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).

fied by repeated fractional distillation using a silica condenser. The water and the nitric acid were proved to be free from chloride by nephelometric tests. Sodium chloride and silver nitrate were purified by crystallization. The stock solutions of the acids were standardized with dry sodium carbonate while those of the salts were prepared determinate by weighing the fused materials. The silver nitrate gave perfectly clear dilute solutions with water. good evidence that it was not contaminated with silver chloride.

In some of the experiments fresh samples of silver nitrate and hydrochloric acid which had been prepared with even more care by another worker were used. The results were entirely consistent with those of the earlier experiments. Volumetric apparatus and weights were carefully standardized.

The Photronic Nephelometer

In order to avoid the difficulties with temperature control and speed of measurement inherent in the visual nephelometer, the apparatus shown in Fig. 1 was constructed. In it an effort was made to keep constant all of the factors which may affect the rate of a precipitation reaction. It was also possible to measure the amount of light scattered by the precipitate at any instant during or after the addition of the precipitating reagent.

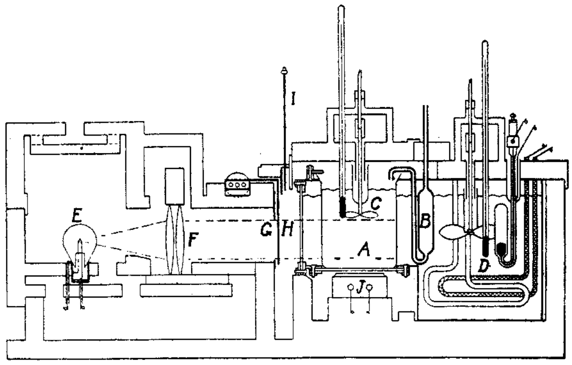

Fig. 1.—Photronic nephelometer.

The precipitate was formed in the beaker A by forcing over into it the solution in the pipet B with air under constant hydrostatic pressure. In this way the addition of the reagent in B was made as uniform and reproducible as possible. Twenty-seven seconds was taken as a standard time of delivery for the pipet. Two calibrations of this pipet yielded the values 10.756 ml. and 10.755 ml. for the volume of solution delivered into the beaker.

The solution in the beaker was stirred before and during the precipitation at a uniform rate (between 350 and 370 r. p. m.). The glass propeller C for this purpose was fitted with a sleeve to prevent possibility of contamination by dirt from the bearings. Stirring was stopped two and one-quarter minutes after the introduction of the silver nitrate from B in order to prevent the coagulation which was brought about by prolonged stirring. On cold days the temperature of the suspension in A would then fall off slightly but never more than a tenth of a degree below the temperature maintained by the thermostat D. This was 25.00 ± 0.02°.

The copper thermostat tank was coated inside with a film of black copper sulfide to absorb stray light. This was easily secured by treatment with ammonium sulfide. It was fitted with thin glass windows held between brass frames with rubber gaskets.

The compact filament of a 6–8 volt 32-candle power automobile headlight bulb served as a satisfactory point source of light. The current, which was supplied by a large storage battery, was adjusted before each measurement of opalescence except at the beginning of an experiment when the readings were too frequent. The adjustments in the final experiments were made so that the potential drop across the filament was 5.1452 volts. The potentiometer employed for this purpose was also used to measure the potential drop across a 0.1-ohm standard resistance connected in series with the filament. This served to detect any changes in the resistance of the filament and was especially useful in discovering poor connections in the lamp socket. Trouble from this source was finally overcome only by soldering the connecting wires directly to the base of the bulb. The lamp was always allowed to warm up for half an hour before measurements were made.

At the operating voltage mentioned no appreciable change was noted either in the luminosity or in the resistance of the filament with time of service. In order to obtain this constancy, however. new filaments were seasoned by operation at six volts for ten or twenty hours. Continued operation at the rated voltage in some of the first experiments resulted in a slow but steady increase in filament resistance and a corresponding loss of luminosity, probably because of evaporation of tungsten.

The filament was turned so that it presented the smallest possible area to the lenses F without having one side of it obstruct the light from the other side. The beam of parallel light from the lenses was limited by the shutters G so that it was of constant vertical height. passing below the thermometer and stirrer and just clearing the bottom of the beaker A. The two shutters H could be moved horizontally by micrometer screws to adjust the width of the beam of light. A slide I was provided to cut off the light entirely when desired.

The constancy of the source of light was checked before and after each experiment by putting in place of A a similar beaker with an inclined piece of ground glass cemented firmly in place and immersed in water. It was necessary to adjust the position of this standard very carefully by means of reference marks and to clamp it firmly in place in order to secure reproducible results. When this was done it was found to be reliable to better than one-half of one per cent. The beakers containing silver chloride suspensions were much less sensitive to changes in position.

