A few series of determinations with additions of water to solutions in ethyl alcohol were made. No very definite conclusions are drawn from them, yet they support, to a certain extent, the suggestion made that the slower rate of migration and the higher viscosities of the ions of the alkali metal, lowest in atomic weight, are due to a greater tendency to combine with molecules of solvent. A maximum of *increase* in viscosity for copper chloride in mixtures of ethyl alcohol and water corresponds with the minimum in conductivity, observed by Jones and Lindsay, in similar solutions, both perhaps being due to a maximum formation of highly associated molecules.

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THE MIGRATION OF COLLOIDS.

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I. PREPARATION AND DIALYSIS OF COLLOIDAL GOLD SOLUTIONS.

MOST of the work described in this paper was done with red colloidal gold, prepared by pouring an ethereal solution of gold chloride (dried at 160° to 170°) into water saturated with ether and acetylene gas.[1] The reduction was completed by the passage of more acetylene, but an excess of this reagent is to be avoided, since otherwise the presence of the supernatant layer of ether has a tendency to turn the red gold blue at the surface between the two liquids, thus often giving a purple or violet tint to the resulting solution. Such red, purple or violet solutions were then dialyzed in tubing of parchmentized paper, so as to remove the hydrochloric acid formed by the reaction. The progress of the purification was followed by measuring the conductivity of the liquid within the dialyzer. The dialysis was carried out by surrounding the parchment tube first with ten times its volume of ordinary distilled water, frequently renewing this until the electrolyte was mainly removed, and then replacing it by conductivity water (of conductivity 1.5×10^{-6} reciprocal ohms). The specific conductivities (κ) (in reciprocal ohms $\times 10^{-6}$) of the four gold

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[1] Blake: *Am. J. Sci.*, **16**, 381 (1903).

solutions used in our migration experiments after the dialysis had been continued for different periods of time, expressed in days, are shown in Table I.

TABLE I.—CONDUCTIVITY OF COLLOIDAL GOLD SOLUTIONS DURING DIALYSIS.

Solution No. 1—red. Final concentration 300 mg. per liter.		Solution No. 2—red, turbid. Final concentration 476 mg. per liter.		Solution No. 3—violet. Final concentration 320 mg. per liter.		Solution No. 4—red. Final concentration 146 mg. per liter.	
Time intervals.	$\kappa \times 10^6$.	Time intervals.	$\kappa \times 10^6$.	Time intervals.	$\kappa \times 10^6$.	Time intervals.	$\kappa \times 10^6$.
3.5	...	7	10.3	0	1690.0	0	1070.0
0.5	12.7	2	8.5	1	206.0	0.25[1]	107.0
4.0	12.3	.	..	0.3	57.7	2	36.6
2.0	...	.	..	2	20.8	1	20.5
3.0	11.2	.	..	1	14.0	1	12.7
2.0	14.7	.	..	7	11.7	.	...
1.0	14.4	.	..	5	9.7	.	...
..	...	.	..	4	11.3	.	...
..	...	.	..	1	9.7	.	...

[1] Running tap water.

It is evident that most of the conducting substance (the hydrochloric acid) is removed within four or five days and that after that time the conductivity remains nearly constant at a value six to eight times that of the conductivity water. It was also proved that the conductivity of the water outside the dialyzer finally remained nearly constant; thus at the end of the experiments with solution No. 3, recorded in the table, the dialyzing tube was placed in about ten times its volume of water having a conductivity of 1.75×10^{-6}; at the end of twenty-four hours the conductivity of this water had increased only to 1.97×10^{-6}, a change which might well have arisen through contamination from the air and sides of the jar. It seems, therefore, justifiable to conclude that the solution contains no more free electrolyte than the outside water, and that most of its conductivity arises from the migration of electric charges on or intimately associated with the gold particles themselves.

Incidentally it is of interest to mention that, as previously observed by Faraday,[1] on long standing the blue gold present in the purple and violet solutions is taken up by fungus growths and that it settles out, leaving the solutions pure red. Thus, after a month gold solution No. 4 had changed from purplish red to

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[1] Faraday: *Phil. Trans.*, 1857, p. 159.

pure red and gold solution No. 3 from violet to purple, which later became red. It may also be noted that a mass of coagulated blue gold was changed to a red colloidal solution by contact with fairly strong ammonium hydroxide for two or three weeks.

II. PREVIOUS WORK ON THE MIGRATION OF COLLOIDS.

Until quite recently most of the work along this line was confined to the migration of mechanically prepared suspensions of visible particles and was connected with investigations on electrical endosmose. All of this earlier work is well summarized in the text-books.[1] It was found that all particles suspended in water migrated toward the anode; except that Quincke[2] states that when the potential gradient was low enough a reversal in their direction took place along the walls of the tube owing to the current of water there flowing toward the cathode. His experiments[3] with lycopodium particles suspended in water show that their rate of migration is directly proportional to the potential gradient, though this conclusion is not definitely drawn by the author. The actual rate of migration of these particles is readily calculated from his data to be 0.00025 cm. per second for a potential gradient of 1 volt per centimeter.

The first extended investigation of the behavior of colloids towards the electric current was carried out by Picton and Linder.[4] They found that various colloids contained in a vertical tube migrated downwards with a sharp surface of demarcation, when a potential difference of suitable sign, which varied with the nature of the colloid, was applied. This boundary could be migrated upwards by reversing the current, but the colloid could not be raised completely from the lower electrode except in the case of dilute solutions containing very fine particles, owing to the effect of gravity. Out of sixteen colloids tested they found that eleven migrated toward the anode and five toward the cathode. They state further that in general the direction of migration is in agreement with the acidic or basic character of the colloid. They noticed, also, that with certain colloids after prolonged action of the current the surface of demarcation which had been steadily moving downward reversed its direction and began to move up-

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[1] See Wiedemann's "Electricität," Vol. II, p. 166 (1883); Lehmann's "Molecularphysik," Vol. I, p. 830 (1888).

[2] Pogg. *Ann.*, **113**, 569, 582 (1861).

[3] *Ibid.*, **113**, 580.

[4] *J. Chem. Soc.*, **71**, 568 (1897).

wards without any change being made in the electrical connections. This phenomenon is generally referred to as the "reverse movement."

These results, so far as the direction of migration is concerned, were confirmed and extended by Spring[1] and by Lottermoser.[2] From these agreeing determinations one may conclude that aqueous colloidal solutions of the noble metals, of metallic sulphides and of mechanically prepared suspensions contain negatively charged particles, whereas basic hydroxides (iron, aluminum, thorium, etc.), together with some dyestuffs, contain positively charged particles.

In 1899 Hardy[3] clearly pointed out the fact that the direction of migration of egg-albumen depends on the nature of the solution, the colloid going to the anode in alkaline solution and to the cathode in acid solution. When the solution was exactly neutral the colloid coagulated. Hardy also observed a "reverse movement," which he attributed to the action of the electrolytes accumulated around the poles by the action of the current. Later he reproduced all the same phenomena with globulin,[4] and determined its rate of migration to be equal to that of the calcium ion.

A pronounced reverse movement was also obtained by one of us[5] with red colloidal gold.

That most colloids are coagulated and precipitated by the passage of the electric current is well established.[6] Zsigmondy found that his red gold solution was simultaneously turned blue. Spring showed, further, that Röntgen rays, the brush discharge, connection with one pole of a Holtz machine, the alternating current from an induction coil and a single pole of an electric circuit are without apparent effect, thus greatly distinguishing these preparations from suspensions of particles in gases.

In 1898 Coehn,[7] extending the idea of contact electrification previously applied to electrical endosmose, showed that in all the cases tested, with one exception, the electricity generated upon either liquid or solid substances by contact, as determined by the

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[1] *Rec. trav. chim. Pays-Bas.*, **19**, 220 (1900).

[2] "Ueber anorganische Colloide," p. 76 (1901), Stuttgart.

[3] *Jour. physiol.*, **24**, 292 (1899).

[4] *Ibid.*, **29**, XXVI (1903).

[5] Blake: *Am. J. Sci.*, **16**, 433 (1903).

[6] Zsigmondy: *Ann. Chem.* (Liebig), **301**, 36 (1898); Bredig's "Anorganische Fermente," 1901, p. 28 (Leipsic); Spring: *Loc. cit.*, p. 209.

[7] *Wied. Ann.*, **64**, 217.

direction of their migration, was always such that the substance having the higher dielectric constant took the positive charge. The dielectric constant of water is the highest known; hence substances suspended in water should be negatively charged. This is generally the case with mechanical suspensions, but it is evident that this theory does not apply to the colloidal solutions used by Picton and Linder, and by Hardy.

The recent work of Billitzer[1] offers a possible explanation of this variance between the ideas based on chemical conceptions and those based on "contact electricity" by applying the theory of the electrical double-layer. Billitzer maintains that colloidal particles of the noble metals act as an oxygen electrode, or after treatment with hydrogen as a hydrogen electrode, toward the surrounding medium, whereas silver acts as a silver electrode. From a consideration of the concentration of the active substance in the particles and of the corresponding ions in the liquid, the potential difference between them may be predicted, and consequently the direction of migration. Conversely, at the concentration at which the direction of migration reverses (Hardy's "iso-electric" point), the potential of the metal toward the liquid is zero. This fact was made the basis of a new method for determining absolute potentials.

In this connection it is interesting to note that Perrin[2] has found that the direction of electrical endosmose through semipermeable plugs, made of different substances, depends on the acid or basic nature both of the plug and of the liquid. Basic plugs in pure or acidified water cause electrical endosmose to the anode; chemically neutral plugs also have this effect in acid solution, but cause the water to flow to the cathode in alkaline solution.

An interesting experiment of Lehmann's[3] should not be omitted in this connection. He found that when a difference of potential was maintained between electrodes immersed in solidified gelatine containing suspended particles, a dark region gradually extended from the anode and a light one from the cathode. Where the boundaries of these regions met, the suspended particles were precipitated and the gelatine melted. It would seem that the extension of the light region was the primary effect of migration,

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[1] *Wied. Ann.*, **11**, 902 (1903).

[2] *Compt. Rend.*, **136**, 1441 (1903).

[3] *Wied. Ann.*, **52**, 455 (1894) ; *Ztschr. phys. Chem.*, **14**, 301.

and that of the dark region was the "reverse movement." This experiment will be referred to again.[1]

Picton and Linder[2] have further found that two different colloids which have the property of migrating in opposite directions precipitate or partially coagulate each other when their solutions are mixed. Biltz[3] has furnished further evidence of this phenomenon. It is evident that even in a single colloidal solution, after the reverse movement has set in, oppositely charged particles must be present and coagulation might be expected to ensue. That in the case of colloidal gold the particles brought together by the reverse movement become neutral and cease to migrate, but without apparent coagulation, has been shown by an experiment made by one of us.[4]

III. APPARATUS AND METHOD USED IN THE MIGRATION EXPERIMENTS.

The apparatus used in these experiments consisted of vertical glass tubes 2.45 or 2.75 cm. in diameter and 30 to 50 cm. in length, closed at both ends with goldbeaters' skin. Holes were blown in the sides of the tube at varous heights to enable the portions of liquid above them to be separately withdrawn at the end of the experiment by means of a pipette, for the purpose of determining their conductivity; during the experiment these holes were closed with rubber bands. The lower end of the tube was placed in an open vessel usually containing 100 cc. of water. Just beneath and in contact with the membrane at the foot of the tube was placed an electrode consisting either of a straight platinum wire or of a platinum ring. Over the top of the tube was placed a slightly wider tube held in place by a rubber band. Into this upper tube a similar electrode was introduced in contact with the membrane, and it was filled with 50 cc. of water. In some cases a slow current of conductivity water was passed through

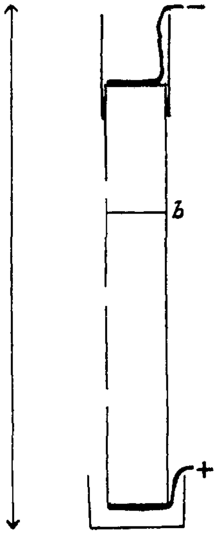

Fig. 1.

