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

Structural Changes Taking Place During the Aging of Freshly Formed Precipitates. I. Aging of Lead Sulfate Precipitated at Room Temperature

BY I. M. KOLTHOFF AND CHARLES ROSENBLUM

A great number of studies have been made on the aging of freshly formed colloidal precipitates,[1] but no data are available on changes taking place in freshly formed microcrystalline precipitates. The investigations of I. M. Kolthoff and E. B. Sandell[2] revealed that freshly formed calcium oxalate, especially when precipitated at room temperature, undergoes a very rapid aging process. The fresh precipitate is extremely imperfect and possesses an internal surface which is a great many times larger than the external surface. On aging, the crystals become more perfect, which results in a rapid decrease of the internal surface, whereas the external surface decreases but very slowly. It is expected that qualitatively most freshly formed microcrystalline precipitates will behave in a similar manner. However, in general, the magnitude of the internal and external surfaces of the fresh precipitate and the speed of aging will be a function of the conditions of precipitation, and of the individual properties of the slightly soluble substance formed. In this paper the results of a study of the aging of freshly formed lead sulfate, precipitated at room temperature, will be described. In consecutive communications the aging of lead sulfate formed under other conditions will be reported.

The total surface of lead sulfate, by which we mean the external surface plus the internal surface which is in open communication with the surrounding liquid, can be approximated by measuring the distribution of thorium B between the precipitate and the solution.[3]

The external surface can be measured with the aid of the microscope, but still better, as is shown in this paper, by the determination of the adsorption of wool violet.[4] For short shaking periods, this dye is adsorbed at the external surface only, since its large size does not allow a penetration into fine capillaries and canals of the imperfect crystals and its subsequent adsorption at the internal surface.

Materials Used.—C. P. lead nitrate and potassium sulfate were thrice recrystallized from water and dried under the proper conditions. Standard solutions were made and standardized by gravimetric procedures. The wool violet 4BN was of the same purity as the product used in a previous study,[4] and the same procedure was applied. Solutions of thorium B were prepared in the same way as described in a former communication.[5] All other materials used were C. P. products and tested for purity.

Experimental Methods

In general the following procedures were adopted.

Procedure A. 1. **Precipitation of Lead Nitrate with a Slight Deficiency of Potassium Sulfate.**—To 10.27 cc. of 0.1000 *M* lead nitrate in a paraffined bottle was added 9.79 cc. of 0.1000 *M* potassium sulfate. The addition of potassium sulfate required forty to forty-five seconds and fifteen seconds for drainage. The bottle was closed with a paraffined stopper and gently shaken for a given time. Then 9.96 cc. of a thorium B solution which was 20% saturated with lead sulfate and of known activity were added from a paraffined pipet, and the whole violently shaken (400 phases p. m.) for a given length of time as specified in the tables. The "age" of the precipitates before the addition of the ThB includes the drainage time for the potassium sulfate solution, the time of gentle shaking, and the time required for the addition of ThB solution. Three shaking periods with ThB of one, three and five minutes were used. The bottles were placed in a centrifuge (time required for balancing cups, etc., was one minute) and centrifuged for four to five minutes. Then three 4.92-cc. samples of supernatant liquid were slowly evaporated on a steam-bath in the partially round-bottomed copper dishes,[5] and the activity of the residues, after radioactive equilibrium, compared with that of an equal volume of a standard thorium B solution of approximately the same activity and with the same potassium and lead nitrate contents as the unknowns.

A. 2. **Precipitation of Potassium Sulfate with a Slight Deficiency of Lead Nitrate.**—This procedure was essentially the same as A 1 except that to 10.29 cc. of 0.1000 *M* potassium sulfate, 9.81 cc. of 0.1000 *M* lead nitrate was added.

Procedure B. **Aging at Higher Temperature.**—The precipitates were prepared in the same way as in A 1 except that glass-stoppered, unparaffined Pyrex flasks of 250 cc. volume were used instead of paraffined bottles. Blank experiments showed that no lead was lost by adsorption on the walls from 0.001 *M* lead nitrate solutions after three

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[1] For literature see H. B. Weiser, "The Colloidal Salts," McGraw-Hill Book Co., New York, 1928; and "The Hydrous Oxides," McGraw-Hill Book Co., New York, 1926.

[2] I. M. Kolthoff and E. B. Sandell, *J. Phys. Chem.*, **37**, 723 (1933).

