EXCHANGE WITH 2-WEEK OLD DIALYZED COLLOID PREPARED BY METHOD II

$M_p = 0.941$; $M_s = 0.135$; $x/m = 13.6$.

	No wool violet		Wool violet present
Time of exch., min.	Apparent % exch.	Apparent mmoles Br^- exch./ mmole AgBr	apparent mmoles Br^1 exch./ mmoles AgBr
2	90.3	0.54	...
5	92.6	.62	...
15	93.9	.66	...
30	(97.1)	(.81)	0.051
60	94.5	.68	.056
120	96.2	.77	.047
180	..	..	.051

TABLE III

EXCHANGE WITH ELECTRODIALYZED COLLOIDS AGED 4 AND 24 HOURS, RESPECTIVELY, AT 90° AFTER A PREVIOUS AGING PERIOD OF 2 WEEKS AT ROOM TEMPERATURE

$M_p = 0.417$; $M_s = 0.108$.

	Aged for 4 hr. at 90°; $x/m = 10.7$		Aged for 24 hr. at 90°; $x/m = 7.4$	
Time of exch., min.	Apparent % exch.	Apparent mmoles Br^- exch./ mmole AgBr	Apparent % exch.	Apparent mmoles Br^- exch./ mmole AgBr
0.5	89.5	0.64		
1	90.3	.65	48.9	0.17
3	86.8	.58	56.0	.21
10	95.5	.82	76.5	.40
30	91.7	.70	75.0	.38
60	89.9	.65	79.0	.44

C. Electron micrographic Studies.—Electron microscope pictures were made of (1) fresh silver bromide colloids, (2) non-dialyzed silver bromide colloids which were 17 hours old, 40 hours old and 4 days old, (3) dialyzed colloids 6 weeks old and (4) non-dialyzed silver bromide colloids which had been aged 4 weeks in the presence of wool violet. In every case the aging was allowed to proceed without shaking.

Some representative photographs are shown in Figs. 7, 8, 9 and 10, the arrow indicating the length of 1 μ.[9] Dimensions of the same order of magnitude as those observed in the colloids aged for 17 hours were found in the colloids aged for 40 hours and for 4 days.

Discussion

(1) The specific surface of a fresh silver bromide colloidal suspension which is low in electrolyte decreases very rapidly when it is allowed to age for one day at room temperature (see curve 1, Fig. 1). There is hardly any difference in the amount of aging during the initial 3 days when the suspension is shaken or not. From the electron micrographs (Figs. 7 and 8) it is evident that during this initial aging period the extremely small primary particles disappear and that the larger particles grow at the cost of the small ones. Hence this type of aging is typical of Ostwald ripening. That Ostwald ripening occurs is substantiated by the fact that the rate of aging increases upon increasing the solubility by the addition of cyanide or bromide (Fig. 5) or by increasing the temperature to 90° (curve 6, Fig. 1).