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[1] See also Bechhold : *Ztschr. phys. Chem.*, **48**, 422 (1904).

[2] *Op. cit.*, **71**, 572. Compare also Spring : *Op. cit.*, **19**, 222.

[3] *Ber. d. chem. Ges.*, **37**, 1095, 1766 (1904).

[4] Blake : *Loc. cit.*

the compartments surrounding the two electrodes. In the vertical tube itself was usually placed one of the completely dialyzed gold solutions already described. This was always allowed to stand in the tube for an hour before the circuit was completed, since otherwise convection currents caused disturbance in the liquid. The electrodes were ordinarily directly connected with the terminals of the 110- or 220-volt street circuit. Owing to the high resistance of the purified colloidal solution the heating effect of the current was inappreciable.

IV. THE PHENOMENA OBSERVED IN THE MIGRATION OF COLLOIDAL GOLD.

The phenomena were found to be simplest in character when the experiments were carried out in the dark, when the electrolytes accumulating around the electrodes were washed away by a continuous current of conductivity water, and when the electrode at the top was made the cathode. In this case the colloidal gold begins at once to move away from the upper membrane with a sharp surface of demarcation between the dark red solution and the perfectly colorless liquid above. This surface moves rapidly downward at first, at a rate of about 12 cm. per hour when a potential gradient of 6 volts per centimeter is maintained. The rate of movement of the surface remains fairly constant as long as it is in the upper part of the tube, after which it continuously decreases. If the current be interrupted when the boundary has moved half way down the tube, the gold solution will be seen by its color to be more concentrated as a whole and scarcely any precipitate will be found on the lower membrane. If the migration be continued, the boundary finally reaches the lower membrane and all the gold is found as a thin layer of a red mud. When conductivity water is added to this it again passes completely in to colloidal solution. The colloid in this new solution can be again migrated down with the production of the same phenomena as before, and the mud again dissolved in water. This process can be repeated indefinitely. It is found that the conductivity of the successive colloidal solutions so obtained diminishes until it becomes not much greater than that of the water used for making up the solutions. This behavior is illustrated by the conductivity values given in Table II, which were obtained by successive migrations of dialyzed solution No. 4, dissolving the mud each time in the original volume of water having a conductivity of 1.3×10^{-6}.

TABLE II.

	$\kappa \times 10^6$.
Dialyzed solution	13.2
Solution after 1st migration	7.7
" " 2nd "	4.2
" " 3rd "	2.7
" " 4th "	2.1
" " 5th "	1.8

In these experiments running water was not used around the electrodes, but 150 cc. of conductivity water were placed at each end. The conductivity of this water increased during the fourth migration around the top electrode to 6.9 and around the bottom to 29.8, and during the fifth migration around the top to 6.5 and around the bottom to 19.9.

In the interpretation of these results it should be recalled that this decrease in conductivity can not be produced by prolonged dialysis of the solution as was shown in §I, and that, therefore, it is not due to the elimination of free electrolyte. It must, in accordance with the well-founded ideas in regard to the factors determining electrolytic conduction, be due to one or more of three other causes—to a decrease in the number of charged gold particles and of the oppositely charged free ions that may be present with them, to a decrease in the rate of migration, or to a diminished charge on each particle. The first assumption would require a coagulation or precipitation of some of the particles, and this is in contradiction with the fact that after four migrations there was no appreciable change in concentration, color, or turbidity when the solution was brought back to its original volume. That the rate of migration of the gold particles is not changed will be shown by the measurements of the rate described in §V. The conclusion seems justifiable that electric charges have been removed from the gold particles, and that they are removed in the form of ordinary ions is shown by the face that electrolytes pass into the anode compartment in considerable quantity. The conductivity of the gold particles seems, therefore to be due to negative ions (probably chlorine ions) associated with them, these being so firmly bound that they are not separated by dialysis, but are removed, probably at the membrane, by the electric force applied.

It was found that strong diffused daylight, falling on one side of a vertical tube in which the gold was being migrated downward, gave rise to a considerable disturbance of the boundary, causing the gold to rise rapidly on the side toward the window and to sink on the opposite side. A convection current was set up in the liquid owing to the heating effect of the sun's rays. The disturbance so produced was not appreciably lessened by surrounding the tube with a glass water-jacket. Investigated in the sun's spectrum obtained with a concave grating, it was found that the disturbance was greatest in those parts of the spectrum where the absorption of light by the solution was the strongest. Thus a red solution was disturbed only by light of wave-length less than that of the yellowish green, and the increased absorption beyond this point toward the violet end of the spectrum was marked. A violet solution was more or less sensitive to all wave-lengths, but especially to those in the yellowish green, at which point the strongest absorption also occurred.[1] Owing to the fact that the migrating surface is not always equally sensitive no quantitative results could be obtained.

This phenomena is doubtless entirely attributable to convection currents in the liquid arising from the heating effect of the light. Two facts tend to show that it is the suspended particles and not the glass that are heated. First, the effect is specific; thus it was obtained with opaque solutions like those of gold, silver, platinum and carbon, but not with transparent ones like quartz, silicic acid, gelatine, or ferric hydroxide. Second, the effect does not persist after the light is shut off, whereas, if a similar disturbance be produced by holding a lighted match a few centimeters from the tube, the effect increases several fold in the next two or three minutes after the match is removed.

Experiments on the rate of migration, conducted in the dark, show no deviation from those conducted in a room with curtains drawn; hence it is not necessary to work in complete darkness. In general, the disturbance is less the larger the bore of the tube.

Another cause of disturbance, especially marked with impure solutions, arises from the accumulation of electrolytes around the cathode, when water is not kept running past the ends of the tube. In such a case the surface of demarcation becomes very sensitive to external influences, and may break up or become indistinct.

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[1] Confirmed by Ehrenhaft, Drude's *Annalen*, (4) **11**, 489 (1903).

This is especially likely to happen while the surface is in the upper third of the tube. The cause of this phenomenon becomes evident from the following consideration of the conditions that must determine the stability of the migrating surface. The rate of migration of the gold particles, as will be shown later, varies directly as the potential gradient. Now the potential gradient must evidently be constantly somewhat greater above the gold surface than immediately below it in order that the boundary may be stable, for in such a case any particles which have accidentally gotten above the surface will be carried back into it in virtue of their greater velocity. But with a constant potential difference between the ends of the tube the potential gradient in any section varies directly as the resistance of the liquid in that section, or inversely as its conductivity. We have already seen that the conductivity of a gold solution is, in part, due to the gold particles themselves and in part to free electrolytes. During the migration the concentration of the free electrolytes remains constant throughout the tube when their accumulation at the ends is prevented by running water; hence the conductivity of the liquid above the boundary is that of the free electrolytes alone, while below the boundary it is that of these electrolytes plus that of the gold particles, so the conditions of stability just stated are fulfilled. On the other hand, when the electrolytes are allowed to accumulate at the cathode they soon enter the upper portion of the migration-tube, and may increase the conductivity of the clear layer of liquid to a value above that of the gold solution below it, thus producing conditions of instability.

If, moreover, the water is not renewed around the anode, and the solution is so dilute that one can see through it, often after half an hour a darker boundary may be seen a few centimeters from the bottom moving quite rapidly up the tube. These darker surfaces do not penetrate into the clear water above the uppermost boundary, but either finally fade away in the middle of the tube or ultimately reverse the direction of their motion and reach the bottom of the tube. This phenomenon may arise from one or both of the two following causes: First, as in the case of disturbance from the cathode, the electrolytes collecting at the anode pass into the tube and decrease the resistance, and the potential gradient in its lower portion, causing the gold particles to move more slowly than those above and hence to concentrate up to the point to which the free electrolyte has penetrated. Secondly, it may be due, in part, to the "reverse movement" frequently mentioned in the literature referred to in §II. This phenomenon requires the assumption of a change in the sign of the charge on the gold particles at the lower membrane. It will be more fully discussed below.

If, after the gold has all migrated to the lower membrane, the water around the electrodes is renewed and the current is reversed, the gold then moves steadily upward until the concentration throughout the whole tube has become nearly uniform. The surface of demarcation is faint and unstable, and if disturbed will not re-form as long as free electrolytes are uniformly distributed throughout the tube. Owing, however, to the accumulation of electrolytes around the anode at the top the surface may become stable in the upper part of the tube, its color continually growing deeper, and its rate of motion decreasing in accordance with the principles previously described (see Table XVII, page 1364).

V. THE RATE OF MIGRATION OF COLLOIDAL GOLD.

The quantitative experiments on the rate of migration were carried out in vertical tubes, arranged as described in §III. The position of the migrating boundary was read by means of a meter-stick placed beside the tube, supported in a metal base, and provided with an index finger touching the tube. It was usually possible to determine the position of the boundary to within 0.5 mm. The experiments were almost all made either in the dark or in a room with the curtains drawn. The potential difference of 110 or 220 volts, ordinarily applied from the street circuit, showed maximum variations of 10 per cent., but the variations were so irregular and of so short duration that their effect was, to a great extent, eliminated.

The experiments will be first presented which show most clearly the relation between potential gradient and rate of migration. Two tubes, each 38 cm. long, one having a diameter of 5 mm. and the other of 13 mm., fitted as usual, were filled with a dialyzed gold solution containing 680 mg. gold per liter and having a conductivity of 16×10^{-6}, and were connected in series with the terminals of a 110-volt circuit. Hence it follows that the potential gradient in the tubes was inversely proportional to the squares of their diameters, or as $13^2 : 5^2$ or 6.76 : 1. It was found that in five and three-quarter hours the boundary moved down a distance of 14.3 cm. in the 5 mm. tube and a distance of 2.1 cm. in the 13 mm. tube, showing that the rate was 6.81 times greater in the smaller tube, in complete agreement with the relative potential gradients.

The following experiment was made with a very concentrated, dialyzed and electrically purified gold solution, containing several grams of gold per liter and having a conductivity of 8.4×10^{-6}, contained in a tube 48.5 cm. long and 2.45 cm. in diameter, with a difference of potential of 110 or 220 volts, alternately applied. In this way the rates due to the different potential gradients can be directly compared even though the rate is not constant for a constant potential difference.

TABLE III.

No.	Applied electromotive in volts.	Time intervals in minutes.	Distance intervals in centimeters.	Rate in centimeters per hour.
1	110	10	0.75	4.5
2	220	10	1.8	10.8
3	110	10	0.8	4.8
4	220	10	1.7	10.2
5	110	10	0.9	5.4
6	220	10	1.75	10.5
7	110	10	0.75	4.5
8	220	10	1.50	9.0
9	110	20	1.10	3.3
10	220	16	3.50	8.1
11	110	9	0.50	3.3
12	220	10	1.15	6.9
13	110	10	0.40	2.4

The accuracy with which the surface could be read is indicated by the number of decimals used in expressing the distances. A comparison of these results with those obtained in a similar experiment with a constant potential difference (see Table IV) shows that for the accuracy obtained the rate varies directly as the potential gradient for the first eight readings. The sudden drop noted at reading No. 9 is attributable to the reverse effect, discussed farther on. It is noteworthy that beyond this point the relative rate of migration is distinctly less for the smaller potential.

The next experiments show the rate of migration during the process of purification of gold solutions by the successive downward migrations and re-solutions described in §IV. The three following experiments were made with dialyzed solution No. 4 in a tube 36.5 cm. long and 2.75 cm. in diameter. A potential difference of 220 volts was applied. Conductivity water was kept slowly flowing by both ends of the tube. The room was darkened by drawing the curtains. The gold was migrated down three times in succession and twice redissolved in conductivity water. The conductivity of the gold solution (κ_S) and that (κ_W) of the water in the tube after gold had migrated out of it was each time determined.

The first column gives the number of the reading, the second the total time in hours, the third the distance from the upper membrane to the boundary, and the fourth the rate in centimeters per hour between the successive readings.

TABLE IV.