[3] This is the method of F. Paneth, *Physik. Z.*, **15**, 924 (1914), and of Paneth and W. Vorwerk, *Z. physik. Chem.*, **101**, 445 (1922), for the determination of the specific surface.

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

[5] I. M. Kolthoff and C. Rosenblum, *ibid.*, **55**, 2656 (1933).

to four hours of violent shaking. After precipitation the flasks were heated to gentle boiling, stoppered, placed in an electric oven and held at 95° for the times indicated in the tables. In cases where the aging was studied in 0.5 and 0.1 N nitric acid, respectively, the calculated amounts of acid were added after the precipitation. After digestion the flasks were cooled to room temperature and the contents filtered on 597 S. & S. white band paper, washed with 10 to 20 cc. of conductivity water and 40–60 cc. of a saturated lead sulfate solution in water. Then the apex of the filter paper was punched through with a pointed glass rod and the precipitate transferred with saturated lead sulfate solution quantitatively into a weighed, paraffined 50 cc. Erlenmeyer flask. The latter with its contents was again weighed and the volume of the liquid phase calculated. The specific surface of the lead sulfate was determined by shaking for one minute with a measured volume (with a paraffined pipet) of thorium B solution of known activity. In various cases the amount of lead sulfate at the end of the experiments was collected and weighed after ignition.

Procedure B was also used in certain aging experiments at room temperature *when the lead sulfate was relatively old.* This was done to check the specific surfaces in an excess of lead nitrate (procedure A 1) where for old precipitates the adsorption was small. Procedure B then yielded much larger adsorptions because of the ten-fold decrease of the lead concentration. Moreover, procedure B was used for the determination of the specific surface of precipitates aged at room temperature according to A 2, thus allowing the calculation of the lead-ion concentration in the supernatant liquids containing an excess of sulfate ions.

In general lead concentrations in the supernatant liquids were determined by precipitation as lead chromate and iodimetric titration of the latter.[5]

Experimental Results

In Table I the "specific surfaces" are given for samples of lead sulfate of various ages prepared at room temperature according to procedure A 1 (slight excess of lead nitrate) after shaking for one, three and five minutes, respectively, with Thorium B.

The Lead Concentration in the Supernatant Liquid.—The tremendous changes of the so-called "specific surface" taking place immediately after the precipitation might be attributed to a greater lead concentration than that calculated from the excess of lead nitrate and the solubility of lead sulfate, due to incomplete precipitation or coprecipitation. Therefore, it was of great importance to make a special study of this point. It was shown that when the precipitates were filtered immediately the filtrates remained perfectly clear after a few days of standing, even when seeded with lead sulfate crystals. Moreover, the precipitates were collected on Gooch crucibles, washed with water and saturated lead sulfate solution and weighed after heating at 500° to constant weight. It was found for example that a precipitate which was collected ninety seconds after precipitation (time

TABLE I

AGING OF LEAD SULFATE AT ROOM TEMPERATURE (26°)

Procedure A 1. Lead concentration after addition of ThB 10.2(±0.4) mg. in 30.02 cc.

$$\text{Specific surface} = \frac{10.2 \times 10^{-3}}{0.297} \times \frac{\text{ThB adsorbed}}{\text{ThB left}} \text{ g. Pb per 1 g. PbSO}_4$$

1 Minute shaking with ThB			3 Minutes shaking with ThB			5 Minutes shaking with ThB		
Age of ppt. at time of addn. of ThB	ThB adsorbed, %	Sp. surface in mg. Pb per 1 g. $PbSO_4$	Age of ppt. at time of addn. of ThB	ThB adsorbed, %	Sp. surface in mg. Pb per 1 g. $PbSO_4$	Age of ppt. at time of addn. of ThB	ThB adsorbed, %	Sp. surface in mg. Pb per 1 g. $PbSO_4$
50 sec.	87.8	222	50 sec.	96.0	728	50 sec.	95.5	728
50 sec.	85.4		51 sec.	95.0		51 sec.	95.5	
2 min. 50 sec.	77.4	122	2 min. 55 sec.	89.9	293	3 min.	94.0	558
2 min. 52 sec.	78.6		2 min. 50 sec.	89.0		3 min. 5 sec.	94.4	
5 min. 26 sec.	66.9	67	6 min. 5 sec.	82.8	168	5 min. 35 sec.	91.6	374
5 min. 27 sec.	65.5		6 min.	83.1		5 min. 30 sec.	91.6	
10 min. 22 sec.	45.4	30	10 min. 24 sec.	72.3	86.5	10 min. 25 sec.	81.5	157
10 min. 24 sec.	48.2		10 min. 24 sec.	70.8		10 min. 20 sec.	82.5	
20 min. 22 sec.	33.3	18.6	20 min. 40 sec.	52.0	36.5	20 min. 24 sec.	60.2	51.3
20 min. 23 sec.	37.4		20 min. 45 sec.	50.9		20 min. 29 sec.	59.5	
20 min. 22 sec.	37.5							
30 min. 21 sec.	21.0	10.1	48 min. 54 sec.	35.4	16.9	48 min. 55 sec.	35.0	21.2
30 min. 21 sec.	24.4		48 min. 51 sec.	30.6		48 min. 25 sec.	41.2	
1 hour 22 sec.	12.5	4.9	1 day 23 hrs.	10.4	4.0	1 day 23 hrs.	10.1	4.0
1 hour 21 sec.	12.3		1 day 23 hrs.	10.6		1 day 23 hrs.	10.8	
1 day 19 hours	4.3	1.54	8 days	2.5	0.88	8 days	3.1	1.0
						8 days	2.6	