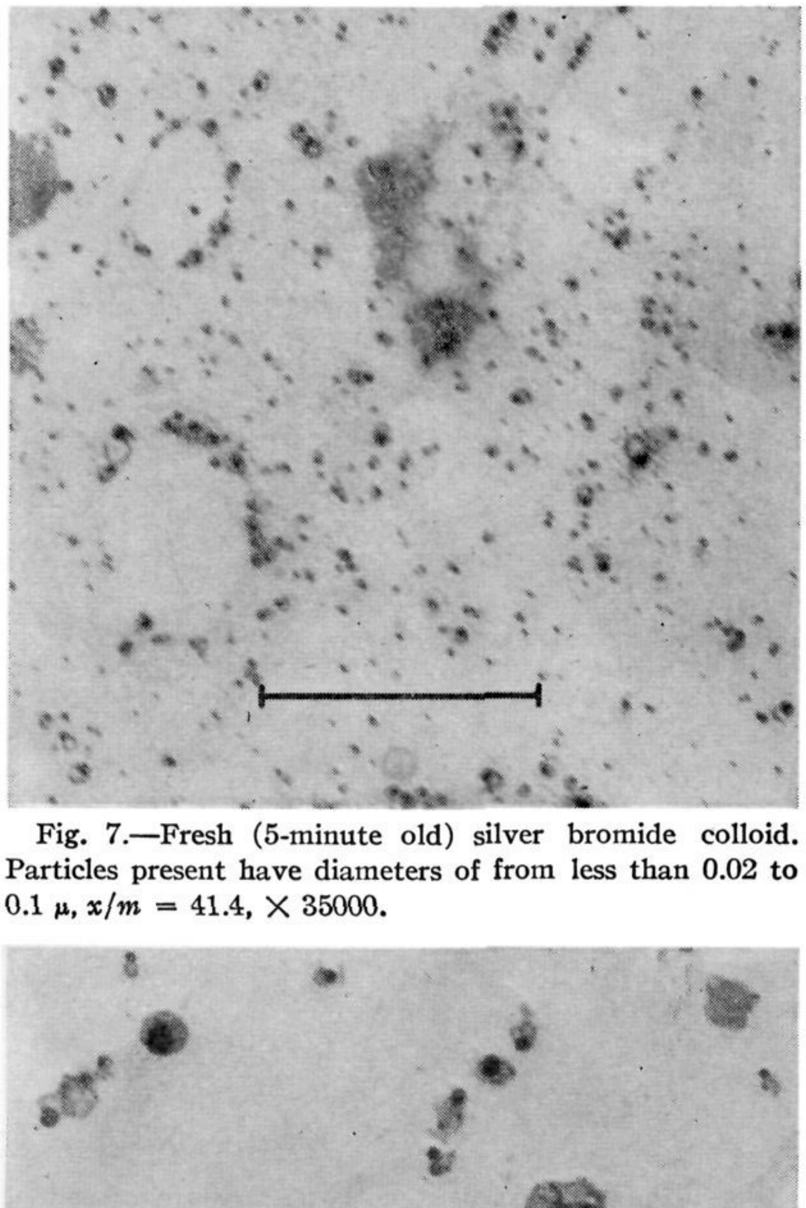

Fig. 7.—Fresh (5-minute old) silver bromide colloid. Particles present have diameters of from less than 0.02 to 0.1 μ, $x/m = 41.4$, × 35000.

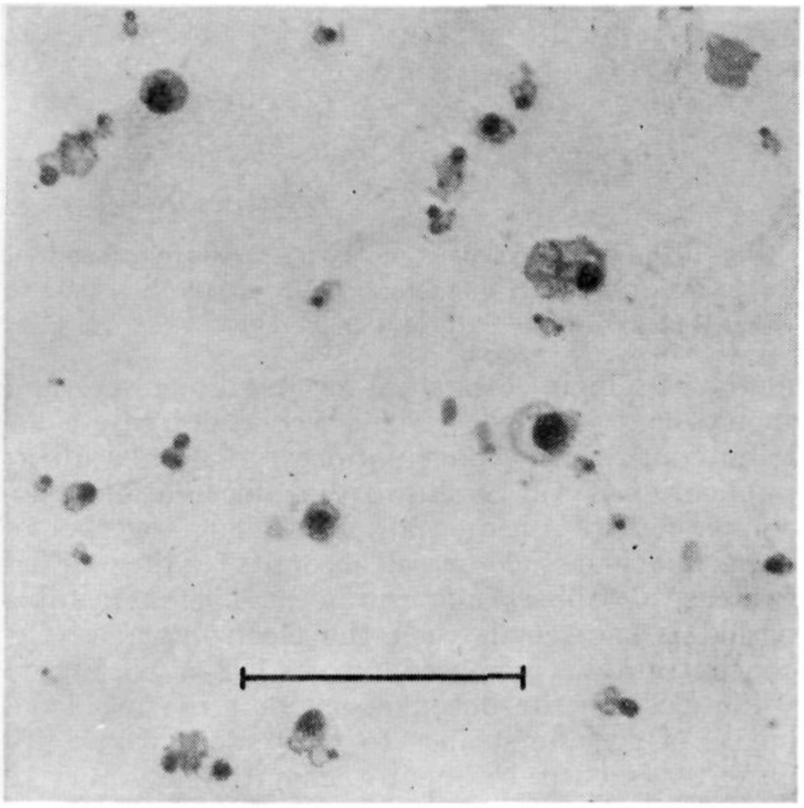

Fig. 8.—Seventeen hour-old non-dialyzed colloid. These particles have diameters of from 0.05 to 0.3 μ; $x/m = 18$, × 35000.

