zero at the point where all of the lead is precipitated, it would then remain very small until all of the barium is precipitated, and it would increase in the usual way with an excess of chromate. It is evident from Fig. 10 that a marked coprecipitation of barium chromate occurs during the precipitation of lead. In the titration of 50 ml. of a mixture which was 0.01 M in lead and 0.01 M in barium nitrate, with 0.2 M potassium chromate at $E_c = -1.0$ v., the first end-point (precipitation of lead) was found about 20% after the equivalence point. The second end-point corresponding to quantitative precipitation of lead and barium was found at the correct location. In a subsequent paper the amperometric titration of barium will be discussed more in detail.

Fig. 10.—Titration of 50 cc. of 0.01 M Pb(NO$_3$)$_2$ in 0.01 M Ba(NO$_3$)$_2$ with 0.2 M K$_2$CrO$_4$ at $E_c = -1.0$ v.

Summary

1. The word "amperometric titration" is coined and the historical development of this type of titration is discussed.

2. Lead can be titrated accurately, precisely and rapidly by amperometric titration with dichromate or chromate, using the dropping mercury electrode as an indicator electrode. The titration can be carried out without applying an external e. m. f.

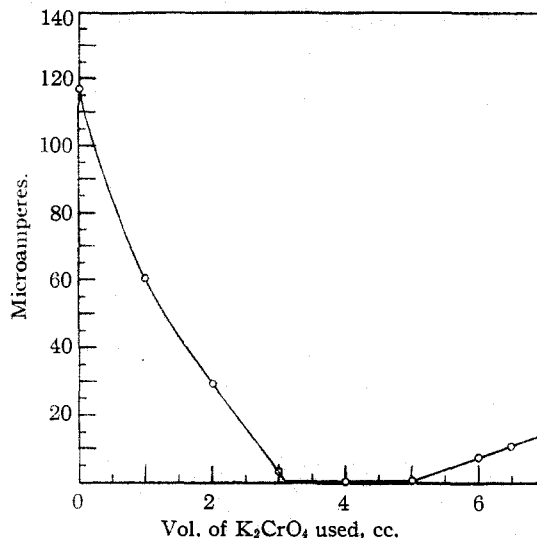3. Even 0.001 M lead solutions can be titrated with a high degree of accuracy.

4. Lead can be titrated amperometrically in the presence of large amounts of barium when the solution is slightly acid with perchloric acid. The fractional precipitation of lead and barium in neutral medium with potassium chromate does not yield good results due to coprecipitation of barium chromate with lead chromate.

Studies on Aging and Formation of Precipitates. XXX. The Determination of the Specific Surface of Silver Bromide by the Radioactive and Dye Methods

BY I. M. KOLTHOFF AND A. S. O'BRIEN[1]

In studies on aging of silver bromide it was of interest to determine the specific surface of various products. Dyes, such as orthochrom T,[2] methylene blue,[3] or pinacyanol[4] have been used for this purpose. In this Laboratory wool violet has proved to be of great value in the determination of the specific surface of various precipitates. For this reason, the adsorption of this dye on silver bromide was studied under varying conditions and compared with the adsorption of methylene blue. In order to know the density of occupation of the adsorbed dye on the saturated surface it was necessary to have available the magnitude of the specific surface of the various products used. Particularly when dealing with freshly prepared, heterodisperse precipitates of silver bromide, consisting of extremely fine particles, it was hardly possible to determine the surface microscopically or ultra-microscopically, as the precipitates could not be peptized completely. For this reason, we have made a study of the radioactive method for the determination of the specific surface, the principles of which originate with Paneth[5] and have been successfully applied in this Laboratory. In the present study it was attempted to determine the kinetic equilibrium in

(1) From a doctor's thesis submitted by Albert S. O'Brien to the Graduate School of the University of Minnesota, June, 1938.

(2) Sheppard and Crouch, *J. Phys. Chem.*, **32**, 751 (1928).

(3) Wulff and Seidl, *Z. wiss. Phot.*, **28**, 239 (1930).

(4) Sheppard, Lambert and Keenan, *J. Phys. Chem.*, **36**, 174 (1932).