for filtration one minute; time of washing five to eight minutes) yielded a weight of 0.2970–0.2975 g.; when collected five to six days after precipitation a weight of 0.2962 g. was found, whereas the calculated weight is 0.2969 g. These and other experiments showed conclusively that the precipitation was virtually complete immediately after the addition of the reagents. Similar experiments were made when sulfate was slightly in excess (see Table IV), and identical results were found.

Lead concentrations in the supernatant liquids of precipitates formed as described in Table I were determined iodimetrically after precipitation as chromate. The age of the precipitates varied between twenty-five seconds and one day; in all cases a lead concentration in the supernatant liquids was found to be between 2.40×10^{-3} and 2.48×10^{-3} molar, with an average of 2.42×10^{-3} *M*. This value agrees with the one calculated from the excess of lead nitrate used and the solubility of lead sulfate under the experimental conditions, thus showing that the figure of $(\mathrm{Pb}^{++}_{\mathrm{solution}})$ accepted in the calculation of the data in Table I is entirely reliable. The fact that the specific surface of the aged precipitate determined according to procedure A 1 gives the same value as that according to B substantiates the above conclusion.

Data on the specific surface obtained with precipitates aged at room temperature according to procedure B are given in Table II. The precipitates were collected by filtration and washed, and the adsorption of Thorium B determined in a saturated solution of lead sulfate in water after one minute of shaking.

TABLE II

AGING OF LEAD SULFATE AT ROOM TEMPERATURE

Conditions of precipitation identical with those in Table I. Specific surface determined according to Procedure B, 1 min. shaking with ThB. Temperature 30–31.8°

Age of ppt., days	1	2	7
Sp. surface in mg. Pb per 1 g. $PbSO_4$	1.53	1.35	0.93

The effect of heating upon the speed of aging in neutral medium and also in the presence of 0.1 and 0.5 *N* nitric acid, respectively, is given in Table III. The calculated amounts of stronger nitric acid were added after the precipitation of lead sulfate from neutral medium. The time of shaking with ThB was limited to one minute.

TABLE III

AGING OF LEAD SULFATE AT 95° IN NEUTRAL MEDIUM AND IN THE PRESENCE OF 0.1 AND 0.5 *N* NITRIC ACID, RESPECTIVELY

Procedure B: 1 minute shaking with ThB. Conditions of precipitation the same as in Table I. Temperature during shaking varied between 29.2 and 30.5° in different experiments.

Concn. of nitric acid in suspension, *N*	Time of aging at 95°	Sp. surface in mg. Pb per 1 g. $PbSO_4$
0	4 hours	1.07
0	1 day	0.91
0	2 days	.72
0.1	5 hours	.61
.1	1 day 2 hours	.36
.1	2 days	.27
.5	4.5 hours	.44
.5	1 day	.53
.5	2 days	.28

The experiments reported in Table IV were performed in the presence of a slight excess of potassium sulfate according to Procedure A 2. In order to calculate the specific surface from the adsorption of thorium B it was necessary to know the lead concentration in the supernatant liquid. This was determined analytically by determining the solubility of lead sulfate in a solution of 0.0652 *M* potassium nitrate and 0.0016 *M* potassium sulfate, this mixture having the calculated composition of the supernatant liquid after the precipitation and the addition of thorium B. A solubility of 0.95×10^{-4} molar lead sulfate at 27° was found. A more reliable value was found from radioactive measurements. The adsorption of thorium B was determined on precipitates prepared according to method A 2 and one day old. Similar precipitates of the same age were filtered, washed and the specific surfaces determined in a saturated solution of lead sulfate in water. In this way a solubility of lead sulfate in the supernatant liquid after the pre-

TABLE IV

AGING OF LEAD SULFATE AT ROOM TEMPERATURE (26°)

Procedure A 2. $\text{Specific surface} = \frac{0.835 \times 10^{-3}}{0.298} \times \frac{\text{ThB adsorbed}}{\text{ThB left}}$ g. Pb per 1 g. $PbSO_4$.