The beakers used in this work were of "Insol" glass. They were selected because of their thin uniform walls which refracted the light but little. They were always cleaned immediately after use. together with the stirrer and thermometer. by a brief treatment with redistilled ammonia followed by careful rinsing. When filled with clear solutions before precipitation these beakers scattered to the photronic cell only about one-half of one per cent. of the light scattered by a silver chloride precipitate of the maximum opalescence met with in this work. Furthermore. a silver chloride suspension which remained constant in opalescence could be transferred from one of the four beakers in use to another without a change of more than 1.5% due to differences in the transparency or the shape of the beakers. Accordingly, no corrections were made for these factors in drawing the curves presented below.

The light scattered by the silver chloride or the ground glass was measured by means of the Weston photronic cell J. A sensitive galvanometer with a resistance of 482 ohms was employed to measure the current from the cell. With the feeble light scattered by the silver chloride precipitates this external resistance resulted in the response of the galvanometer being proportional to the amount of light received by the cell.[5]

To correct for unavoidable changes in illumination (such as those caused by replacing a bulb) the galvanometer deflections obtained with the silver chloride suspensions were divided by those obtained with the standard ground glass before and after each experiment. This ratio has been taken as a measure of the opalescence of the suspensions. As is usual in nephelometric work no correction has been made for the fact that light scattered by distant portions of the suspension is partly absorbed and rescattered by the portions of the suspension nearer to the photronic cell. This neglect is justified by the small concentration of the suspensions.

Since the variation of the response of the photronic cell with changing wave length of light[5] is similar to that of the human eye, the results obtained with this instrument should be proportional to the opalescences observed visually in the usual forms of nephelometer. This assumption is made the more reasonable by the fact that the filament which served as a source of light was operated at less than its normal voltage and consequently emitted light poor in the short wave lengths for which the relative response of the photronic cell is most markedly greater than that of the human eye.

In the near future it is planned to extend the scope of the instrument by employing either color filters or a monochromator to gain some idea of the change in color of the suspensions. This will be useful in interpreting the data in terms of rate of precipitation, particle size and rate of coagulation. Meanwhile, it may be noted that there was but little variation in the colors of the suspensions when they were removed from the instrument. All had the bluish-white appearance familiar to everyone who has precipitated silver chloride from dilute solutions.

The speed of response of the cell was tested by suddenly raising the shutter with the ground glass standard in place in the instrument. With the feeble illumination here employed (less than one foot candle in all cases) the fatigue effect noted in the manufacturer's publication[5] was reversed. That is, the response of the cell shortly after illumination was slightly less than the final response. This effect may have contributed slightly to the rounding off of the bend in the opalescence–time curves which show a sudden increase to a maximum opalescence. A fatigue effect of the kind described by the manufacturers was observed when the illumination was suddenly cut off from the cell. A perceptible current continued for five minutes after the illumination ceased, although this became less than 1% of the "illuminated" current after one minute. These observations may be of use to others planning to employ these cells.

TABLE I

EXPERIMENTS WITHOUT NITRIC ACID

Final concn. of $HCl \times 10^4$	Average opalescence	Deviation from the mean, %	Number of expts.
0.086	4.67	8.6	3
.518	7.36	10.5	2
3.97	5.56	12.6	12
6.13	0.49	10	3
8.29	.82	5.5	2
21.3	3.32	2.0	4
43.0	2.33	0.2	2

TABLE II

EXPERIMENTS IN WHICH NITRIC ACID WAS ALSO PRESENT AT A FINAL CONCENTRATION OF 0.0782 *N*

Final concn. of $HCl \times 10^4$	Average opalescence	Deviation from av., %	Number of expts.
3.97	8.26	1.6	3
21.3	6.60	1.5	4
43.0	6.13	1.1	2
215	6.56	0.9	3

Reproducibility of Experiments

Figure 2 indicates the type of results which may be obtained with this instrument and the degree of reproducibility. Each set of solid black points represents the opalescence observations in a single experiment. These experiments were all carried out by adding one pipet full of 0.001 *N* silver nitrate to 300 cc. of dilute hydrochloric acid both with and without added nitric acid. There was thus produced a suspension of silver chloride having a concentration of 3.46×10^{-5} or about

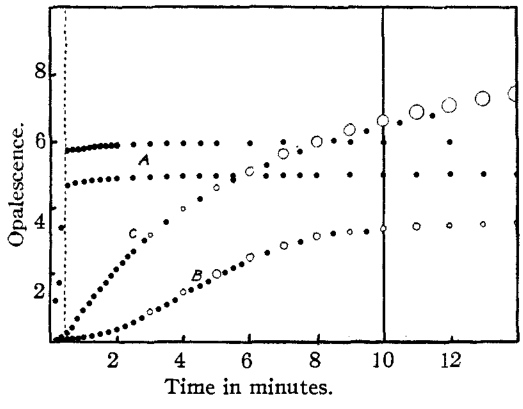

Fig. 2.—The change with time in the opalescence of silver chloride precipitates.