Solution No. 4. First migration down. $\kappa_s = 12.7 \times 10^{-6}$; $\kappa_w = 3.7 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.167	2.00	12.00
2	0.33	4.10	12.60
3	0.50	5.80	10.20
4	0.67	8.00	13.20
5	0.83	10.30	13.80
6	1.00	12.35	12.30
7	1.17	13.60	7.50
8	1.42	15.50	7.60
9	1.58	16.35	5.10
10	1.75	17.20	5.10
11	2.00	18.25	4.20
12	2.25	19.05	3.20
13	2.67	20.45	3.36
14	3.25	22.15	2.91
15	4.25	24.25	2.10
16	4.83	25.30	1.80
17	5.83	26.20	0.90
18	6.17	26.40	0.60

TABLE V.

Solution No. 4. Second migration down. $\kappa_s = 7.8 \times 10^{-6}$; $\kappa_w = 3.9 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.267	2.70	10.13
2	0.43	4.25	9.30
3	0.60	5.65	8.40
4	0.77	7.00	8.10
5	0.93	8.10	6.60
6	1.13	9.20	5.50
7	1.33	10.25	5.25
8	1.58	11.55	4.80
9	1.92	12.85	4.35
10	Surface suddenly broken up at $t = 2.4$, distance = 15.		
11	5.08	17.85	2.50
12	5.58	19.20	2.70
13	6.08	21.40	4.40
14	6.75	23.60	3.30
15	7.25	25.10	3.00
16	7.75	26.05	1.90

TABLE VI.

Solution No. 4. Third migration down. $\kappa_s = 5.1 \times 10^{-6}$; $\kappa_w = 2.1 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.167	1.90	11.40
2	0.35	3.90	10.90
3	0.52	5.60	10.20
4	0.68	7.10	9.00
5	0.85	8.70	9.60
6	1.27	12.10	8.16
7	1.52	13.50	5.60
8	1.78	15.15	6.19
9	2.04	16.50	5.40
10	2.28	17.65	4.60
11	2.53	18.80	4.60
12	2.95	20.60	4.32
13	3.38	22.30	3.92
14	3.88	24.15	3.70
15	4.60	26.20	2.86
16	5.93	28.90	2.03

The following series of experiments were made like the preceding ones, except that they were carried out in complete darkness and that the water was not flowing around the ends of the tube. The migration was, moreover, repeated five times. The tube used was 48.5 cm. in length and 2.45 cm. in diameter. Another portion of the same gold solution was used for these experiments.

TABLE VII.

Solution No. 4. First migration down. $\kappa_s = 13.2 \times 10^{-6}$; $\kappa_w = 4.0 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.55	3.5	6.4
2	0.97	6.4	6.8
3	1.47	10.3	7.8
4	1.80	13.2	8.7
5	2.13	16.6	10.2
6	2.38	18.5	7.6
7	2.63	20.0	6.0
8	3.05	21.7	4.8
9	3.55	23.3	3.2
10	4.05	24.6	2.6
11	4.38	25.3	2.1[1]
12	32.38	41.8	1.03

[1] Change water at ends.

TABLE VIII.

Solution No. 4. Second migration down. $\kappa_s = 7.6 \times 10^{-6}$; $\kappa_w = 2.8 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.67	4.6	6.90
2	1.00	6.7	6.30
3	1.67	10.6	5.85
4	2.38	14.1	4.90
5	2.72	15.7	4.80
6	3.22	18.0	4.60
7	3.72	19.9	3.80
8	4.22	21.7	3.60
9	4.72	23.4	3.00
10	7.13	30.8	3.06

TABLE IX.

Solution No. 4. Third migration down. $\kappa_s = 4.2 \times 10^{-6}$; $\kappa_w = 2.5 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.317	3.00	9.46
2	0.52	4.80	9.00
3	0.85	7.70	8.70
4	1.78	14.80	7.61
5	2.02	16.40	6.86
6	2.72	20.45	6.43
7	3.22	22.90	4.90
8	5.13	30.10	3.76
9	5.72	32.15	3.51
10	7.92	39.00	3.11

TABLE X.

Solution No. 4. Fourth migration down. $\kappa_s = 2.7 \times 10^{-6}$; $\kappa_w = 2.4 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.25	2.05	8.20
2	0.50	4.00	7.80
3	0.75	6.05	8.20
4	1.58	13.00	8.34
5	2.08	17.25	8.50
6	2.58	21.15	7.80
7	3.08	24.00	5.70
8	4.52	29.60	3.91
9	5.72	33.05	2.87
10	8.15	38.15	2.51
11	10.62	43.60	1.80

Final κ aq. top (150 cm³.) = 6.9×10^{-6}.
Final κ aq. bottom (150 cm³.) = 29.8×10^{-6}.

TABLE XI.

Solution No. 4. Fifth migration down. $\kappa_s = 2.1 \times 10^{-6}$; $\kappa_w = 2.1 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimers per hour.
1	0.25	2.30	9.2
2	0.50	4.20	7.6
3	0.75	6.25	8.2
4	1.00	8.25	8.0
5	1.25	10.30	8.2
6	1.50	12.35	8.2
7	1.72	14.15	8.3
8	1.97	16.30	8.6
9	2.22	18.50	8.8
10	2.47	20.50	8.0
11	2.72	22.65	8.6
12	2.97	24.60	7.8
13	3.85	31.20	7.5
14	4.10	32.70	6.0
15	5.27	39.50	5.8
16	6.19	44.50	5.5
17	6.69	46.30	3.6

Final κ aq. top (150 cm³.) = 6.5×10^{-6}.
Final κ aq. bottom (150 cm³.) = 19.9×10^{-6}.

Attention may first be directed to the comparative rates of migration at the beginning of the experiments when the potential gradient throughout the solution is uniform and is readily calculated from the applied electromotive force and the length of the tube. It will be seen that even in the early stages the rates in most cases decrease. To determine the true initial rate we have extrapolated for time zero from the first few rates under the assumption that the change in rate is a linear function of the time. The values so obtained from the results of the three experiments of the first series are 12.0, 11.0 and 11.8 cm. per hour respectively, and the potential gradient in these cases was 6.03 volts per centimeter. The average of these values corresponds to 1.92 cm. per hour for a potential gradient of 1 volt per centimeter. The initial rates for the last four experiments of the second series, similarly extrapolated, are 8.0, 9.8, 8.2 and 8.3 cm. per hour, with a potential gradient of 4.54 volts per centimeter. The average of these values corresponds to 1.89 cm. per hour for unit potential gradient, in approximate accordance with the result of the first series. The agreement of the rates in the separate experiments of either series shows that the rate of migration is independent of the conductivity of the gold solution and of the extent to which it has been freed from electrolytes. Since on each migration only an insignificant quantity of gold is precipitated in an insoluble form on the lower membrane and, therefore, the solution always contains the same quantity of gold and since there is no free electrolyte in the dialyzed solution used at the start in excess of that present in the water outside the dialyzer, and since at any rate the free electrolytes must have been almost wholly removed after the first migration when the few cubic centimeters of soluble mud were dissolved in conductivity water, this decrease in conductivity of the gold solution must be due to a decrease in the total charge on the particles, arising from the separation of the ions of hydrochloric acid associated with them, indicating either a partial coagulation of the gold insufficient to increase the turbidity of the solution, or that more than one ion was originally associated with each particle. Since the particles are negatively charged, chlorine ions are probably directly attached to them, while hydrogen ions remain in the neighborhood to maintain the electrical neutrality of the solution.

Except in the first experiment of each series the rates of migration show a steady decrease, usually, however, showing a rather sudden decrease at a point from one-third to one-half the distance down the tube. The gradual decrease in the rates is due to the fact that the total resistance of the continually lengthening layer of clear water above the boundary continually increases, whereas the specific resistance of the gold solution continually decreases, owing to the fact, already noted, that the concentration of the gold solution continually increases during the migration. Hence the potential gradient in the gold solution continually decreases, and, consequently, the rate of migration. This increase in the conductivity of the migrating solution may be determined approximately by pipetting it out after the boundary has moved part way down the tube. Thus in one experiment the specific conductivity of the gold solution, concentrated by the migration, was found to have increased 26 per cent. after its average concentration had increased 37 per cent. It has been found, in fact, that a formula based on the assumption that the gold below the boundary remains uniformly distributed throughout the experiment and that its specific conductivity varies directly as its concentration, while the specific conductivity of the water above the boundary remains constant throughout the experiment at the value actually determined by pipetting it out at the end of the experiment, enables one to predict to within a few millimeters the total distance the boundary will have moved during any interval of time. It will be shown, however, that the concentration of the gold solution does not remain uniform and that other factors materially influence the rate when the potential gradient is small. Hence the formula just mentioned can be only an approximation, which we allude to, however, in support of the ideas regarding the conditions determining the stability of the boundary enunciated in §IV.

The irregularity in the beginning, rates of the first experiment of the second series (Table VI), is attributable to the accumulation of electrolytes around the cathode in accordance with principles already discussed (page 1348).

The magnitude of the sudden drop in the rate between successive readings, as well as the percentage of the distance from the top of the tube at which it occurs in the foregoing experiments, is shown in Table XII.

An inspection of the following tables containing the rates will show that no other changes in the rate for smilar intervals of time are nearly so great as those here set opposite the percentage distances from the top, as is also shown in the foregoing table for the readings adjacent on either side to the reading at which the reverse effect occurs. It is plain that the method of making the readings precluded the possibility of detecting the maximum rate of de-

TABLE XII.

Series 1.

Table No.	Reading No.	Percentage change of rate per minute.	Percentage distance from top of tube.	Conductivity of gold solution × 10⁶.
	5–6	—1.1		
IV	6–7	—3.9	34	12.7
	7–8	+0.1		
V	10–11	Surface broken up	(39)	7.8
	5–6	—0.6		
VI	6–7	—2.1	33	5.1
	7–8	+0.5		

Series 2.

Table No.	Reading No.	Percentage change of rate per minute.	Percentage distance from top of tube.	Conductivity of gold solution × 10⁶.
	4–5	+0.8		
VII	5–6	—1.7	34	13.2
	6–7	—1.4		
	5–6	—0.1		
VIII	6–7	—0.6	37	7.6
	7–8	—0.1		
	5–6	—0.1		
IX	6–7	—0.8	42	4.2
	7–8	—0.2		
	5–6	—0.3		
X	6–7	—0.9	44	2.7
	7–8	—0.3		
	12–13	—0.1		
XI	13–14	—1.3	64	2.1
	14–15	—0.1		

crease, such as more frequent readings would have disclosed. The position at which this sudden decrease occurs is usually about one-third the distance down the tube, but it is still farther down in extremely pure solutions. This sudden decrease in the rate may be due to one or both of the two following causes: (1) To a sudden decrease in the potential gradient at the boundary, due to the arrival of a denser layer of hydrogen ions from the anode; (2) to a decrease in the resultant negative charge on the gold in the boundary, considered as a whole, due to the arrival of positively charged gold particles originating at the anode membrane. It was found by actual measurement of the conductivity of the electrically concentrated gold solution after a migration part way down the tube that the conductivity of the gold solution had greatly increased. From a consideration of the observed rates of migration in the different sections of the tube, and from a consideration of the relative values of κ_g and κ_w, already defined, as well as from the approximate agreement of the rates of migration with those calculated from the formula mentioned on page 1356, it may easily be seen that the average potential gradient in the electrically concentrated gold solution up to the time the reverse effect occurs might well be only one-half or one-third the average potential gradient at the boundary up to that time. It will be shown that the rate of migration of the boundary is approximately that of the univalent ions of neutral inorganic salts. Hence the observed sudden retardation in the rate of migration, if due to any influence originating at the anode, must be due to the arrival of hydrogen ions. This will appear more fully farther on.

It will now be shown that any increase in the conductivity at the boundary produced by the arrival of hydrogen ions from the anode, with consequent decrease in the potential gradient at that point, is insufficient to account for the observed phenomena. In dilute solutions the motion of the boundary is either entirely arrested at a point about one-fourth the way down the tube, or its direction of motion reversed. In cases where the boundary thus becomes stationary the gold is slowly carried to the lower membrane in insensible portions, the color below the boundary gradually fading away in the next few hours.[1] This effect could be due only to a complete neutralization of the particles forming the boundary. The actual simultaneous migration of gold up the tube as a dense layer, starting at the bottom, has already been alluded to (page 1348) and considered more fully in §XIII. This behavior can be explained only on the assumption that the hydrogen ions carry the gold along with them to some extent. It is plain that in so far as positively charged particles thus brought to the boundary tend to neutralize its charge, taken as a whole, the rate of migration would not be dependent solely on the potential gradient.