(5) F. Paneth, *Physik. Z.*, **15**, 924 (1915); *Z. Elektrochem.*, **28**, 113 (1922); Paneth and W. Vorwerk, *Z. physik. Chem.*, **101**, 445, 480 (1922).

the exchange between a radioactive bromide solution and inactive bromide in the surface of the silver bromide. When equilibrium is established, the following relation holds

$$\frac{Br^*_{surf.}}{Br^*_{sol.}} = \frac{Br_{surf.}}{Br_{sol.}} \tag{1}$$

or

$$Br_{surf.} = \frac{Br^*_{surf.}}{Br^*_{sol.}} \cdot Br_{sol.} = R. \ Br_{sol.} \tag{2}$$

in which the asterisk denotes the radioactive bromine. The application of equation (1) or (2) requires the limitation of the exchange to the surface layer only.

Experimental

Preparation of Radioactive Bromide.—Ethyl bromide (c. p.) was dehydrated over anhydrous calcium chloride, filtered and stored in glass-stoppered bottles. One ml. of an approximately 0.08 molar bromine solution in carbon tetrachloride was added to 1 liter of ethyl bromide. After thorough mixing, the flask was suspended at the center of a ten-gallon (40-liter) crock of water. The water was used to reflect the neutrons back into the flask. Soft glass bulbs, about 5 mm. in diameter, containing approximately 100 mg. of beryllium and from 100 to 140 millicuries of radon were secured through the courtesy of Dr. D. Hull of the Division of Physical Chemistry in this University. After radiating from sixteen to twenty hours the bulb was removed and the bromine reduced and extracted by shaking the ethyl bromide in a separatory funnel with 40 ml. of 0.1 molar sodium acid sulfite solution. The ethyl bromide left was dehydrated again and used in subsequent experiments. The aqueous layer containing the radioactive bromide was transferred to a 250-ml. Erlenmeyer flask and the dissolved ethyl bromide boiled off at reduced pressure. The solution was about 0.0013 molar in bromide. Water or solutions of inactive potassium bromide were added to it until the desired volume and bromide concentration were obtained. The four and one-half hour isotope was used in the present experiments, as the thirty-four hour isotope does not have much opportunity to build up and the isotopes of shorter life have almost decayed before the readings are started. In our work no readings were made before three hours had elapsed from the time of the removal of the beryllium–radon bulb.

Measurement of Radioactivity.—A great number of copper dishes of uniform dimensions was prepared and a measured volume of the radioactive solution was evaporated on a steam-bath in a copper dish; if the solution was acid it was neutralized before evaporation. The radioactivity of the residue was measured by placing the dish in the holder under the aluminum window of an ionization chamber. The amplifying circuit, constructed with the valuable aid of Dr. C. S. Copeland, was essentially the one recommended by DuBridge and Brown,[6] details of which are given in the thesis of the junior author.[1]

In all the experiments, the "rate of drift" method was used in measuring the activity of the residue, by determin-

ing the rate of the drift of the galvanometer light across an arbitrary number of cm. on a scale.

Materials Used.—Most of the chemicals were of c. p. quality and recrystallized if desirable. A product of wool violet 5BN, purified in the laboratories of the National Aniline Company, was used without further purification. The sample of methylene blue used satisfied the requirements of the "U. S. Pharmacopoeia X."

Analytical.—The dye concentration was determined colorimetrically using a photoelectric colorimeter. Solutions containing small amounts of suspended silver bromide were made entirely clear by addition of sodium thiosulfate. The latter salt did not affect the absorption spectrum of wool violet. In some cases the wool violet concentration was also determined by the chemical method using ceric sulfate or permanganate as oxidizing agents.

The concentration of (inactive) bromide in solution ($Br^-_{sol.}$ in equation 2) was determined by the hypochlorite procedure following the directions of Kolthoff and Yutzy.[7]

Products of Silver Bromide

Well Aged "Product E."—A 200-g. portion of silver bromide was precipitated by adding 0.4 M potassium bromide to a slight excess of 0.4 M silver nitrate. After washing the precipitate thoroughly with large quantities of water, it was suspended in 0.5 M potassium bromide and drastically aged for three days in a stoppered bottle at 95°. The product was then collected on a sintered glass filter, washed thoroughly with water, then with ethanol and finally with ether. It was air-dried until the odor of ether was no longer perceptible. It was then heated at 90° for two hours, ground in an agate mortar and kept in a brown bottle in a desiccator over anhydrous calcium chloride.