Curves	Concn. $HCl \times 10^4$	Concn. $HNO_3 \times 10^4$	Concn. $AgCl \times 10^4$
A	3.97	0.0	0.346
B	21.3	0.0	.346
C	21.3	782	.346

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[5] Technical Data on the Weston Photronic Cell, Manufacturer's Publication.

two and a half times the concentration of a saturated solution of silver chloride in pure water. The concentrations of the acids given with Fig. 2 are the final values allowing for the dilution and reaction with the silver nitrate. The dotted line indicates the time when the addition of the silver nitrate was complete.

As may be seen the points fall on a smooth curve giving a clear picture of the change with time in the opalescence of a given suspension of silver chloride. The form of this time–opalescence curve was found to be satisfactorily reproducible in duplicate experiments. The absolute value of the opalescence in a given suspension was not as easy to reproduce, especially when the silver nitrate was precipitated in a small concentration of hydrochloric acid without the addition of extra electrolytes. The degree of reproducibility with a larger concentration of chloride both with and without nitric acid is shown in Fig. 2 by the open circles. These are drawn to include all points obtained at even minute intervals in four independent experiments of each kind. In order to give some idea of the reproducibility with smaller concentrations of chloride the two curves A were selected from a series of twelve duplicate experiments so that the difference between them is very nearly the average deviation from the mean of this series.

Tables I and II, which give a summary of the opalescences observed after ten minutes in all experiments which were repeated, contain also columns giving the average deviation from the mean of the opalescences measured at this time, expressed as percentage of the mean opalescence. It is clear that the reproducibility increases as the concentration of chloride increases and also when a comparatively large concentration of nitric acid is present.

Summary

An apparatus has been described for studying the rate of development of opalescence when precipitates are formed in dilute solutions and results have been presented to show the degree of reproducibility attained with it when silver chloride is precipitated in dilute solutions with an excess of hydrochloric acid both with and without the addition of nitric acid.

CAMBRIDGE, MASS. RECEIVED FEBRUARY 8, 1934

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 31]

Thermodynamic Properties of Fused Salt Solutions. VIII. Lead Chloride in Silver Chloride

BY EDWARD J. SALSTROM

The following investigation represents a continuation of a series of thermodynamic studies on fused salts and their solutions.

The lead chloride used in the cells and as a source of electrolytic chlorine was of "Merck c. p." grade containing a maximum impurity of 0.06%. The silver chloride was also obtained from commercial sources, having a maximum impurity limit of 0.014%. A pure silver wire served as the negative electrode while chlorine obtained by the electrolysis of fused lead chloride and bubbled over a treated[1] graphite rod dipping into the cell melt served as the positive electrode. The two salts were carefully weighed out in the desired proportions, fused together in a Pyrex cylinder, mixed by stirring and poured into the cell container.[2] Both the contents of the cell and the chlorine generator were then carefully freed from moisture, oxidation and hydrolysis products by bubbling dry hydrogen chloride through the liquid for at least a half hour. This hydrogen chloride was obtained by dropping concentrated sulfuric acid upon hydrochloric acid and dried by passing over glass beads wet with concentrated sulfuric acid. Apparatus and the method of obtaining measurements have been previously described.[2]

Other investigations, notably those of Lorenz and co-workers,[3] Hildebrand and Ruhle,[4] and Wachter and Hildebrand[5] have been made with the chlorine electrode. With the exception

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(1) Salstrom, THIS JOURNAL, **55**, 2426 (1933).

(2) Salstrom and Hildebrand, *ibid.*, **52**, 4650 (1930).

(3) Lorenz, "Die Electrolyse geschmolzener Salze," Dritte Teil, Elektromotorische Kräfte, Verlag Wilhelm Knapp, Halle a. S., 1906; *Z. physik. Chem.*, **62**, 119 (1908); **63**, 109 (1908); *Z. angew. Chem.*, **39**, 88 (1926).

(4) Hildebrand and Ruhle, THIS JOURNAL, **49**, 722 (1927).

(5) Wachter and Hildebrand, *ibid.*, **52**, 4655 (1930).