It was found in experiments similarly conducted that the initial rate is independent of the concentration of the gold solution for

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[1] See Blake: *Am. J. Sci.*, **16**, 434.

variations of a hundredfold. So, also, gold solution No. 3, after treatment with hydrogen under a pressure of two feet of water for times varying from two hours to two months, gave the same initial rate of migration from the cathode as before such treatment, and the same as gold solution No. 4. The same initial rate in the same direction was obtained when an excess of ammonia was added to the solution, with or without the hydrogen. The red gold solution formed by treating coagulated blue gold with ammonia (see page 1341) also migrated from the cathode with nearly the same initial rate.

It was found that gold solution No. 2, which was originally somewhat turbid, migrated as usual for the first ten days. Thereafter part of the gold was coagulated and rendered insoluble by each successive migration, the gold thus thrown out forming a red precipitate with network structure on the lower membrane. This red precipitate turned blue on drying, as does the soluble red mud, and as does pure red silver.[1] The following tables of rates, obtained with solutions No. 2, during the second and third migrations, may be given to illustrate this behavior, more especially as it is also the behavior of most colloidal solutions. The tube was 33.1 cm. long and 2.75 cm. in diameter. The water at the ends, though not running, was kept below 10×10^{-6}. The potential difference was 110 volts. Strong light was excluded from the room.

Practically none of the gold was precipitated during the first migration, which gave decreasing rates after the first increase which occurs in impure solutions (see Table VI). A considerable part of the gold was precipitated in each of the subsequent experiments, one-sixth having been rendered insoluble in all three migrations. It is evident that this precipitation of the gold would render its concentration in the lower part of the tube less than it would otherwise have been, thus lowering the conductivity and increasing the potential in this part of the tube, and lessening the retardation of the boundary by positively charged particles originating at the anode-membrane. As a matter of fact, no increase in the depth of color of the solution during the migration can be seen with gold solutions showing such constant rates nor with most of the other colloidal solutions tested. It is doubtless for

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[1] Blake: *Am. J. Sci.*, **16**, 282 (1903).

TABLE XIII.

Solution No. 2. Second migration down. $\kappa_s = 7.3 \times 10^{-6}$; $\kappa_w = 2.7 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters. per hour.	$\frac{\text{Distance}}{\text{Time}}$.
1	0.38	2.05	5.35	5.35
2	0.55	3.00	5.70	5.45
3	0.72	4.05	6.30	5.62
4	0.88	5.07	6.12	5.76
5	0.98	5.71	6.40	5.83
6	1.20	7.00	5.95	5.83
7	1.37	8.00	6.00	5.84
8	1.57	9.30	6.50	5.92
9	1.73	10.40	6.60	6.01
10	1.90	11.45	6.30	6.03
11	2.07	12.61	6.96	6.09
12	2.28	14.05	6.65	6.17
13	2.48	15.65	8.00	6.31
14	2.68	17.15	7.50	6.40
15	2.85	18.90	10.50	6.63
16	3.02	20.00	6.60	6.62
17	3.18	20.60	3.60	6.48
18	3.35	21.15	3.30	6.31
19	3.52	21.61	2.76	6.14
20	3.68	22.11	3.00	6.01
21	4.13	23.25	2.53	5.63
22	4.38	23.85	2.40	5.45
23	4.63	24.20	1.40	5.23
24	5.13	25.02	1.64	4.88
25	5.67	25.90	1.65	4.57
26	7.75	28.10	1.06	3.63

TABLE XIV.

Solution No. 2. Third migration down. $\kappa_s = 3.8 \times 10^{-6}$; $\kappa_w = 2.2 \times 10^{-6}$.

No.	t. Time in hours.	s. Distance in centimeters.	Rate in centimeters per hour.	$\frac{\text{Distance}}{\text{Time}}$.
1	0.33	1.83	5.32	5.32
2	0.50	2.78	5.70	5.56
3	0.67	3.78	6.00	5.64
4	0.83	4.80	6.14	5.78
5	1.00	5.73	5.58	5.73
6	1.22	7.03	6.00	5.76
7	1.38	8.10	6.42	5.87
8	1.58	9.37	6.35	5.93
9	1.75	10.33	5.76	5.90
10	2.00	12.13	7.20	6.07
11	2.17	13.15	6.12	6.07
12	2.33	14.13	5.88	6.06
13	2.58	15.83	6.80	6.14
14	3.42	19.73	4.68	5.77
15	3.92	21.03	2.60	5.37
16	4.28	22.13	3.00	5.17
17	4.78	23.18	2.10	4.85
18	5.50	25.33	2.63	4.52
19	7.43	28.03	1.47	3.77

these reasons that the rate is so nearly constant. The initial values correspond to a rate of 1.60 cm. per hour for unit potential gradient.

In experiments made a few days later than the foregoing the first migration gave nearly constant rates and an insoluble red precipitate formed on the lower membrane, showing that the solution itself was unstable, a property indicated by its original turbidity.

VI. DIFFUSION OF COLLOIDAL GOLD.

The gold from a portion of solution No. 4 was migrated clear to the bottom of the tube, which was 33.1 cm. long and 2.75 cm. in diameter. The potential difference of 220 volts was left on twelve hours longer and then the circuit was broken. The gold began to diffuse quite rapidly up the tube, the boundary becoming faint and indistinct. After a few hours the concentration of the gold in the boundary increased until no irregularities in the density of the gold solution could be detected. Thereafter the surface remained sharp and perpendicular to the axis of the tube for weeks. After the first week a faint pink tint could be detected in the water above the gold. The experiment was carried out in a room with drawn curtains. The ends of the tube were left in contact with water, as in the migration, fresh water having been added shortly before the circuit was broken. The rates of diffusion are given in the following tables:

TABLE XV.

Time in hours.	Distance from bottom of tube in centimeters.	Rate in centimeters per hour.	*k*.		Variations of *k* for 1 millimeter of distance.
4.5	0.60	0.13	0.040	Day (surface indistinct)	
21.5	1.20	0.03	0.034	Night	0.039
31.5	1.55	0.03	0.038	Day	
46.5	2.20	0.04	0.052	Night	
55.5	2.40	0.02	0.052	Day	
70.5	2.65	0.02	0.050	Night	
78.5	2.90	0.03	0.054	Day	0.050
95.5	3.20	0.02	0.052	Night	
119.0	3.40	0.01	0.049	Day and night	
126.0	3.60	0.03	0.051	Day	
142.0	3.80	0.01	0.051	Night	
151.0	3.90	0.01	0.050	Day	
165.5	4.00	0.01	0.048	Night	
174.5	4.10	0.01	0.048	Day	
190.5	4.20	0.01	0.049	Night	
199.5	4.30	0.01	0.046	Day	
214.0	4.30	0.00	0.043	Night	
237.5	4.50	0.01	0.043	Day and night	0.045

The following experiment was similarly conducted with the gold migrated downward from a portion of solution No.3 in a tube 36.5 cm. long and 2.45 cm. in diameter. The experiment was carried out in the dark.

TABLE XVI.

Time in hours.	Distance from bottom of tube in centimeters.	Rate in centimeters per hour.	k.	Variation of k for 1 mm. of distance.	Temperature water at bottom.
5.0	1.20	0.240	0.144	Surface indistinct	21.0
9.5	1.45	0.033	0.105	0.096	20.5
24.5	2.05	0.040	0.086		22.0
33.0	2.30	0.029	0.080		22.8
49.0	2.80	0.031	0.080		20.8
59.5	3.15	0.034	0.083	0.079	20.5
74.0	3.45	0.021	0.080		20.0
81.5	3.60	0.020	0.079		20.5
96.0	3.90	0.021	0.079		20.6
106.0	4.05	0.015	0.077		20.7
119.0	4.35	0.023	0.080		21.0
128.0	4.45	0.011	0.078		18.0
145.0	4.75	0.018	0.078		19.4
155.0	4.85	0.010	0.076		19.4
169.0	5.05	0.014	0.075		18.7
178.0	5.20	0.017	0.076		18.8
192.0	5.40	0.014	0.076		18.0
200.0	5.45	0.006	0.074		19.5
215.0	5.60	0.010	0.073		19.0
224.0	5.70	0.011	0.073		18.2
239.0	5.80	0.007	0.070	0.073	18.0

If this is a true diffusion of the gold, the rate should vary as its concentration in solution. Under the given conditions the concentration of the gold solution would vary as $1/s$, where s is the distance of the moving boundary from the lower membrane.

Hence putting

$$\frac{ds}{dt} = \frac{k}{s}, \qquad (1)$$

when k is a constant, we have

$$k = \frac{s^2}{2t},$$

if $s = 0$ when $t = 0$. The values of k thus calculated are included in the tables and are constant within 2 or 3 mm., although the value of k tends to decrease. The beginning values are rendered uncertain by reason of the slight disturbance in the surface produced by the rapid diffusion at first as well as by the fact that the lower membrane is slightly convex downward, owing to the weight of the liquid. The bulk of the "solid" red gold at the start introduces errors which may be neglected until great accuracy is desired. The relative values of the constant in the two experiments ($80/50 = 1.6:1$) is in approximate agreement with the amounts of gold deposited on the lower membranes from the two solutions, which were in the ratio of 2.4 : 1. This constant represents the rate of diffusion for the concentration existing in the gold solution, if uniform, when the boundary is 1 cm. from the bottom, as may readily be seen by putting $s = 1$ in formula (I). The rates for this concentration, equal to 4.82 and 11.68 grams of gold per liter, respectively, are of the same order of magnitude as those obtained with electrolytes in concentrated solution diffusing into pure water. It was found that with ordinary precautions these solutions, even though containing several grams of gold to the liter, gave no measurable lowering of the freezing-point of water and no measurable osmotic pressure.

It is plain that this diffusion of the gold would lessen the rate of migration downward under the conditions of the foregoing experiments, and that the percentage retardation due to this cause would increase as the potential gradient falls. This is indicated in the last few readings of Table III, as already pointed out, the concentration of the gold in that experiment having been very great.

VII. THE EFFECT OF GRAVITY ON THE RATE OF MIGRATION.

The phenomena occurring in the upward migration of colloidal gold under the given conditions are described in § IV. The following downward and upward migrations were made with solution No. 2 contained in a tube 33.1 cm. long and 2.75 cm. in diameter, with a potential difference of 110 volts. After the first migration down, the water at the ends was changed and the current reversed, giving the first migration up. The water at the ends was again changed and the gold migrated down again. Then the water at the ends was changed again, giving the second migration up. The amount of electrolyte eliminated at the ends continually diminished. Strong light was excluded from the room.

Solution No. 2.

TABLE XVII.

First migration up.

No.	Distance from bottom in centimeters.	Rate in centimeters per hour.
..	4.10	....
1	7.50	2.46
2	8.68	2.95
3	9.60	2.76
4	10.55	2.85
5	Surface broken up.	
6	21.45	3.72
7	22.20	4.50
8	22.80	3.00
9	23.57	3.85
10	24.60	3.43
11	28.70	2.90
12	29.60	2.70
13	30.70	2.64

TABLE XVIII.

Second migration up.

No.	Time in hours.	Distance from bottom in centimeters.	Rate in centimeters per hour.
..	....	4.55	....
1	0.25	5.10	2.20
2	2.07	10.90	3.20
3	2.32	11.90	4.00
4	2.57	12.95	4.20
5	2.82	13.90	3.80
6	3.07	14.90	4.00[1]
7	3.32	15.85	3.80
8	3.57	16.60	3.00
9	3.82	17.60	4.00
10	4.07	Unreadable.	....

[1] Surface disturbed.

The following experiment was similarly conducted with solution No. 4 after the first migration down. The tube was 36.5 cm. long and 2.75 cm. in diameter, the potential difference 220 volts. The experiment was carried out in the dark.