Fresh Silver Bromide from 0.1 M Solutions (Product B).—Separate samples weighing 0.094 g. were prepared by adding 5 ml. of 0.102 M potassium bromide to 5 ml. 0.1 M silver nitrate. The samples were not made air-dry, but kept in suspension and investigated immediately after preparation.

Fresh Silver Bromide from 0.43 M Solutions (Product A).—Separate samples weighing 2 g. were prepared by adding 25 ml. of 0.423 M potassium bromide to 25.5 ml. of 0.423 M silver nitrate. Further treatment will be described below.

Determination of Surface by Radioactive Method

Aged Silver Bromide (Product E).—The speed of exchange of radioactive bromide in solution with inactive bromide in the precipitate was determined by shaking at 25° 2-g. samples of product E with a mixture of 4 ml. of 0.001 N potassium bromide and 10 ml. of 0.00104 N radioactive bromide.

The results are plotted in Fig. 1, in which the amount of exchanged bromide is expressed in equivalents per gram of silver bromide. When the exchange is limited to the surface only this amount of exchanged bromide corresponds to the specific surface ($Br_{surf.}$ in equation 2). From the figure it is seen that the amount of bromide exchanged increases continuously and fairly rapidly with the time of shaking. From the relatively large amount of bromide exchanged it

(6) DuBridge and Brown, *Rev. Sci. Instr.*, **4**, 532 (1933).

(7) Kolthoff and Yutzy, *Ind. Eng. Chem., Anal. Ed.*, **9**, 75 (1937).

is evident that during the shaking much of the radioactive bromide is being incorporated into the solid. This must be due to recrystallization.
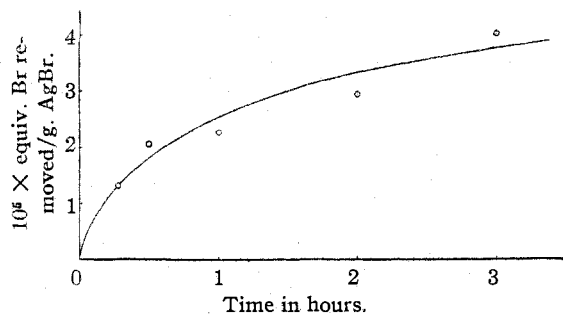

Fig. 1.—Penetration of radioactive bromide ions into aged AgBr.

The speed of recrystallization of this well-aged silver bromide decreases with decreasing temperature. The slope of the exchange curve was found to be much less at 0° than at 25°, but even at this lower temperature most of the radioactive bromide removed from the solution was being incorporated in the precipitate and only a small fraction was present on the surface.

In previous work carried out in this Laboratory and elsewhere[8] it was found that recrystallization and perfection, even of fresh and highly imperfect precipitates, can be prevented by coating the surface of the particles with a layer of a suitable dye. Therefore, experiments were carried out in which the speed of exchange was determined with aged and fresh silver bromide after the particles had been covered with a layer of wool violet or methylene blue or gelatin.

In the following experiments 2 or 4 g. samples of product E were shaken with 4 ml. of a 0.1% solution of wool violet or of methylene blue in 0.001 M bromide. After shaking for thirty minutes, 10 ml. of a radioactive solution which was 0.00107 M in bromide was added and the mixture shaken for a given period of time, after which the activity of the supernatant liquid was determined. The results are given in Table I and plotted in Fig. 2 (lines 1 and 2).

TABLE I

Speed of Exchange of Br* with AgBr (Product E) in the Presence of Wool Violet or Methylene Blue

AgBr in g.	Time of shaking with Br*, hr.	Wool violet adsorbed R	Br⁻ exchanged × 10⁵ in equiv. per 1 g. AgBr	Methylene blue adsorbed R	Br⁻ exchanged × 10⁵ in equiv. per 1 g. AgBr
2	1	0.354	0.248		
2	2	.374	.262	0.318	0.223
2	3	.380	.266	.332	.232
2	4	.403	.282	.346	.242
2	5	.41	.287		
4	1	.735	.257	.602	.211
4	2	.769	.268	.624	.218
4	3	.784	.274	.638	.226
4	4	.800	.280	.677	.237
4	5	.834	.292		