After about one day of aging at room temperature the specific surface of a colloid prepared by

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[9] In Fig. 7 the particles are distorted in one direction, probably because of a slight deformation during exposure of the formvar coating on the grid. This figure shows the extremely small dimensions of the particles present in the fresh colloid.

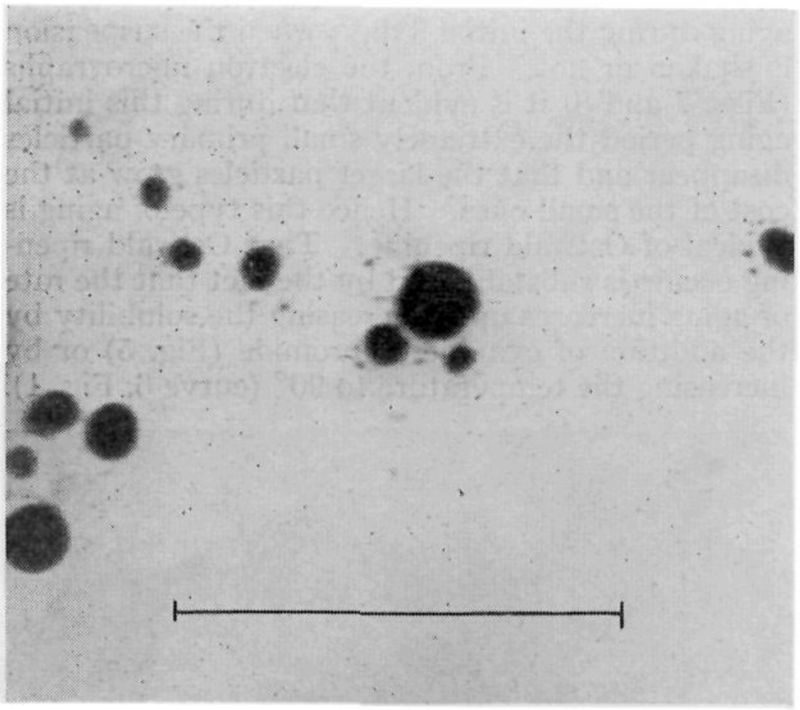

Fig. 9.—Six-week old dialyzed colloid. Particle diameters are from 0.06 to 0.3 μ, × 57000.

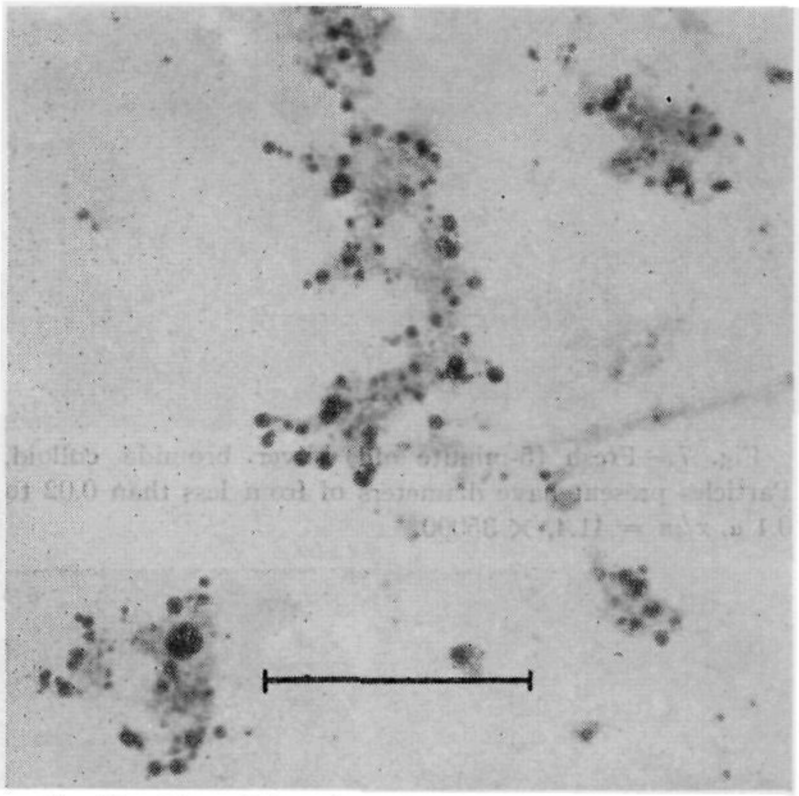

Fig. 10.—Non-dialyzed colloid aged 4 weeks in presence of wool violet. Particle diameters are from less than 0.02 to about 0.15 μ; x/m = 38.6, × 33000.