TABLE XIX.

Solution No. 4. First migration up.

No.	Time in hours.	Distance from bottom in centimeters.	Rate in centimeters per hour.
1	0.25	1.9	7.6
2	0.67	4.8	6.8
3	0.92	6.8	8.0
4	1.17	8.5	6.8
5	1.47	10.5	6.7
6	1.92	14.1	8.0
7	2.25	Surface broken up.	

The average rate of migration upward, derived from the nearly constant rates of Table XVIII, is 3.42 cm. per hour for a potential gradient of 3.32 volts per centimeter, if uniform, corresponding to a rate of 1.03 cm. per hour for unit potential gradient. The nearly constant rates given in Table XIX give an average of 7.34 cm. per hour for a potential gradient of 6.03 volts per centimeter, or 1.22 cm. per hour for unit potential gradient. The rates of migration downward for the same potential gradients were 1.60 cm. and 1.90 cm. per hour, respectively. There seems, therefore, to be a gravity effect on the rate of migration which increases with the potential gradient. We have seen that with zero potential gradient the surface slowly moves up the tube owing to diffusion. With small potential gradients amounting to a few tenths of a volt per centimeter the difference in the rate down and up is scarcely distinguishable. The results are not sufficiently extended, however, to permit one to draw any certain conclusion beyond this, that the gravity effect is not larger than half the difference between the rates up and down, or 0.34 cm. per hour for a potential gradient of 6.03 volts per centimeter. Subtracting this from 1.90 cm. per hour we obtain 1.56 cm. per hour, or 0.00043 cm. per second, the velocity of the sodium ion. The results are not sufficiently accurate to enable one to say that the rate of migration of colloidal gold differs from that of any of the ions of neutral inorganic salts of univalent elements.

The constancy of the rate in the upward migrations is conditioned by the fact that the potential gradient in the pure water above the gold is nearly uniform and that the most advanced gold particles practically move under that potential gradient.

It was found that a solution of red gold containing 0.68 gram per liter falls into pure water at the rate of 1.3 cm. per minute. The phenomenon could not be distinguished from a similar experiment made with a solution of potassium permanganate containing the same amount of dissolved substance per liter. Since this rate is so much greater than the rate of migration with the potentials usually applied, it is evident why the current cannot raise the gold from the lower membrane when the cathode is at the bottom.[1]

VIII. COLLOIDAL PRUSSIAN BLUE.

It was of considerable interest to apply the foregoing method of investigation to other colloids in order to test the generality of its applicability and, if possible, to discover new relations between the properties of these substances. Accordingly, the following experiments were made with colloidal Prussian blue, formed by the action of ferric chloride on an excess of potassium ferrocyanide in solution. The resulting precipitate was purified to some extent by three or four filtrations with a porous cell. A little of the blue material went into the cell, but most of it remained outside. One gram of this material, air-dried, was dis-

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[1] *Cf.* p. 1341.

solved in a liter of ordinary distilled water ($\kappa_w = 15 \times 10^{-6}$), the conductivity of the resulting solution being 187.8×10^{-6}. The tube used in these experiments was 33.1 cm. in length and 2.75 cm. in diameter. The voltage between the terminals was 220, with the cathode at the top. Fifty cc. of water were placed at each end of the tube. Strong light was excluded from the room.

TABLE XX.

Prussian blue solution. First migration down.

$\kappa_s = 187.8 \times 10^{-6}$; $\kappa_w = 11.0 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.167	2.0	12.0
2	0.33	4.0	12.0
3	0.50	5.9	11.4
4	0.67	7.7	10.8
5	0.83	9.3	9.6
6	1.00	10.7	8.4
7	1.25	12.8	6.8
8	1.50	13.7	5.2
9	2.25	16.3	3.1
10	2.58	17.1	2.4
11	3.08	17.9	1.6
12	3.83	19.2	1.7
13	4.17	19.5	0.90
14	4.83	20.2	1.05
15	5.67	21.0	0.96
16	6.33	21.7	1.05
17	8.50	23.5	0.81
18	11.00	24.8	0.52
19	22.00	28.5	0.16

TABLE XXI.

Prussian blue solution. Second migration down.

$\kappa_s = 56.5 \times 10^{-6}$; $\kappa_w = 4.0 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.28	3.3	11.8
2	0.50	4.3	4.6
3	0.83	5.4	3.3
4	1.83	8.0	2.6
5	2.17	8.9	2.7
6	2.67	9.9	2.0
7	4.25	12.7	2.0
8	5.25	14.3	1.6
9	6.75	16.2	1.3
10	7.75	17.3	1.1
11	24.42	30.5	0.46

TABLE XXII.

Prussian blue solution. Third migration down.

$\kappa_s = 16.4 \times 10^{-6}$; $\kappa_w = 2.6 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.183	2.3	12.5
2	0.33	3.4	7.3
3	0.53	4.7	6.6
4	0.70	5.6	5.4
5	1.17	7.7	4.5
6	1.50	8.9	3.6
7	1.83	10.1	3.6
8	2.42	11.9	3.09
9	3.08	13.5	2.40
10	4.00	15.3	1.96
11	4.75	16.6	1.73
12	5.75	18.3	1.70
13	6.83	20.2	1.75
14	8.08	22.1	1.52

TABLE XXIII.

Prussian blue solution. Fourth migration down.

$\kappa_s = 6.7 \times 10^{-6}$; $\kappa_w = 3.4 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.15	2.1	14.0
2	0.25	3.2	11.0
3	0.35	4.3	11.0
4	0.50	5.5	8.0
5	0.75	7.6	8.4
6	1.00	9.5	7.6
7	1.83	14.4	5.9
8	2.33	16.7	4.6
9	3.00	19.2	3.75
10	3.67	21.3	3.45
11	4.33	23.2	2.85
12	5.08	25.0	2.16
13	6.67	28.1	1.96

These results confirm the indications obtained with gold both as to the general march of the experiments and the magnitude and direction of the rate of migration. The initial values in the four experiments give an average rate of 1.88 cm. per hour for unit potential gradient, whereas that obtained for gold was 1.90 cm. per hour for substantially the same potential gradient. The reverse effect is especially pronounced, more particularly as it occurs so near the beginning of the experiment. This is best seen in the last migration, since the solution was at first so impure that the heating effect of the current and other disturbing influences due to electrolytes might not be negligible. In the last experiment the reverse effect (reading No. 3) occurred after 0.35 hour at a point 4.3 cm. down the tube, whereas the hydrogen ions, under the given potential gradient, 6.65 volts per centimeter, if uniform, would have moved up to this point in exactly the same time. The potential gradient in the Prussian blue solution would have changed but little in that time.

Hence it seems certain that the sudden decrease in the rate of migration attributed to the reverse effect, both of colloidal gold and of colloidal Prussian blue, is due to the arrival of hydrogen ions liberated at the anode, whether with or without associated colloidal particles.

IX. COLLOIDAL PLATINUM.

Platinum electrodes were sparked for about twenty minutes under water having a conductivity of 1.1×10^{-6}. The resulting solution had a conductivity of 2.9×10^{-6}. This solution was placed in a tube 33.1 cm. long and 2.75 cm. in diameter, and joined to the 220-volt circuit with the cathode at the top. After the platinum had been migrated clear to the bottom of the tube the water at the ends of the tube was changed and the platinum migrated up. The experiments were carried out in the dark.

Platinum solution, fresh.

TABLE XXIV.

First migration down. $\kappa_s = 2.9$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.25	2.2	8.8
2	0.50	4.5	9.2
3	1.00	9.2	9.4
4	1.50	14.1	10.2
5	2.00	18.5	8.4
6	2.35	20.9	6.9
7	3.93	28.0	4.9

TABLE XXV.

First migration up.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.88	5.2	5.9
2	1.13	6.8	6.4
3	1.52	8.6	4.7
4	1.95	10.9	5.3
5	2.85	15.3	4.9[1]
6	3.33	17.1	4.3[1]
7	3.83	20.6	7.0[1]
8	4.33	Surface broken up	

[1] Surface irregular.

The following experiments were similarly conducted with part of the same solution two days later, after the particles visible under the microscope had largely settled out and the conductivity had increased to 4.6×10^{-6}.

TABLE XXVI. TABLE XXVII.

Platinum solution, two days old.

First migration down. $\kappa_s = 4.6 \times 10^{-}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.25	2.7	10.8
2	0.50	5.1	9.6
3	0.75	8.2	12.4
4	1.00	10.8	10.4
5	1.80	18.8	10.0
6	2.10	20.2	4.7
7	2.35	21.1	3.6
8	2.63	22.1	3.4
9	2.85	22.8	3.2

First migration up.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.25	1.7	6.8
2	0.50	3.6	7.6
3	0.75	5.1	6.0
4	1.00	6.4	5.2
5	1.27	7.7	4.9
6	1.50	9.0	5.6
7	1.75	10.1	4.4[1]
8	2.00	Unreadable	..

[1] Surface irregular.

The rates obtained in both experiments are a little less than those obtained for gold, both in the migration down and in the migration up, being respectively 1.5 cm. and 0.95 cm. per hour for unit potential gradient, whereas the corresponding rates for gold for substantially the same potential gradient were 1.90 and 1.22 cm. per hour. The difference in the initial rates in the two experiments is so great, however, that little significance can be attached to the variation pointed out. The gravity effect is about the same, being 0.28 cm. per hour for a potential gradient of 6.65 volts per centimeter. The reverse effect is marked in the experiment recorded in Table XXVI.

X. QUARTZ SUSPENSIONS.

Rock quartz was pulverized in an agate mortar and suspended in conductivity water. It was found that most of the powder settled out over night, forming one or more sharp surfaces of demarcation, but leaving a uniform turbidity behind. Particles showing the Brownian movement were readily visible under the microscope in all these surfaces. The effect is especially beautiful in reflected sunlight, and is visible between crossed nicols. On adding a little barium chloride solution the Brownian movement was instantly stopped and the quartz precipitated, although no aggregates seemed to form. In the following migration experiments, two suspensions of powdered quartz were used, each of which had stood over night. The supernatant liquid, containing one surface of demarcation (which settled at the rate of 0.3 cm. per hour), as well as the uniform turbidity, was decanted and migrated down in a tube 33.1 cm. long and 2.75 cm. in diameter. The difference of potential was 220 volts, with the cathode at the top. The experiments were conducted in ordinary daylight.

TABLE XXVIII.

Quartz suspension No. 1. First migration down. $\kappa_s = 5.6 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.30	2.5	8.3
2	0.45	3.9	9.3
3	0.62	5.9	12.0
4	0.78	7.9	12.0
5	0.92	9.8	14.25
6	1.20	11.9	7.4
7	2.20	16.1	4.2
8	2.50	17.0	3.0
9	2.83	17.6	1.8
10	3.47	18.6	1.8
11	4.28	19.8	1.5
12	4.70	20.4	1.03
13	4.95	20.7	1.2
14	5.95	22.1	1.4
15	7.17	24.0	1.6
16	7.67	24.6	1.2

TABLE XXIX.

TABLE XXX.

Quartz supension No. 2.

First migration down. $\kappa_s = 3.8 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.28	2.5	8.8
2	0.42	3.8	9.7
3	0.62	5.7	9.5
4	0.92	8.5	8.0
5	1.12	10.6	10.5
6	1.37	13.8	12.8
7	1.70	17.7	11.7
8	1.92	20.4	12.5
9	2.08	22.3	11.4
10	2.25	23.8	9.0
11	2.43	25.1	7.1

First migration up.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.12	0.8	6.9
2	0.23	1.6	6.0
3	0.35	2.4	6.0
4	0.50	3.3	6.0
5	0.70	4.3	5.0[1]
6	1.00	5.7	4.7[1]
7	1.52	8.4	5.2[1]
8	2.33	13.1	5.8
9	2.70	15.7	7.1
10	2.83	16.8	8.2
11	3.33	20.0	6.4

[1] Surface irregular.

TABLE XXXI.

Quartz suspension No. 2.

Second migration down.