(8) Compare also Mare, Z. physik. Chem., **61**, 385 (1908); **67**, 470 (1909); **68**, 104 (1909); **73**, 685 (1910); **75**, 710 (1911); also, Stevenson, Kolloid Z., **10**, 249 (1912).
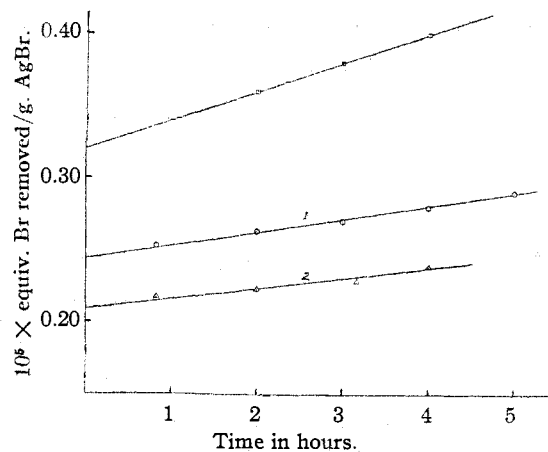

Fig. 2.—Specific surface of aged silver bromide: ⊙, wool violet coated AgBr; △, methylene blue coated AgBr; ⊡, gelatin coated AgBr.

The results of experiments carried out in the presence of gelatin are given in Table II and also in Fig. 2.

TABLE II

Speed of Exchange of Br* with AgBr (E) in the Presence of Gelatin (First Shaken 16 Hrs. before Addn. of r.a.Br⁻)

Time of shaking with Br*, hr.	With 10 mg. of gelatin R	Br exchanged × 10⁵ in eq. p.g. AgBr	With 1 mg. of gelatin R	Br exchanged × 10⁵ in eq. p.g. AgBr
1	0.584	0.409		
2	.664	.464	0.516	0.361
3	.736	.515	.549	.384
4	.756	.530	.572	.400

A comparison of the data in Figs. 1 and 2 reveals that adsorbed wool violet, methylene blue and gelatin almost completely prevent the further recrystallization of the aged silver bromide. Extrapolation to a time of shaking of zero should, in the presence of an inhibitor, yield the number of equivalents of bromide in the surface of 1 g. of silver bromide (E). In this way a specific surface of 0.24×10^{-5} equivalent of bromide per gram was found in the presence of wool violet and of 0.21×10^{-5} equivalent per gram in the presence of methylene blue. The values found in the presence of gelatin were somewhat greater, 0.33×10^{-5} in the presence of 1 mg., and 0.37×10^{-5} in the presence of 10 mg. of gelatin. These higher values may be attributed to the fact that the samples had been shaken for sixteen hours with the gelatin solution, and only for half an hour with the dye solutions; more peptization may have occurred after the longer period of shaking with gelatin. It is of interest to note that the slope of the line in the presence of 1 mg. of gelatin is much less than in the presence of 10 mg.

From the agreement of the values of the specific surface found in the presence of the acid dye wool violet and the basic dye methylene blue and from the fact that the specific surface was found to be independent of the amount of silver bromide shaken, it may be concluded that the "dye radioactive method" yields good results in the determination of the specific surface of aged silver bromide.

Fresh Silver Bromide (Product B).—The speed of penetration of radioactive bromide into fresh precipitates of silver bromide is extremely great. Consequently, the radioactive method cannot be used in the determination of the specific surface of fresh silver bromide unless the recrystallization is prevented by the addition of dyestuffs. In the following experiments 2 ml. of a 0.1% solution of wool violet in 0.001 M bromide was added to 10 ml. of the freshly prepared suspension of product B which contained 0.094 g. of silver bromide. After shaking for ten to fifteen minutes 10 ml. of about 0.008 M radioactive bromide solution was added and the suspensions further shaken for various periods of time, after which the activity was determined in an aliquot part of the supernatant liquid. Similar experiments were performed in which 2 ml. of 0.1% solution of methylene blue in 0.001 M bromide was added to the fresh suspension instead of wool violet. In all these experiments the concentration of bromide in the radioactive suspension was 0.004 M. In order to increase the percentage of activity removed, the experiments were repeated at a smaller final bromide concentration of 0.00175 M (with wool violet) and of 0.00166 M (methylene blue). All of the results are reported in Table III and those at the smaller bromide concentration are given graphically in Fig. 3.
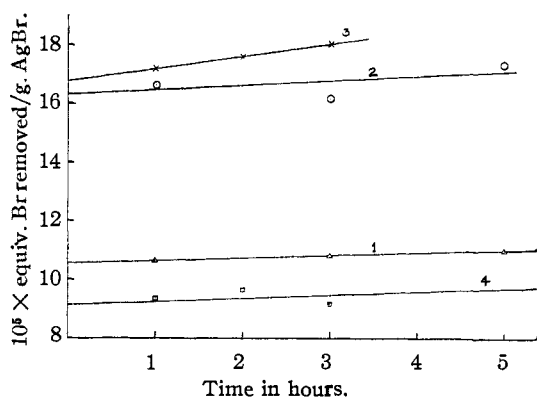