Age of ppt. at time of addition of ThB	Sp. surface in mg. Pb per 1 g. $PbSO_4$ (1 min. shaking with ThB)[a]	Sp. surface in mg. Pb per 1 g. $PbSO_4$ (5 min. shaking with ThB)[a]
1 minute	213	700
3 minutes	145	
10.5 minutes	98	700
30 minutes	16.7	
1 hour	11.0	54
1 day 21 hrs.	1.32	

[a] Each value is the average of at least four determinations.

cipitation and the addition of thorium B was found to be 1.34 × 10^{-4} molar, and this figure was used in the calculation of the specific surface of lead sulfate in the experiments reported in Table IV.

The specific surface was also determined according to procedure B. The values found in this way with *fresh* precipitates were three to four times smaller than according to method A 2. This is not surprising since the filtering and washing takes about twenty minutes, and the aging of the precipitate on washing with water may be faster than in the supernatant liquid. With precipitates which had been aged for more than one hour the agreement between the two procedures was very gratifying. The specific surface of a precipitate which had been aged for nineteen and one-half hours at 26° was found to be 1.42 mg. and after four days of aging, 1.23 mg. of lead per 1 g. of lead sulfate (procedure B).

Adsorption of Wool Violet during Aging Process.—Precipitates of lead sulfate were prepared as described in Tables I and IV. After the time of standing indicated in Tables V and VI, 10.02 cc. of a wool violet solution of known concentration was added. In all cases the mixture was then shaken (400 phases p. m.) for intervals of between one and ten minutes, centrifuged and the dye concentration in the supernatant liquid determined colorimetrically by comparison with dye solutions of known concentration in media having the same composition as the supernatant liquids. It was found that adsorption equilibrium was attained within one minute of shaking. This indicates that the external surface does not change on aging when it is coated with a layer of the dye. This result is in harmony with the fact previously found[4] that adsorbed dye inhibits the speed of recrystallization of lead sulfate particles to virtually zero. From the amount of dye adsorbed per 1 g. of lead sulfate and the results of a previous study,[4] the "specific surfaces" of the precipitates expressed in mg. of lead per 1 g. of lead sulfate were calculated. All data reported in Tables V and VI are the averages of six independent sets of measurements which gave quite reproducible results agreeing within very close limits. For the sake of brevity all computations are omitted and only the average values are reported.

TABLE V

ADSORPTION OF WOOL VIOLET BY AGING LEAD SULFATE (26°)

10.29 cc. 0.1000 *M* $Pb(NO_3)_2$ + 9.81 cc. 0.1000 *M* K_2SO_4. Initial dye concentration in supernatant liquid is 115.4 mg. per liter.

Age of ppt. before adding dye soln.	Dye adsorbed, %	Dye adsorbed per 1 g. of $PbSO_4$ in mg.	Sp. surface calcd., mg. Pb per 1 g. $PbSO_4$
75 sec.	41.9	4.90	2.65
16 minutes	37.6	4.40	2.38
1 hour	33.8	3.95	2.13
16 hours	27.4	3.21	1.74
4 days	27.0	3.16	1.71

TABLE VI

ADSORPTION OF WOOL VIOLET BY AGING LEAD SULFATE (26°)

Initial dye concentration in supernatant liquid is 258 mg. per liter.

