inserted, one end under the mica gasket and touching the bomb, the other end above the gasket and in contact with the cover, the wire being looped so as to touch the mixture in the bomb. A current of 4 amperes is used to fuse the wire, one terminal in contact with the bomb, the other applied to the cover. After a minute or two, cool the bomb in a little water, unscrew the clamp and dissolve the mass, treating exactly as in the coke analysis.

This method compares very well with Eschka's method and requires much less time and cheaper apparatus while there is less liability of contamination with impure chemicals and exposure to gas flames. The peroxide used seldom contained any sulphates. The following are some of the results obtained:

Coal and coke.	Per cent. sulphur by Eschka's method.	Per cent. sulphur by peroxide method.
River View coal	1.69	1.64
" " "	1.59	1.57
Hocking Valley, pea	1.95	1.96
" " slack	1.690	1.694
Coke (mixture)	1.26	1.21
Pittsburg coke	0.89	0.88
Connelsville coke	1.67	1.73
Coke mixture	2.027	2.031

DETROIT, October 18, 1902.

A STUDY OF MAGNESIUM AND MANGANOUS HYDROXIDES AND OF BARIUM SULPHATE WITH RESPECT TO THE PHENOMENA OF ADHESION AND OF SOLUTION.

BY HARRISON EASTMAN PATTEN.

Received November 27, 1902.

THE work on aluminum,[1] iron,[2] zinc,[3] and chromium[4] has shown that the action of their hydroxides in carrying down other substances into precipitation is chemical, and under certain conditions not proportional to the mass of precipitate. I have examined the action usually expressed by the equation

$$MgCl_2 + 2KOH = Mg(OH)_2 + 2KCl;$$

also

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[1] "A Thermochemical Analysis of the Reaction between Alum and Potassium Hydroxide." *Am. Chem. J.*, 8, 23.

[2] "A Study of Ferric Hydroxide in Precipitation." *Ibid.*, 19, 512.

[3] Unpublished.

[4] "Chromic Hydroxide in Precipitation." *Ibid.*, 18, 608; also "Recherches sur le sulfate chromique, ses transformations et les acides complexes qui en derivent." *Ann. chim. phys.*, 7, 4 (1895).

$$MgCl_2 + 2KOH + K_2SO_4 = Mg(OH)_2 + 2KCl + K_2SO_4$$

to ascertain whether magnesium hydroxide acts in a similar manner.

SOLUTIONS.

Solutions as described below were used in the work:

(1) For the magnesium solution, 20.2963 grams of crystallized magnesium chloride was made up to 1 liter at 20°. This solution contained 0.0070 gram chlorine, and 0.00308 gram magnesium oxide per cubic centimeter.

(2) A dilute solution of potassium hydroxide, standardized by oxalic acid and gravimetrically. It contained 0.0261 gram potassium hydroxide per cubic centimeter.

(3) A dilute solution of sulphuric acid, standardized against the potassium hydroxide solution both volumetrically and gravimetrically (weighed as K_2SO_4). It contained 0.04206 gram sulphuric acid per cubic centimeter.

As a preliminary step, the amount of potassium hydroxide required for exact precipitation of the magnesium in Solution (1) was determined.

GENERAL METHOD.

The filtrates were analyzed and the percentage of each constituent found deducted from that of the total introduced. The difference gives the percentage of the constituent in the precipitate, which may not be analyzed directly, since washing or diluting the solution in which the precipitate is formed changes its composition. In the case of magnesium, the precipitated hydroxide is soluble in water.

A blank determination of the magnesium chloride was made: 50 cc. magnesium chloride stock solution was made up to 500 cc. at 20°, four portions were drawn off with a 50 cc. pipette and the magnesium oxide and chlorine determined in duplicate.

$$MgO\begin{cases}0.0207 \text{ gram}\\0.0207 \text{ gram}\end{cases} \qquad Cl\begin{cases}0.0040 \text{ gram}\\0.0042 \text{ gram}\end{cases}$$

Experiments were now made with 44.24 cc. sulphuric acid, neutralized to potassium sulphate by the equivalent amount of potassium hydroxide, and 50 cc. stock solution of magnesium chloride as constant factors, the magnesium being precipitated by varying amounts of potassium hydroxide. The above constituents were made up to 500 cc. at 20°, allowed to stand twenty minutes, well shaken and four portions of mixed precipitate and solution drawn off with a dry 50 cc. pipette and labeled "totals". The solution and precipitate remaining was thrown upon a dry filter-paper, the clear filtrate brought back to 20°, and five portions drawn off with a 50 cc. pipette and labeled "filtrates".

The "totals" for magnesium oxide were redissolved by hydrochloric acid in some excess, ammonia added to alkaline reaction and the magnesium precipitated cold as magnesium ammonium phosphate, and weighed as pyrophosphate.

The "totals" for chlorine were redissolved by nitric acid, precipitated hot with silver nitrate solution, and the magnesium removed by a wash-water containing 25 cc. concentrated nitric acid and 0.1 gram silver nitrate per liter. The chlorine was then weighed as silver chloride.

The "filtrates" for magnesium oxide and chlorine were analyzed in the same manner as the "totals". As in the work with aluminum, chromium, iron and zinc, it was assumed that re-solution by hydrochloric or nitric acid would liberate any constituents carried down in the precipitation with potassium hydroxide.

It was considered unnecessary to determine the potassium oxide in the "totals" and "filtrates," for two reasons: first, because in all the foregoing work in this line no carrying down of potassium was observed short of re-solution in the alkali; second, the negative results of the work on magnesium oxide, chlorine and sulphur trioxide in this investigation indicate the absence of such action.