method I remained constant for about one week and then decreased slowly. This second decrease is attributed to a slow coagulation. In a subsequent publication it will be shown that flocculation is accompanied by a cementing and fusing together of the primary particles which accounts for the marked decrease of the specific surface. The metastable period is shortened when the electrolyte (KNO_3) concentration is increased (curves 1, 2 and 3, Fig. 1) *while close to the flocculation point the rapid decrease of specific surface to very small values apparently is entirely due to cementing together of particles.* As a matter of fact the flocculation point of silver bromide can be sharply defined on the basis of the very rapid decrease of the specific surface (Fig. 3).

The rate of slow flocculation as represented by the rate of change of specific surface of the particles after the flat portions in the curve increases with increasing potassium nitrate concentration and also with shaking.

Small concentrations of potassium bromide and cyanide eliminate the metastable period of the colloid (Fig. 5) while similar and even considerably larger concentrations of potassium nitrate have no appreciable effect. Apparently the enhanced Ostwald ripening in the presence of cyanide or bromide gives rise to the formation of particles of such size that they are not small as compared to the thickness of the double layer and thus cause a decreased stability of the colloidal particles.[10] In the presence of small concentrations of potassium bromide or cyanide the decrease in surface in the first portion of the curves 2 and 4 in Fig. 5 it is due to Ostwald ripening, but after one or two days mainly to flocculation.

Dialysis of the fresh suspension gives rise to a stable colloid. During the period of dialysis the particles undergo Ostwald ripening and reach such dimensions that they become relatively stable. An increase of the solubility by raising the temperature to 90° or by adding a little cyanide or bromide causes a marked further decrease of the specific surface (Fig. 6) because of a continued Ostwald ripening.

Wool violet adsorbed on the particles prevents Ostwald ripening. From electron micrographs (Fig. 10) it appears that some agglomeration not accompanied by a cementing together (decrease of surface) occurs when a fresh colloidal suspension is kept a long time in the presence of wool violet.

(2) Previous work[4] on exchange with r.a. bromide was carried out with freshly flocculated precipitates of silver bromide, the specific surface of which is of the order of one thirtieth that of a freshly prepared colloid. The instantaneous homogeneous exchange even at 0° between a fresh colloid and r.a. bromide in the solution found in the present work cannot be attributed to recrystallization of the particles by way of solution because the Ostwald ripening is too slow a process as compared to the extremely rapid exchange. The results must be attributed to a high thermal mobility of the bromide ions throughout the extremely small particles of silver bromide. In an interpretation of the theory of photographic emulsions, Mitchell[11] postulated that in addition to Frenkel defects (vacant silver lattice and interstitial silver ions in the lattice) there occur coupled pairs of positive and negative ion vacancies. These Schottky defects could account for the high mobility of the bromide ions throughout the tiny particles. Homogeneous exchange was practically instantaneous even after aging for 9 days at which time the specific surface had decreased four times. More striking and instructive are the experiments carried out with well aged dialyzed colloids. With such a colloidal suspension, which had undergone an additional aging for 4 hours at 90° an apparent exchange of 90% was obtained within 30 seconds and this value hardly changed when the time of exchange was extended to one hour (Table III). Even after several hours

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(10) E. J. W. Verwey, J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier Publ. Corp., New York, N. Y., 1948.

(11) J. W. Mitchell, *Sci. Industr. Photogr.*, **19**, 361 (1948).

no complete exchange between all the bromide in the particles and bromide in solution was observed.