Age of ppt. before adding dye soln.	Dye adsorbed, %	Dye adsorbed per 1 g. of $PbSO_4$, mg.	Sp. surface calcd., mg. Pb per 1 g. $PbSO_4$
78 seconds	22.4	5.86	3.61
15.75 min.	18.4	4.82	2.96
58 minutes	15.0	3.93	2.42
17 hours	8.3	2.14	1.32
4 days	6.9	1.83	1.13

Discussion of the Results

1. The "specific surfaces" of fresh precipitates of lead sulfate increased very much with the time of shaking with thorium B. During this shaking, two processes occur. There is a kinetic exchange between the lead ions in the external and internal surfaces and those in the solution. The final equilibrium is not established until after a longer period of shaking,[5] although it has taken place for the greatest part after one minute. The second process, namely, the perfection of the freshly formed lead sulfate crystals, causes the thorium B adsorbed at the internal surface to be incorporated in the aging crystals. Because of the latter process the specific surfaces found after longer periods of shaking with thorium B are therefore much greater than correspond to the size of external and internal surface at the particular age of the precipitate. Since the two processes occur simultaneously, it is impossible to determine the exact value of the "specific surfaces" of the fresh precipitates. It is known that one minute of shaking is insufficient for the establishment of kinetic equilibrium; on the other hand, some thorium B is removed from solution by incorporation in the perfecting crystals. Therefore it appears likely that the one-minute period of shaking yields the approximate value of the sum of the external and internal

surfaces. The fact that virtually the same specific surfaces were found in an excess of lead and an excess of sulfate supports this assumption.

2. The appearance of the precipitates was examined under the microscope. They were heterodisperse but distinctly crystalline, and consisted of needles with a width of 0.75–1 μ and a length of 1–5 μ. No distinct changes of the average crystal size were noticed during the first hour of aging. Although the freshly formed crystals had the appearance of being quite massive, their specific surfaces as measured by the adsorption of thorium B were unusually large (Tables I and IV) and decreased twenty to forty times after one hour of aging. As a matter of fact the freshly formed precipitates behave as if all of the lead ions are present on the surface. The results in Table I for example show that when the fresh precipitates are shaken for three to five minutes with thorium B a specific surface of 728 mg. of lead per 1 g. is found. A similar result was obtained when the potassium sulfate was slightly in excess (Table IV); after five minutes of shaking with thorium B the specific surface amounted to 700 mg. of lead per 1 g. Since 1 g. of lead sulfate can contain at most 683 mg. of lead ions, it is apparent that the thorium B distributes itself homogeneously throughout the fresh precipitate, in spite of the fact that the latter has the appearance of compact crystals when viewed under the microscope. The freshly formed crystals therefore must be entirely porous or have a spongy structure, all of the lead ions in the inside being in open communication with the exterior. On standing, an extremely rapid aging process occurs in the interior of the crystals, resulting in a perfection of the latter without a growth of the particles. There is a possibility that the freshly formed lead sulfate precipitates in the form of a metastable modification which is quickly transformed into the stable form, thus causing a destruction of the primary crystals separating out. This point is being investigated in greater detail. However, it is suggested that such an explanation does not appear very probable, considering the fact that the external shape of the crystals does not change during the most drastic part of the aging process. The speed and kind of aging are the same for precipitates formed in a slight deficiency of potassium sulfate (Table I) as for those formed under reverse conditions (Table IV). This is clearly demonstrated in Fig. 1.

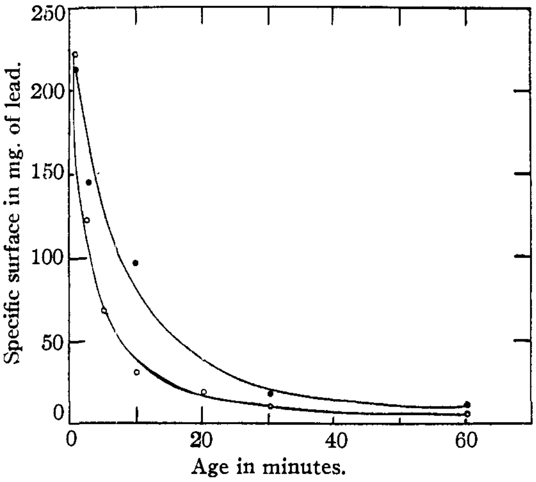

Fig. 1.—○, excess $Pb(NO_3)_2$; ●, excess K_2SO_4.

The final state of the aging process is reached very slowly. Even after a few days of standing (see Tables I, II and IV) a further decrease of the specific surface is found. However, during this long aging process a distinct growth of the particle size is noticed from microscopic observations, and is also indicated by the decrease of the adsorption of wool violet. Therefore the drastic and most rapid aging, starting immediately after precipitation, results in an inner perfection of the crystals, whereas on longer standing a slow crystal growth occurs as a secondary process.

3. An increase in the temperature accelerates the rate of perfection and of crystal growth tremendously, as may be inferred from the digestion experiments described in Table III. If the digestion is carried out in the presence of nitric acid, large and transparent crystals are found after a relatively short time.