$\kappa s = 1.9 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.25	2.5	10.0
2	0.40	3.7	8.0
3	0.57	5.3	9.6
4	0.87	8.0	9.0
5	1.00	9.3	9.7
6	1.25	12.0	10.8
7	1.45	14.1	10.5
8	2.25	20.5	8.0
9	2.65	23.1	6.5
10	3.00	25.3	6.3
11	3.67	28.8	5.25

TABLE XXXII.

Second migration up.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	1.23	6.7	5.5
2	1.90	10.9	6.3
3	2.48	14.0	5.3
4	2.93	15.5	3.3
5	3.37	18.0	5.8
6	4.03	20.7	4.05
7	4.53	Surface irregular.	

The results obtained with quartz are practically identical with those obtained with platinum, both down and up, even including the reverse effect (Table XXVIII, reading No. 5). In all the other experiments with quartz the formation of a precipitate on the lower membrane could readily be observed from the start, although the effect of settling would be inappreciable in the given time. It is probable that the unstable particles present in the quartz and platinum hydrosols were without effect on the rate of migration, since the migrating surface, both down and up, would be composed of the stablest particles.

The decrease in the rate going up, which usually occurs after the first few readings, is probably due to the effect of the hydrogen ions coming down the tube, thus lessening the potential gradient by their presence.

The results obtained with platinum and quartz seem quite remarkable. We have here, especially with quartz, the migration of particles whose diameter is approximately 1 μ with a velocity almost equal to the ionic rate of migration, in a solution as free from ions as could be obtained without unusual care. The spark discharge itself would, it is true, furnish an abundant supply of ions or ionic charges in the case of colloidal platinum, but the source of the negative charges on the quartz particles is not evident. The phenomenon of electrical endosmose, whereby water is usually carried to the cathode through porous walls of inert materials, as well as the fact that the quartz particles are negatively charged, indicate that the particles are not simply inert bodies swept along by the ions resulting from the electrolysis. Besides, if the platinum and quartz are carried by hydroxyl ions, one would expect that the rate of migration would exceed that obtained for gold, where, especially in the first migration, the particles seem to be associated with chlorine ions. The effect of such impurities as carbonic acid must likewise be considered. The fact that the rate of migration of gold was the same for five successive migrations, however, whereby the chlorine must have been almost completely removed, indicates that the rate of migration of a boundary of colloidal gold would not be much changed if some other ion took the place of chlorine. That single gold particles migrate upward with the hydrogen ion in the "reverse movement" has already been pointed out. That they can be carried back and forth across the tube an indefinite number of times in the same experiment without a stable boundary, and that their primary direction of migration is quite independent of the acid or alkaline, oxidizing or reducing nature of the solution, will be shown farther on, thus indicating that the quartz and platinum are no more remarkable than the gold in their relations to ions.

It may be pointed out, further, that the magnitude of the gravity effect is apparently the same for gold, platinum and quartz, even though the density of the quartz is so much less than that of the metals. This probably arises from the fact that the largest suspensible particles of the different substances bear a constant inverse relation to their density. Thus the largest particles of quartz suspensible for a week or more are approximately 0.5 μ in diameter, whereas practically all of the microscopically visible particles of platinum settle out in a day or two. The growth of fungus in either case, building the colloidal particles into its mycelium,[1] renders it difficult to obtain precise information in this direction.

XI. FERRIC HYDROXIDE.

Ferric hydroxide precipitated from ferric chloride solution by an excess of ammonia at the boiling temperature, washed by decantation several times, then filtered and washed, was shaken up with a small amount of ferric chloride in solution. Disintegration gradually took place, with a continual lessening of the turbidity,

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[1] *Cf.* p. 1341.

until, after some time, the liquid was scarcely turbid. The liquid was then dialyzed for more than a week against running tap water, then for several weeks against ordinary distilled water, frequently changed. When the dialysis was stopped the conductivity of the colloidal solution scarcely changed in twenty-four hours when dialyzed against fresh ordinary distilled water. Three months later this solution was diluted with two volumes of conductivity water, the resulting solution having a conductivity of 35.7×10^{-6}, and containing 1.850 grams ferric oxide per liter. Migrated downward (toward the cathode) with a potential difference of 220 volts in a tube 33.1 cm. long and 2.75 cm. in diameter, this solution gave the following results, the experiment being carried out in ordinary daylight.

TABLE XXXIII.

Colloidal "ferric hydrate."

First migration down. $\kappa_s = 35.7 \times 10^{-6}$: $\kappa_w = 75.1 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.
1	0.167	2.0	12.0
2	0.42	4.0	8.0
3	0.62	5.6	8.0
4	0.95	8.1	7.5
5	1.67	14.5	8.9
6	2.33	20.2	8.5
7	3.67	30.2	7.5

Final κ water around anode (50 cc.) $= 1130 \times 10^{-6}$ (smelled strongly of chlorine).

Final κ water around cathode (50 cc.) $= 10.5 \times 10^{-6}$.

The rates given in the foregoing table closely resemble those obtained in other solutions where precipitation took place. In this experiment the formation of the precipitate could be watched, as the solution was transparent. The colloidal material was migrated clear to the bottom of the tube, where it became entirely insoluble in water, gelatinous and adhesive, still containing large amounts of chlorine. The density of the color of the colloidal solution remained constant during the migration. The large amount of conducting material eliminated around the anode (see table), together with the fact that the conductivity of the water in the tube was greatly increased during the migration (see κ_w in the table) show that the chlorine thus liberated had been in stable union with the colloid. In this connection it is interesting to note that none of this chlorine is precipitated from the original solution by silver nitrate, even on boiling. Complete congelation gelatinizes the colloid and frees the chlorine (silver nitrate test). No lowering of the freezing-point could be detected.

Experiments made to determine the coagulative power of electrolytes when added to this solution confirmed the conclusion arrived at by Duclaux[1] that the polyvalent anions, as well as the hydroxyl ion, replace the chlorine in the compound $x\mathrm{Fe(OH)_3}.y\mathrm{FeCl_3}$. A nearly similar conclusion was arrived at by Hardy.[2]

XII. SILICIC ACID.

A very stable and pure solution of silicic acid may be obtained by dialyzing a water solution of solid water-glass (A), or the same solution to which a large excess of hydrochloric acid has been added (B). Either solution is finally acid to litmus and phenolphthaleïn, has a puckering taste, and is free from chlorine and sodium. The solutions, originally containing 100 grams of solid water-glass to the liter, contained (A) 5.63 grams, $\kappa = 67.6 \times 10^{-6}$, (B) 14.73 grams silica per liter, $\kappa = 100 \times 10^{-6}$. Neither solution gave any lowering of the freezing-point. Solution (B) was readily coagulated by a small amount of $m/300.\mathrm{AlCl_3}$, but neither solution was coagulated perceptibly by any other of the common electrolytes tested, except in strong or alkaline solution, or at the boiling temperature. Boiling alone was without effect. The following rates were obtained with solution (B) in a tube 37.85 cm. long and 1.2 cm. in diameter with a potential drop of 220 volts between straight platinum wire electrodes. The experiment was carried out in ordinary daylight.

TABLE XXXIV.

Colloidal silicic acid. First migration down and up. $\kappa_3 = 100 \times 10^{-6}$.

Distance from top. Centimeters.	Rate in centimeters per hour.	Distance from top. Centimeters.	Rate in centimeters per hour.
1.45	3.22	13.20	3.00
4.10	4.18	14.80	3.20
4.95	3.40	15.80	3.33
8.30	4.47	16.80	3.00
9.40	4.12	18.00	3.00
7.85	−5.5[1]	19.35	2.70

[1] Spontaneous double reversal.

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[1] *Compt. Rend.*, **138**, 809 (1904).

[2] *Proc. Roy. Soc.*, **66**, 120 (1900).

TABLE XXXIV.—(*Continued.*)

Colloidal silicic acid. First migration down and up. $\kappa_s = 100 \times 10^{-6}$.

Distance from top. Centimeters.	Rate in centimeters per hour.	Distance from top. Centimeters.	Rate in centimeters per hour.
8.30	3.37	20.15	2.40
8.95	3.25	21.40	1.67
9.80	3.00	22.60	1.29
10.50	3.50	23.60	1.40
11.20	3.50	24.10	1.43
12.60	3.23	Change water at ends and reverse current.	
24.55	...	19.15	1.00
24.17	3.80	18.85	0.90
23.10	4.28	18.50	1.05
22.25	4.25	18.30	0.67
21.10	5.75	18.00	1.00
20.80	1.20	17.55	0.75
20.30	2.00	17.30	0.63
20.00	1.20	17.07	0.73
19.85	1.00	16.77	0.62
19.60	1.00	16.40	0.62
19.40	1.00	15.55	0.68

Final κ aq. top $= 16.9 \times 10^{-6}$; final κ aq. bottom $= 13.7 \times 10^{-6}$.

The rate of migration of silicic acid is seen to be distinctly less than that of the colloids previously worked with, the potential gradient in this experiment being substantially the same as that in the first series of experiments with gold, where the initial rate of migration was 1.90 cm. per hour for unit potential gradient, as against 0.55 cm. per hour in this experiment. The reverse effect was so great as temporarily to reverse the direction of migration of the boundary. The migrating boundary could be detected only by the difference in the index of refraction and in the second migration down finally stopped at a point one-tenth the distance from the bottom. The water above the boundary was then removed and the silicic acid found to be solid. This solid substance, insoluble in water and structureless when air-dried, lost 85.5 per cent. of water over calcium chloride within forty-eight hours, when its weight became constant for thirty hours. Ignited before the blast-lamp, this latter substance lost 16.1 per cent. of water, corresponding within the limits of error (the ignited silica was quite hygroscopic) to the formula $H_4Si_3O_8$.

	Calculated. Gram.	Found. Gram.
H_2O	0.0485	0.0470
SiO_2	0.2436	0.2451

XIII. THE REVERSE MOVEMENT IN THE MIGRATION OF COLLOIDS.

The "reverse effect" has been shown to be a general characteristic in the migration of colloids. The following experiments show further that this reverse effect is not due solely to the hydrogen ions migrating up the tube, but that part, at least, of the colloid itself is also moved in the direction opposite to that of the primary migration (see page 1358). It was found that the direction of migration, though not the rate, could be best studied in tubes placed horizontally, closed at both ends with goldbeaters' skin, with compartments at the ends containing the electrodes, past which conductivity water could be kept running. The electrodes and the tubes supplying the water entered the end compartments through rubber stoppers, as shown in the photographs. The water escaped through a hole cut in the upper side of the rubber band connecting the end tubes with the migration tube.

The colloidal solutions placed in the migration tube were as follows: A concentrated dialyzed and electrically purified red gold solution made in the manner previously described; a violet gold solution made by dialyzing against ordinary distilled water the red gold solution obtained by sparking gold electrodes in a 0.001-normal sodium hydroxide solution with a current of 10 to 12 amperes;[1] a concentrated red gold solution, prepared by digesting coagulated blue gold with ammonia (see page 1341); a greenish yellow silver solution prepared by sparking silver electrodes in conductivity water and dialyzing to remove the silver hydroxide with which the solution is contaminated.[2] The conductivities of these solutions varied from 5×10^{-6} to 80×10^{-6}. The results obtained with them were scarcely distinguishable, however, as will be shown. The migration tube was 24.2 cm. long and 2.75 cm. in diameter. The distance between the electrodes was 26.6 cm. The voltage was 220.

Under these conditions, with conductivity water running past the ends of the tube so fast that its conductivity is but slightly increased, usually from 2×10^{-6} to 4×10^{-6}, the following

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[1] A more concentrated and more stable red gold solution may be obtained by sparking gold electrodes in the presence of a solution of hydrochloric acid having a conductivity of 200×10^{-6}.

[2] Blake: *Am. J. Sci.*, **16**, 431 (1903). The cathode lost 0.0507 gram, the anode 0.0698 gram. The conductivity increased from 3.3×10^{-6} to 17.5×10^{-6} during the sparking. A considerable amount of slime was deposited on the cathode from the undialyzed solution but not from the dialyzed solution under the given conditions.