Fig. 3.—Specific surface of fresh silver bromide:
×, AgBr from 0.1 N reagents, wool violet–gelatin;
△, AgBr from 0.1 N reagents, wool violet coating;
⊙, AgBr from 0.1 N reagents, methylene blue coating;
□, AgBr by method A, wool violet coating.

Experiments were also carried out in the presence of a mixture of gelatin and wool violet. Gelatin alone does not prevent entirely the recrystallization of fresh silver bromide. As wool violet is effective in preventing further recrystallization, the method could be used in the determination of the specific surface of silver bromide aged in the presence of gelatin.

In the experiments reported in Table IV, 2 mg. of wool violet was added to the fresh suspension of product B, and after ten minutes of shaking 10 mg. of gelatin dissolved in 2 ml. of 0.001 M bromide. After further shaking for one hour the radioactive bromide solution was added. In other experiments the suspension was first shaken with 10 mg. of gelatin and subsequently for one hour in the presence of wool violet–radioactive bromide solution. The results are given in Table IV and on curve 3 in Fig. 3.

TABLE III

SPEED OF EXCHANGE OF Br* WITH FRESH SILVER BROMIDE (B) IN THE PRESENCE OF 2 MG. OF WOOL VIOLET OR 2 MG. OF METHYLENE BLUE

Time of shaking with Br*, hr.	Dye used	(Br⁻) in final suspension 0.004 M Br⁻ exchanged $\times 10^5$ in equiv. per g. of AgBr		(1) in final suspension 0.00175 to 0.00166 M Br⁻ exchanged $\times 10^5$ in equiv. per g. of AgBr	
		R		R	
1	W.V.	0.123	11.6	0.260	10.7
2	W.V.	.134	12.7		
3	W.V.	(.119)	(11.2)	.264	10.8
4	W.V.	.141	13.3		
5	W.V.			.268	11.0
1	M.B.	.189	17.4	.428	16.7
2	M.B.	.189	17.4		
3	M.B.	.208	19.2	.416	16.2
4	M.B.	.212	19.6		
5	M.B.			.445	17.3

TABLE IV

SPEED OF EXCHANGE OF Br* WITH FRESH SILVER BROMIDE (B) IN THE PRESENCE OF 2 MG. OF WOOL VIOLET AND 10 MG. OF GELATIN

Time of shaking with Br*, hr.	First shaken 10 min. with W. V., then gelatin added Br⁻ exchanged $\times 10^5$ in equiv. per 1 g. of AgBr		First shaken 1 min. with gelatin, then W. V. added Br⁻ exchanged $\times 10^5$ in equiv. per 1 g. of AgBr	
	R		R	
1	0.254	17.0	0.260	17.4
2	.306	20.5	.263	17.6
3	(.259)	(17.3)	.286	19.1

In a similar way fresh product A yielded an exchange of 9.0×10^{-5} equivalent of bromide per gram (see line 4 in Fig. 3).

Determination of Specific Surface by the Dye Method.—The adsorption of wool violet on fresh and old products of silver bromide was determined from solutions being either 0.001 M in silver or 0.001 M in bromide. Independent of the age of the silver bromide, it was found that the amount of dye adsorbed on the saturated surface is twice as great from the silver as from the bromide solutions. Fresh silver bromide coated with dye did not age on further shaking, the amount of dye adsorbed remaining constant with time. In this respect the silver bromide behaves like other fresh precipitates. A summary of the results obtained with the various products is given in Table V. In all of the experiments it was ascertained that the final dye concentration was large enough to have the surface saturated with the dye. In the experiments with methylene blue paraffin lined bottles were used.