4. The specific surfaces of the fresh precipitates calculated from the adsorption of wool violet (Tables V and VI) are much smaller than those found with thorium B. On the other hand, there is a good agreement between the two methods when applied to aged precipitates. Lead sulfate aged for four days at room temperature in the presence of a slight excess of lead nitrate yielded a specific surface of 1.71 mg. of lead per 1 g. according to the dye method and 1.25 according to the radioactive method. When aged in the presence of a slight excess of sulfate these values were 1.13 and 1.23, respectively. Apparently the dye is adsorbed on the external surface only, and its size is too large to allow a penetration into

the pores of the fresh precipitate which must be of the order of a few Ångström units.

The radioactive method therefore gives the sum of the external and the non-isolated internal surface, whereas the dye method gives the external surface only. That the latter conclusion holds true could be shown by extraction of the dye after the adsorption process. Upon washing the colored precipitates with water, the dye was very slowly removed; alcohol, however, gave a much more efficient decoloration, leaving the precipitates only faintly violet. Most effective was an extraction with less than 5 cc. of 1–2 N nitric acid and washing out the acid with water. In all cases a pure white precipitate resulted after such a treatment.

5. From the lead determinations made in the supernatant liquids of precipitates formed in the presence of a slight excess of lead nitrate (conditions as in Table I) it may be inferred that even the fresh precipitates do not adsorb lead nitrate. This conclusion is in harmony with that derived in a previous study[5] although the fresh precipitates prepared in the present investigation had a specific surface which was at least 200 to 400 times larger than that of well aged lead sulfate preparations used before.

Summary

1. Lead sulfate, freshly precipitated at room temperature from 0.1 M lead nitrate and 0.1 M potassium sulfate solutions, consists of distinct microscopic needles. The crystals are entirely porous; all of the lead ions within the fresh precipitate behave as though present at the surface. On standing a tremendously rapid aging occurs, resulting in a perfection of the primary crystals separated. A distinct crystal growth is noticed only after long periods of aging.

2. The entire aging process is much accelerated by digestion, especially in the presence of nitric acid.

3. The sum of the external and internal surfaces of freshly formed lead sulfate is determined by measuring the adsorption of thorium B, whereas the adsorption of wool violet gives the magnitude of the external surface only.

MINNEAPOLIS, MINN. RECEIVED JANUARY 15, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF RADCLIFFE COLLEGE AND HARVARD UNIVERSITY]

Studies of the Precipitation of Silver Chloride. I. The Photronic Nephelometer

BY CHARLES H. GREENE

Since the original investigations of Richards and Wells,[1] but little work has been done upon the nephelometric determination of small quantities of silver. Lamb, Carleton and Meldrum[2] and later Kolthoff and Yutzy,[3] have studied the determination of small quantities of chlorine by this method; Johnson[4] has pointed out that the precipitates of silver chloride may not be precisely similar in the two cases, but may be expected to behave somewhat differently, depending upon whether silver ion or chloride ion is present in excess. Wells,[1b] indeed, noted such differences, but Johnson's experimental work for the most part tends to show that any differences do not cause noticeable errors in the usual "Equal opalescence" end-point of precise chloride–silver titrations.

In a further study of this problem an instrument was constructed in which silver chloride could be precipitated under carefully controlled conditions, and the opalescence of the precipitate measured by means of a photo voltaic cell much more quickly and accurately than in the usual visual nephelometer. It is the purpose of this paper to describe this instrument, which may be termed a "photronic nephelometer," and enough of the results which have been obtained with it in the study of the precipitation of silver chloride to illustrate the type of data which the instrument will supply and the accuracy of which it is capable. In subsequent papers the complex phenomena which are encountered when silver chloride is precipitated in dilute solutions will be considered.

Materials

Conductivity water was used in all preparations and experiments. Hydrochloric acid and nitric acid were puri-

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(1) (a) Richards and Wells, *Am. Chem. J.*, **31**, 235 (1904); (b) Wells, *ibid.*, **35**, 99 (1906); (c) Richards, *ibid.*, **35**, 510 (1906).

(2) Lamb, Carleton and Meldrum, THIS JOURNAL, **42**, 259 (1920).

(3) Kolthoff and Yutzy, *ibid.*, **55**, 1915 (1933).

(4) (a) Johnson, *J. Phys. Chem.*, **35**, 540 (1931); (b) **35**, 2244 (1931).