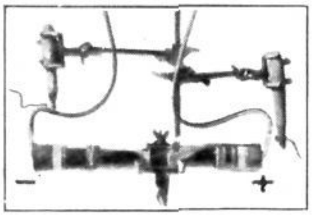

Fig. 2.
Bredig's gold solution,
after one hour.

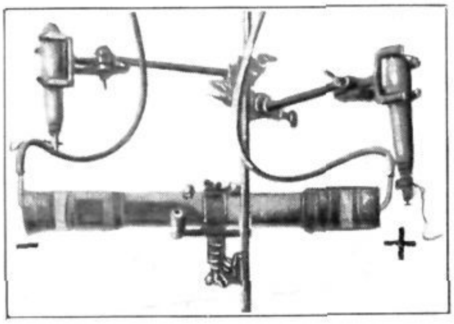

Fig. 3.
Ether-acetylene gold solution, after
one hour.

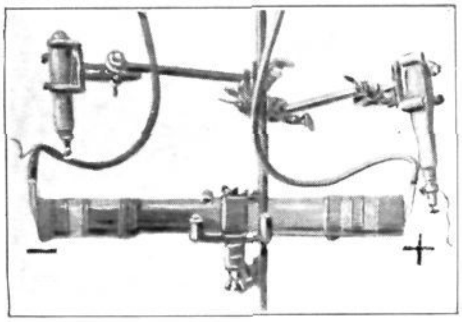

Fig. 4.
Same as Fig. 3, one hour later.

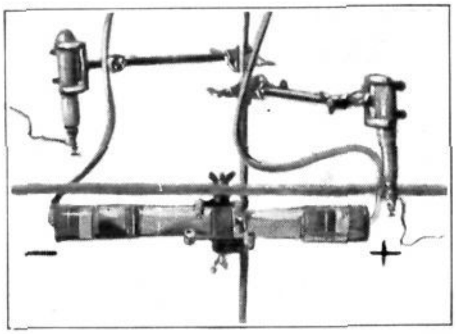

Fig. 5.
Bredig's silver solution, water at
ends not running.

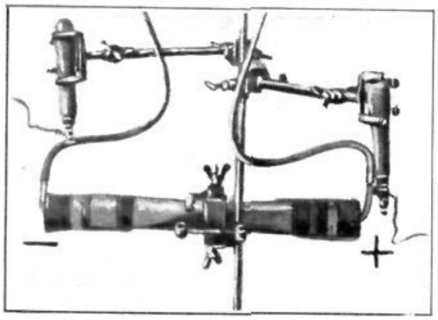

Fig. 6.
Same as Fig. 5, one-half hour later,
water running.

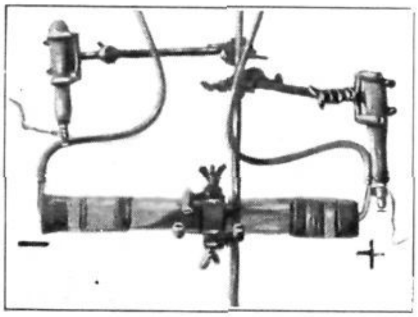

Fig. 7.
Same as Fig. 6, two hours later.

Fig. 8.
Gelatine, coagulated at *g*.

phenomena occur when contact is made. The colloid at once moves 1 or 2 mm. away from the cathode membrane with a sharp vertical surface of demarcation. This boundary then stops, the upper edge of it breaks and the colloid along the top of the tube moves rapidly toward the anode, leaving a streak of clear water behind. When this clear streak has nearly reached the anode membrane a V-shaped clearing occurs somewhere near the middle of the tube (Fig. 2), gradually extending downward and widening toward the anode (Fig. 3). Meanwhile a heavy solution of the colloid gathers on the bottom of the tube next to the anode membrane. This heavy solution soon begins to move back along the bottom of the tube toward the cathode, whether the current is kept running or is turned off, evidently due to gravity in the latter case. When the current is kept running, the heavy solution soon accumulates against the cathode membrane. The colloid still remaining in dilute solution in the upper portion of the cathode end of the tube, as well as the heavy solution accumulated against the cathode membrane and extending as a thin layer on the bottom of the tube throughout its entire length, now assume an unending variety of formations, some of the more characteristic of which are shown in the photographs (Figs. 4 to 7). The conditions governing these motions have not been fully ascertained. Although further work in this direction is contemplated, a preliminary statement may be made here. If the current is allowed to run for several hours without changing the water at the ends of the tube, then the colloid may be made to migrate from either pole by allowing pure water to flow slowly through the compartment surrounding the pole from which the repulsion takes place; after several hours the colloid is sometimes again attracted to the pole at which the pure water is flowing. On one occasion a deposit of soluble mud (red gold) which had formed on the anode membrane was removed by the action of the current.

An experiment made with the same silver solution in the same sort of vertical tube used for the migration experiments shows further the complexity and sensitiveness of the reverse movement and indicates another cause for the instability of the migrating surface with gold and other colloids in the upper portions of the tube. It was found that when the silver solution was contained in a tube 48.5 cm. long and 2.45 cm. in diameter and a potential difference of 220 volts was applied with the cathode at the top, in the dark, the colloid moved 1 or 2 cm. away from the upper membrane in the first ten minutes and then moved back again the next ten minutes. When fresh water was added at the top, this process was repeated many times. It thus appears that the initial rate of migration of colloidal silver, independent of the "reverse movement," is about the same as that of gold.

XIV. EXPERIMENTAL CRITICISM OF BILLITZER'S HYPOTHESES.

It will be evident at once that the results thus far recorded are very different from what would be expected from a consideration of the hypotheses propounded by Billitzer in the work cited in §II. In this connection it will be convenient to distinguish the "reverse movement," above described, from a change in the direction of the primary migration, which we shall speak of as a "reversal." A direct attempt to repeat the work of Billitzer on the change in the direction of migration of colloids due to the presence of various electrolytes, failed to reveal any reversals with Bredig's platinum or with red colloidal gold solutions like those used in the migration experiments, whether the colloid was uncontaminated, or mixed with urea as in Billitzer's experiments. The experiments were tried with the apparatus used by Billitzer—a U-tube—and with vertical tubes like those heretofore described. The amount of electrolyte added to the solution to reverse the direction of migration was varied from a trace to amounts so large that the migrating surface was broken up by the heating effects of the current. The voltage was 110 or 220.

Billitzer added gelatine also to his solutions to prevent the coagulation of the metallic colloid by the electrolytes added, according to principles now well recognized.[1] The effect of adding 0.5 gram per liter of the purest commercial gelatine to the platinum solution whose rate of migration has already been given, is shown in the following table of rates similarly obtained. The tube was 48.5 cm. long and 2.45 cm. in diameter, with 100 cm^3. of conductivity water at the top and 150 cm^3. at the bottom. The voltage was 220, with the anode at the top. Strong light was excluded.

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[1] We are informed by private correspondence that the amount of gelatine added was variable and "recht viel," especially with the platinum solutions.

TABLE XXXV.

Bredig's platinum hydrosol + 0.5 gram gelatine per liter.

$\kappa_s = 31.8 \times 10^{-6}$.

Anode at the top.

No.	Time in hours.	Distance from top in centimeters.	Rate in centimeters per hour.	Surface No.
1	1.17	0.05	0.43	1 Clear above this surface.
2	3.17	0.0	....	
3	3.17	42.1	(2.0)	
4	3.37	41.2	4.5	
5	4.12	40.3	1.2	2 Darker below the surface.
6	4.53	Indistinct, settling.		
7	4.53	0.8	....	
8	22.53	5.9	0.33	
9	24.53	6.4	0.25	
10	30.03	9.4	0.75	3 Same as Surface No. 1.
11	51.03	15.2	0.28	
12	53.03	15.8	0.30	
13	69.03	18.9	0.19	
14	70.0	Rising	....	
15	75.42	16.0	....	

The history represented by the foregoing rates is easily told. At first, part of the material was carried to the lower membrane without a surface of demarcation. At reading No. 3 this material had already migrated 6.4 cm. up the tube (42.1 cm. from the top).[1] Meanwhile all the material had slowly migrated 0.5 cm. downward from the top and then migrated back to its original position (reading Nos. 1 and 2). Surface No. 2 then continued to migrate upward for an hour or so (reading Nos. 4 to 6). It then reversed and simultaneously a new surface—No. 3—formed at the top. This surface slowly migrated downward for a couple of days, and then began to rise. The rate going up is much greater than the rate going down. When the cathode was at the top, the results were equally unsatisfactory, the first migration being towards the cathode.

One might surmise that such an effect as that just described was due to mixed influences, evidently introduced by the gelatine added. An idea as to what these influences are may be gathered from the migration of gelatine alone, similarly placed, except that the cathode was at the top and the solution contained 2 grams of gelatine per liter.

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[1] *Cf.* Lehmann's experiment, p. 1343.

TABLE XXXVI.

Migration of gelatine. Cathode at the top. $\kappa_s = 68 \times 10^{-6}$.

No.	Time in hours.	Distance in centimeters.	Rate in centimeters per hour.	
1	1.17	4.5	3.9	Read by index-of-refraction surface.
2	1.58	6.2	4.1	
3	1.92	6.2	0.0	Current off.
4	2.58	6.2	0.0	
5	3.08	7.9	3.4	
6	4.58	9.1	2.4	
7	19.17	14.5	0.35	Top of gelatine coagulated.
8	21.67	15.2	0.28	
9	25.67	15.9	0.17	
10	42.0	Coagulated down to 23.5, ragged.		
11	216.0	No further change—photograph.		

The index-of-refraction surface used at first as the surface of demarcation of the gelatine was especially sharp, like that of silicic acid. All the gelatine was finally collected in the middle of the tube, as shown in the photograph (Fig. 8), where it coagulated and adhered to the glass. Hence the gelatine migrated away from both poles. That the downward migration was not due to gravity is shown by the result obtained by breaking the current, when the gelatine, not yet coagulated, remained unchanged (reading Nos. 3 and 4).

The gelatine solution was originally acid to phenolphthaleïn and the electrolytes eliminated around the anode contained sulphuric acid. Since the original gelatine solution was acid, the gelatine should, in agreement with the results obtained by Hardy with egg albumen and globulin, have been repelled more strongly from the anode than from the cathode. This was the case, even though the cathode repulsion was aided by gravity. In fact, when the poles were reversed (separate experiment) all the gelatine was finally found on the bottom of the tube in the coagulated state.

These facts show that it would be practically impossible to trace the movements of colloidal platinum in the presence of gelatine and as distinguished from the gelatine, owing to mutual influences. It should be remembered that in the experiment recorded in Table XXXV the two substances were present in nearly the same proportion, since Bredig's platinum hydrosol usually contains about 0.2 gram platinum per liter, and that the platinum alone migrates to the anode and the gelatine the more actively to the cathode. This conflict, continually modified by the action of the electrolytically freed acid and alkali on the gelatine, and by the coagulation of the gelatine, resulted in several reversals of the direction of migration, as is shown in the table. That one colloid will not diffuse through another was discovered by Graham. That suspended particles are carried down by the precipitation of gelatine and gums has been known for a long time. Hence it was scarcely to have been expected that platinum would migrate through gelatine uninfluenced by it. Billitzer found, in fact that his "platinum" (gelatine and platinum) moved to the cathode when considerable amounts of the (acid) electrolytes were present, as we have seen the gelatine alone would do. Hence the platinum was evidently carried along by the gelatine. With less of the acid electrolytes present Billitzer found that the "platinum" moved to the anode. Since in the presence of less acid the gelatine would tend less strongly to migrate toward the cathode, it is probable that in this case the platinum, tending to migrate to the anode, carried the gelatine along with it to some extent. The fact that the direction of migration is often opposite in the two arms of the U-tube makes it difficult to interpret Billitzer's results, but it would seem that most of his "reversals" obtained with "platinum" may be thus accounted for.