From this behavior it is concluded that the Schottky defects do not extend throughout the larger particles but are only present in the outer layers. Thus a rapid diffusion of bromide ions can occur through these layers with Schottky defects but not through the inner core free of these defects. From the diameter, d, of the particles (Table V) and the number of mmoles of bromide exchanged per mmole of silver bromide in the Schottky layers the thickness of the shell can be estimated. Let the radius of the core in which no exchange occurs be r_x and the radius of the particle be r_0, then

$$\text{thickness of Schottky layer} = (r_0 - r_x) = r_0(1 - (\text{fraction of AgBr in core})^{1/3})$$

TABLE IV

THICKNESS OF SCHOTTKY LAYERS IN SILVER BROMIDE

Product	$r_0 \times 10^{-7}$ cm. (see Table V)	Mmoles Br^- exch. mmole AgBr (Schottky layer)	$(r_0 - r_x) \times 10^7$, cm.
Fresh	5.8	1.00	>6
9 days old	14	0.90	7.5
2 weeks old, dialyzed	17	.65	5
Electrodialyzed, then aged, 4 hr. at 90°	22	.63	6
Electrodialyzed, then aged 24 hr. at 90°	33	.37	5

The thickness of the Schottky layers in particles of 9-day old colloid was calculated to be 75 Å. and that of the well-aged dialyzed colloid 50 Å. corresponding to 27 and 18 layers, respectively. These thicknesses compare favorably with those estimated by Grimley and Mott[12] who state that the concentration of vacant lattice sites (Schottky) in a region of the order of 10^{-6} cm. (100 Å.) thick near the interface of silver bromide exceeds by several powers of ten their concentration in the bulk of the crystals.

(3) In agreement with previous work[4,13] our results show that an adsorbed layer of wool violet apparently limits the exchange to the surface layer only. With this assumption an extrapolation to zero time of a plot of mmoles Br^- exch./mmoles AgBr *vs.* time of exchange in the presence of wool violet gives us a measure of the percentage surface. This quantity has been determined over a fairly wide range of specific surfaces of the silver bromide and has been found to be almost proportional to the values of x/m. From the number of mmoles Br^- surface (per mmole of silver bromide) the number of bromide ions on the surface per adsorbed wool violet molecule can be found.

Assuming spherical particles of silver bromide, the diameter of the particles can be calculated from the equation

$$d = \frac{6 \times 10^2\alpha}{\text{spec. surf.}} = \frac{1.73 \times 10^{-5}}{\text{spec. surf.}} \text{ (in cm.)}$$

using a value for α of 2.89 Å. as the distance between a bromide and silver ion.

TABLE V

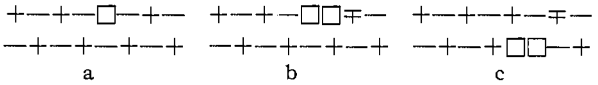
PARTICLE DIAMETERS CALCULATED FROM R. A. EXCHANGE DATA IN PRESENCE OF WOOL VIOLET

Product	x/m	% Surface (from exch.)	No. of Br^- ions on surf. per W.V. molecule ads.	Diameter $\times 10^6$, cm.
Fresh	53.7	15.0	11	1.2
5 min. old then aged 4 wk. in presence of wool violet	38.6	11.6	12	1.5
9 days old, non-dialyzed	13.4	6.2	19	2.8
2 weeks old, dialyzed	13.6	5.0	15	3.5
Electrodialyzed then aged 4 hr. at 90°	10.7	..	..	4.3[b]
Electrodialyzed then aged 24 hr. at 90°	7.4	..	..	6.7[b]
Fresh[a] (flocculated)	..	2.0	15	8.7
Aged[a] (flocculated)	..	0.046	22	380

[a] From Kolthoff and O'Brien.[4] [b] Calculated from x/m values.

The order of magnitude of the calculated diameters of the particles compares favorably with the range of particle diameters observed with the electron microscope. A fresh colloid gave a range of particle diameters from less than 0.02 to about 0.1 μ, as compared to the calculated average diameter of 0.012 μ. With the dialyzed colloids the electron microscope gave a range from 0.06 to 0.3 μ compared to 0.04 μ found from surface adsorption and exchange.

It is only possible to speculate why adsorbed wool violet limits the exchange with bromide to the surface layer only. The formation of Schottky defects may be understood by considering the following pictures.



In a, a bromide ion in the surface next to a silver hole may become adsorbed on the neighboring silver ion b thus creating a Schottky defect which can change position with an ion pair in the second layer c, etc. The entire process is a kinetic one and not a static one, Schottky holes being formed and destroyed continuously. Adsorbed wool violet may prevent the change from a to b and freeze the surface bromide ions.

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MINNEAPOLIS, MINNESOTA

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[12] T. B. Grimley and N. F. Mott, *Disc. Faraday Soc.*, [1] 3 (1947).

[13] A. Langer, *J. Chem. Phys.*, **11**, 11 (1943).