Discussion of Results

1. The radioactive method applied in the presence of wool violet or methylene blue yields identical results with well-aged silver bromide. It was found that 0.046 and 0.039%, respectively, of the bromide was present in the surface of silver bromide E. Fresh product B yielded by the "wool violet–r.a." method a specific surface of 10.5 $\times$ 10^{-5} equiv. of bromide per gram, corresponding to the presence of 2.0% of all the bromide in the

TABLE V

ADSORPTION OF WOOL VIOLET (W.V.) AND METHYLENE BLUE (M,B.) ON FRESH AND AGED SILVER BROMIDE (SHAKEN FOR THIRTY MINUTES)

Product AgBr	Amt. taken, g.	Medium	Dye	Final concn. of dye mg. per l.	Dye removed in %	Dye absorbed in mg. per g. AgBr	Dye absorbed in moles per g.
E	10	0.001 N Ag	W.V.	54	79	0.158	2.08×10^{-7}
E	10	.001 N Ag	W.V.	160	36	.150	
E	10	.001 N Br	W.V.	150	48	.090	
E	10	.001 N Br	W.V.	150		.085[a]	1.17×10^{-7}
E	5	.001 N Br	M.B.	210	19	0.070–0.076	1.95×10^{-7}
B	0.19	.001 N Ag	W.V.	110	45	12.1	1.59×10^{-5}
B	.19	.001 N Br	W.V	160	21	5.4	0.71×10^{-5}
B	.094	.001 N Br	M.B.	107	35	7.6	2.0×10^{-5}
A	2	.0005 N Ag	W.V.	326	52	10.85	1.43×10^{-5}
A	2	.0005 N Br	W.V.	256	49	4.90	0.65×10^{-5}

[a] After centrifuging, most of the supernatant liquid was decanted and the dye concentration was determined in the mother liquor. The weight of the remaining precipitate and mother liquor was determined and the total amount of dye in this mixture measured after dissolving it in sodium thiosulfate. From the known weight of the precipitate and the dye concentration of the mother liquor and of the total amount of dye in the mixture, the amount of dye adsorbed on the precipitate was calculated.

surface. With the slightly aged product A the values were 9.1×10^{-5} equiv. per g. corresponding to 1.7% surface.

The "methylene blue–r.a." method with the fresh product B yielded a value of the specific surface which was 60% greater than that obtained with the "w.v.-r.a." method, although both methods gave identical results with the aged product E. The difference found with the fresh product undoubtedly is to be attributed to an adsorption of bromide in the form of methylene blue bromide on the active surface of the fresh product. In agreement with this interpretation it is found that the ratio of adsorbed wool violet (from excess of silver) to methylene blue on the saturated surface of aged product E is equal to 0.158/0.073 = 2.16, while this ratio on fresh product B is 12.1/7.6 = 1.6, showing that the adsorption of methylene blue as compared with wool violet is greater on the fresh than on the aged product. The specific surface of product B determined by the "r.a. method" in presence of a mixture of wool violet and gelatin is found equal to that found with the "r.a. methylene blue" method. The radioactive bromide solution used was slightly acid; at the positive side of the isoelectric point, positively charged gelatin particles are adsorbed and also an equivalent amount of bromide, explaining the difference between the "r.a. w.v. gelatin" and the "r.a. w.v." methods on the one hand and the similarity between the former and the "r.a. methylene blue" method on the other.

2. Taking the value of the specific surface

determined by the "r.a. w.v." method as a standard, it is possible to calculate the number of bromide ions on the surface per molecule of adsorbed wool violet or methylene blue. A summary of the data is given in Table VI.

TABLE VI

DENSITY OF OCCUPATION OF WOOL VIOLET AND METHYLENE BLUE ON SATURATED SURFACE OF FRESH AND AGED SILVER BROMIDE

Dye	Medium	No. of bromide ions in surface per 1 molecule adsorbed dye		
		Product E	B	A
W.V.	0.001 N Ag	10.9	6.6	6.4
W.V.	.001 N Br	20.2	14.8	14.2
M.B.	.001 N Br	11.6	5.2	