In attempting to repeat Billitzer's experiments with colloidal silver a true reversal, or primary migration from the anode, was obtained without the addition of gelatine. Silver nitrate or nitric acid was added to the undialyzed colloidal silver solution until the normality was about 0.008 or 0.004, respectively. When either of these solutions was placed in one of the vertical tubes used for the migration experiments with gold under exactly similar conditions, in the dark, with 50 cm^3. of water at each end, with the anode at the top, the colloid migrated down about 1 cm. in the first half hour and then remained stationary for twenty-four hours. The same thing was obtained when urea was added, and a primary migration from the anode was also obtained in a U-tube under the conditions prescribed by Billitzer, except that no gelatine was added to the solution. The conductivity of these solutions was about 1000×10^{-6}; it was somewhat less, however, when urea was present. It may be added that urea alone tends to prevent the coagulation of metallic colloids either by electrolytes or by the electric current.

XV. THEORETICAL DISCUSSION.

The theoretical aspect of the experimental results of this investigation may be entirely included under the relation of colloids to electrolytes. The most probable explanation of the observed phenomena is that the migration of colloids by the electric current is due to the association of the colloidal particles with ions. From this point of view it is very remarkable that the rate of migration of the colloidal particles[1] and associated ions should be of the same order of magnitude as that of free ions.

An idea as to the nature of the union between the ions and the colloidal particles may be best obtained from the experiments relating to the "reverse movement" of the colloid when migrated in horizontal tubes. It was shown for gold prepared by three different methods, and for silver prepared by Bredig's method, that the colloid could be repelled from both poles simultaneously or repeatedly swept back and forth across the tube from one pole to the other by varying the strength of the acid accumulated at the anode and of the base accumulated at the cathode by the action of the current. The concentration of acid or base necessary to produce this effect was only that accumulated from ordinary or conductivity water and the enclosing vessels by the action of the current for a few minutes under the given conditions. In fact, no lower limit was found for the conductivity of the water at the one end of the tube necessary to produce the foregoing effects, provided that of the water at the other end was still less. This behavior may be due to the fact that the colloidal particles are swept along by the hydrogen ions coming from the anode and by the hydroxyl ions coming from the cathode, with the formation of a cloud of neutral particles at the point where the two influences meet (see Figs. 5, 6 and 7). The fact, often noted, and clearly shown in Fig. 5, that this neutral cloud forms at a point very nearly three-eighths of the distance from the cathode to the anode when the tube is undisturbed, confirms this belief, since this is the ratio of the rate of migration of the hydroxyl to the hydrogn ion. The greater mobility of the hydrogen and hydroxyl ions compared to any other ions they may be associated with to maintain the electrical neutrality of all parts of the solution may be

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[1] On the size of colloidal particles, see Lobry de Bruyn: *Rec. trav. chim. Pays-Bas* 19, 251 (1900); Siedentopf and Zsigmondy: Drude's *Annalen*, 4, 1 (1903); Ehrenhaft: *Ibid.* 11, 489 (1903).

assigned, as was done by Hardy,[1] as a sufficient reason why the colloidal particles would be swept along by the hydrogen and hydroxyl ions, after the primary migration is over, and not swept in the opposite direction by the other ions just mentioned. The fact that Billitzer's hypotheses bearing on this subject could not be confirmed indicates that the colloidal particles are not ion-electrodes in equilibrium with the solution surrounding them, and the results obtained regarding the gradual purification of colloidal gold solutions, first by dialysis of free electrolytes, then by electrolysis of associated electrolytes, renders it highly probable that the union in question is similar to that occurring in so-called "adsorption" phenomena. It would seem, in fact, that the union is quite stable and that the sign of the electric charge is generally reversed only at the electrodes. This tendency of the ions to attach themselves to colloidal particles in water may be identical with that noted in gases by J. J. Thomson and others.

Until more is known about the great resistance encountered by the ions during electrolysis it would be idle to speculate as to why the presence of an associated colloidal particle does not increase that resistance, even though the colloidal particle is surrounded by a water envelope.[2] In this connection it is interesting to note that Smoluchowski,[3] applying the theory of the electrical double layer devised by Helmholtz to explain the phenomenon of electrical endosmose, and using as the potential between the layers of the double sheet the value calculated by Helmholtz from Wiedemann's observations on electrical endosmose, has deduced the conclusion that the rate of migration of particles suspended in water should be of the same order of magnitude as that of the ions. That the rate should be independent of the size and shape of the particles was previously deduced by Lamb.[4] We find, therefore, a theoretical explanation of the otherwise remarkable fact that the association of colloidal particles with ions does not greatly retard their rate of migration, a fact which seems to indicate that the electrical double sheet existing around a single charged particle may be only that due to a single ion associated with it. It is only necessary to add, in view of the experimental confirmation which these theories have received in the foregoing

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[1] *Jour. physiol.*, **29**, cit.

[2] See Parks : *Phil. Mag.*, 4, 240 (1902) ; **5**, 517 (1903) for literature to date.

[3] *Bull. Acad. Sci. de Cracovie*, March, 1903, p. 182 ; *Ref. Phys. Chem. Rev.*, I, p. 124.

[4] Brit. Assn. Report, 1887, p. 502.

pages, that the electrical moment of the double sheet would seem to offer a sufficient explanation of the permanent suspensibility of particles whose density is greater than that of the suspending medium and to place them in the same state as that of heavy ions so far as suspensibility is concerned.

That the density of the suspended particles is greater than that of water is shown in a number of ways. Thus Cholodnyj[1] showed that the density of silver in colloidal solution is equal to that of the metal in the massive state. A density of the gold particles greater than one would be necessary to account for the falling of gold solutions into pure water, as noted on page 1365. A marked gravity effect was obtained in the vertical migrations by noting the difference in the rate up and down, and in the horizontal migrations by noting the actual settling of the colloid to the bottom of the tube. So, also, when quartz particles, which retained the optical properties of massive quartz, were precipitated by the addition of an electrolyte, no aggregation could be detected under the microscope, showing that the settling was not due to a condensation of the colloidal substance.

Not only the migration and the permanent suspensibility of colloidal particles may be thus attributed to the presence of ions, the diffusion observed with colloidal gold may likewise be due to the diffusion of the ions associated with it. However that may be, it is plain that the fact that the gold does diffuse offers a probable explanation of the Brownian movement in this case.

Another interesting phenomenon is also shown most clearly in the diffusion experiments, that is, the stability of the boundary or surface of demarcation.[2] According to the law applicable to the gold solution as a whole, that is, that the rate of diffusion varies as the concentration of the gold in solution, the concentration of the gold solution at any moment should be greatest at the bottom, gradually falling to zero at the top. We have seen that a dense boundary forms, however, as though the gold might migrate faster in the gold solution than into pure water. The stability of the boundary is strikingly shown, also, in the migration experiments made in vertical tubes, in which the boundary usually remains unbroken to the end of the experiment, even though subjected to the many influences revealed by the migrations made in

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[1] *J. Russ. Phys. Chem. Soc.*, **35** (2), p. 585 (1903); *Ref. Phys. Chem. Rev.*, I, p. 125; *Chem. Centrbl.*, 1904, **I**, p. 634.

[2] *Cf.* Barus: Bull. 36, U. S. Geol. Survey.

horizontal tubes. It is plain that the rate of migration of the boundary obtained in the vertical tubes is, on account of the component forces acting in it, only a minimum value for the rate of migration of the single untrammeled particles.

It may be remarked in conclusion that the relation between colloidal particles and ions pointed out in this work may be expected to throw some light on the principles involved in the coagulation of colloids by electrolytes.

SUMMARY.

It has been shown by this investigation that:

(1) Colloidal gold solutions, prepared by the action of an ethereal solution of gold chloride on an aqueous solution of acetylene, retain, even after prolonged dialysis against conductivity water, a constant conductivity five or six times as great as that of the water outside the dialyzer.

(2) This conductivity is almost completely lost by repeatedly migrating the gold downwards with the electric current against a membrane of goldbeaters' skin and redissolving it in pure water, and is to that extent, at least, attributable to electrolytes associated with or "adsorbed" by the gold.

(3) Red gold was obtained as a soluble mud by migrating it against a membrane of goldbeaters' skin; from this, mud solutions of any desired concentration and of great purity were prepared.

(4) Colloids may readily be made to migrate downward with a sharp boundary or surface of demarcation when the colloidal solution is placed in a vertical tube.

(5) This boundary is not readily disturbed by slight temperature changes; neither is it disturbed by the action of light unless the colloidal material is opaque.

(6) The rate of migration of this boundary, under optimum conditions, was determined for gold, platinum, silver, Prussian blue, "ferric hydrate," silicic acid and gelatine.

(7) The rate of migration of colloids is determined primarily by the potential gradient and is directly proportional to it.

(8) The boundary is stable when the potential gradient just above the boundary is greater than that just below it.

(9) The potential gradient, and hence the rate of migration in the different sections of the tube, may be calculated approximately from a knowledge of the initial conductivity of the colloidal solution and of the water above the migrating surface.

(10) An influence due to the force of gravity becomes manifest during the migration.

(11) Gold solutions fall rapidly through pure water without mixing with it.

(12) The soluble mud obtained by downward migration, when placed under pure water, diffused upward into it at a rate comparable with that of electrolytes diffusing from concentrated solutions into pure water.

(13) A reverse effect, consisting either in a sudden retardation of the downward movement of the boundary or in a reversal of its direction, occurs in the migration of colloidal solutions in vertical tubes. This is due, in part, to changes in the potential gradient arising from the decomposition products of electrolysis, and in part to a reverse movement of the colloid itself where precipitation by the current is not complete.

(14) The reverse movement of colloids can best be studied by migrations carried out in horizontal tubes closed at the ends with goldbeaters' skin past which conductivity water may be kept flowing.

(15) The reverse movement was thus shown to be complex, the colloid being carried repeatedly back and forth between the poles as though swept along by the hydrogen and hydroxyl ions after the primary migration had taken place.

(16) A change in the direction of the primary migration was obtained with colloidal silver, but not with gold or platinum, by adding certain electrolytes to the solution.

(17) Gelatine migrates simultaneously from both electrodes.

(18) When a mixture of gelatine and platinum in colloidal solution is migrated, each colloid exerts an influence on the migration of the other.

(19) The "reversals" obtained by Billitzer were probably due to the effect of the migration of the gelatine, superimposed on that of the metallic colloids present with it.

(20) The rate of migration of the boundary, independent of gravity, diffusion and the reverse effect, in the case of colloidal gold, platinum, silver, Prussian blue, "ferric hydrate" and quartz, is approximately that of the univalent ions of neutral inorganic salts.

(21) These facts are in agreement with the deductions of Lamb and Smoluchowski, based on the theory of the electrical double

layer, according to which the rate of migration of solid particles suspended in water should be independent of the size and shape of the particles, and should be of the same order of magnitude as the rate of migration of the ions.

(22) The charge on the colloidal particles is probably due to associated ions, which determine the migration, diffusion and permanent suspensibility of the particles.

This investigation will be continued during the following year.

NOTE.

A Contact Process for the Preparation of Ammonia-free Water. —The preparation of ammonia-free water in chemical and water laboratories has usually been limited to one or two tedious processes. Although otherwise inexpensive, the time required and the necessary strict attention to sources of ammonia from corks and joints, as well as the continual testing of the product, have made this chemical a decided luxury. Difficulty in getting certain rather poor waters absolutely satisfactory by the usual distillation induced the author to try the contact process which is described in this article.

A standard method for the preparation of ammonia-free water is tersely described in Richards and Woodman's "Water, Food and Air," as follows: "The ammonia-free water used in this laboratory is made by redistilling distilled water from a solution of alkaline permanganate in a steam-heated copper still........ only the middle portion of the distillate is collected." Modifications of this method are the only procedures described in the literature on water analysis for ammonia-free water, one exception being the method of Weems, Gray and Myers,[1] *using* sodium peroxide.

It is sufficient to say that either process is inefficient and troublesome, even if the final product is satisfactory, which, indeed, is not always the case.

I will now describe a process by which waters containing any ordinary amount of carbonaceous or nitrogenous material can be rendered perfectly free from the same, and the whole done by a process extremely simple in outline.

[1] *Proc. Iowa Acad. Sciences*, **10**, 112, and abstract *J. Soc. Chem. Ind.*, **22**, 1016.