The density of occupation of adsorbed wool violet on the aged product E, even in the presence of an excess of silver, is very small as compared to that found with other precipitates such as lead sulfate, barium sulfate, and lead chromate. In the latter cases the dye probably is oriented with its polar groups perpendicular to the surface of the polar adsorbents, whereas with the less polar silver bromide the adsorbed dye may be in a more flat position on the surface.[9] The fact that the density of occupation in an excess of silver is twice as great as in an excess of bromide suggests that in the latter case the dye is held in a monomolecular layer and that an extra layer is adsorbed as silver salt when the solution contains an excess of silver. On fresh precipitates the density of occupation of adsorbed wool violet is

(9) Compare Rabinovich and Natanson, J. Phys. Chem. U. S. S. R., 11, 434 (1930); and espec. Leermakers, Carroll and Staud, J. Chem. Phys., 5, 873 (1937); Sheppard, Lambert and Walker, ibid., 7, 265 (1939).

about 1.7 (excess silver) to 1.4 (excess bromide) times as great as on the aged products. It is not possible to say whether this is due to a changed orientation of the adsorbed dye or to other causes.

On the aged product 1 molecule of methylene blue was found to be adsorbed per 11.6 bromide ions on the surface. This value is in fair agreement with that reported by Wulff and Seidl[3] of 7.6 for a well-aged product the surface of which was measured microscopically and found to be about 2.5 times as great as that of our product E. The increased density of occupation of methylene blue on the fresh products has been explained above.

3. From a practical point of view the wool violet method either in an excess of silver or in an excess of bromide seems satisfactory for the determination of the specific surface of silver bromide of varying ages. The values found by the wool violet method are in satisfactory agreement with those found by the "w.v. r.a." method. In Table

TABLE VII

COMPARISON OF VARIOUS METHODS FOR DETERMINATION OF SPECIFIC SURFACE

	"r.a. w.V."	W.V. (Ag+)	W.V. (Br⁻)	"r.a. M.B."	M.B.
Surface B/ Surface E	47	77	64	73	104
Surface B/ Surface A	1.16	1.12	1.10		

VII is given the ratio of the specific surfaces of the products determined by different methods.

Summary

1. A rapid incorporation of radioactive bromide into well-aged silver bromide occurs when a solution of the former is shaken with the solid.

2. Adsorbed wool violet and methylene blue limit the exchange between solution and solid to the surface layer only. Use of this is made in the radioactive determination of the specific surface of fresh and aged products of silver bromide. Adsorbed gelatin inhibits the recrystallization of aged silver bromide.

3. Wool violet is found suitable for the determination of the specific surface of silver bromide. From a solution containing an excess of silver the amount of dye adsorbed is twice as great as that from a solution containing an excess of bromide.

4. The saturated surface of an aged product of silver bromide contained per 10.9 bromide ions 1 molecule of wool violet (excess Ag^+) or per 20.2 bromide ions 1 molecule of wool violet (excess Br^-), and per 11.6 bromide ions 1 molecule of methylene blue (excess Br^-). With a fresh product the following figures were found: 6.5, 14.5, and 5.2, respectively.

Studies on Aging and Formation of Precipitates. XXXI. The Aging of Silver Bromide

BY I. M. KOLTHOFF AND A. S. O'BRIEN[1]

In previous studies it has been found that fresh imperfect precipitates perfect themselves as a result of repeated recrystallizations which take place mainly in liquid films around the primary particles. Consequently, lattice material may deposit in interstices of an agglomerate of primary particles, thus cementing the latter together and causing a marked decrease of the specific surface of the precipitate.[2] The speed of this kind of aging was found to be determined by the solubility of the precipitate in the aging medium or more exactly in the liquid film around the particles. Ostwald ripening involving the growth

of large particles at the cost of small ones was found to be of secondary significance with regard to the type of aging discussed above.

In the present paper studies on the aging of freshly prepared silver bromide are reported. It was found again that the speed of aging increased with increasing solubility of the precipitate. However, when the solubility had reached a certain minimum value, further decrease of the solubility did not affect the still fairly large speed of aging. Evidence is given in this paper that this relatively rapid aging is due to a thermal aging of silver bromide which also occurs in the dry state even at room temperature.

In general the aging was followed by two methods: (a) by determining the decrease of the

(1) From a doctor's thesis submitted by Albert S. O'Brien to the Graduate School of the University of Minnesota, June, 1938.

(2) Compare S. E. Sheppard and R. H. Lambert, *Colloid Symposium Monograph*, 6, 276 (1928).