No good method of separating the magnesium oxide from the sulphur trioxide in "totals" and "filtrates" being available, two different methods were used to ascertain whether the sulphur trioxide enters into the reaction.

(1) The amount of magnesium oxide precipitated in presence of *potassium sulphate* by a definite amount of potassium hydroxide, should be greater than the amount precipitated in absence of the sulphate—*if sulphur trioxide enters into the reaction.*[1]

(2) Magnesium oxide or chloride should be carried down into precipitation by barium sulphate. The four elements already mentioned show this reciprocal action, as does also manganese, of which I shall speak later.

[1] Series II., "Chromic Hydroxide in Precipitation," *loc. cit.;* "A Study of Ferric Hydroxide in Precipitation," *loc. cit.*

TABLE I.

Experiment.	KOH.	"Total" MgO.		"Filtrate" MgO.		"Precipitate." MgO.	"Total" Cl.		"Filtrate" Cl.		"Precipitate." Cl.	"Precipitate." % MgO.
I	2	0.02065 0.02071	0.0207	only a trace		0.0207	0.0036 0.0035	0.0036	0.0037 0.0040	0.0038	0.0000	100.00
II	6 (2) 300 cc. $MgCl_2$	0.1190+ 0.1190−	0.1190	0.0026 0.0020	0.0023	0.1167	0.2082 0.2085	0.2084	0.2086 0.2088	0.2087	0.0000	98.06
III	6 (1½) 300 cc. $MgCl_2$	0.1174 0.1180	0.1177	0.0281 0.0276	0.0278	0.0899	0.2080 0.2085	0.2083	0.2081 0.2087	0.2084	0.0000	76.38
New solution IV	1½ + K_2SO_4	0.1926 0.1927	0.1926	0.0480 0.04807	0.0480	0.1446	0.3445 0.3443	0.3444	0.3442 0.3438	0.3440	0.0004	75.07
V	1½	0.1928 0.1931	0.1929	0.0484 0.0481	0.0482	0.1447	0.3431 0.3432	0.3431	0.3427 0.3429	0.3428	0.0003	75.07
VI	1 + K_2SO_4	0.1936 0.1942	0.1939	0.0958 0.0963	0.0960	0.0979	0.3430 0.3425	0.3427	0.3433 0.3429	0.3431	0.0000	50.46
VII	1	0.1941 0.1940	0.1940	0.0968 0.0966	0.0966	0.0974	0.3426 0.3429	0.3427	0.3427 0.3426	0.3426	0.0001	50.46

Experiment I.—The system was made up according to the equation $MgCl_2 + 2KOH = Mg(OH)_2 + 2KCl$, using 50 cc. of magnesium chloride solution to 22.2 cc. potassium hydroxide solution. No potassium sulphate was introduced here since the object was to determine if chlorine were carried down into precipitation by the magnesium hydroxide. No chlorine was found in the precipitate (see Table I, Exp. I). A trace of magnesium was obtained in the filtrate by further addition of potassium hydroxide, showing that magnesium chloride is not completely precipitated by 2 molecules of potassium hydroxide. As the mass of precipitate was so small, for this concentration, and as "adhesion" in the cases of chromium, iron, aluminum and zinc hydroxides is more marked in concentrated solutions, the next two experiments were made up each with six 50 cc. portions of magnesium chloride solution instead of one 50 cc. portion as in this experiment.

Experiment II.—The system was made up according to the equation $MgCl_2 + 2KOH = Mg(OH)_2 + 2KCl$ (see Table I, Exp. II., for results). This shows no chlorine carried down into precipitation. Since adhesion is more marked at incomplete precipitation than at complete precipitation, in the next experiment I used 1½ KOH.

Experiment III.—The system was made up according to the equation $MgCl_2 + 1\frac{1}{2}KOH = ?$ (see Table I, Exp. III, for results). Here again no chlorine is carried down by the precipitate.

The stock supply of magnesium chloride being now exhausted, a new solution (4) was made up: 203 grams $MgCl_2 + 6H_2O$ were dissolved in water and diluted to 1000 cc. of solution at 20° C. One 50 cc. portion was drawn off and made up to 500 cc. at 20° C. Of this solution each 50 cc. contained:

$$MgO\begin{cases}0.1926 \text{ gram}\\0.1925 \text{ gram}\end{cases} \qquad Cl\begin{cases}0.3445 \text{ gram}\\0.3440 \text{ gram}\end{cases}$$

For 50 cc. of stock solution of magnesium chloride (4), 212.5 cc. potassium hydroxide were required to precipitate completely the magnesium. The calculated amount of potassium hydroxide was 207 cc.

Now the attempt was made to ascertain if sulphur trioxide is carried down into precipitation. As was stated in "General

Method," no good means of separation being at hand a difference method was resorted to. The work on chromium and iron showed that in a partially precipitated system (which had been filtered or allowed to settle) further precipitation was caused by the addition of a little sulphate solution, and in some cases[1] no definite precipitate was obtained unless some soluble sulphate was present. From this influence of sulphur trioxide on the amount of hydroxide formed at fractional precipitation, I assume that if sulphur trioxide is carried down into precipitation by magnesium hydroxide, the amount of magnesium hydroxide precipitated by, say, 1.5 molecules of potassium hydroxide will be greater in the presence of sulphur trioxide than in its absence. If then, the amount of magnesium hydroxide precipitated by 1.5 molecules of potassium hydroxide is the same with and without sulphur trioxide present, I conclude that no adhesion takes place.

For results see Experiments IV, V, VI, VII, Table I, and the accompanying plate, curve 6.

The same amount of magnesia is precipitated in Experiment IV with potassium sulphate present as in Experiment V with potassium sulphate absent; likewise in Experiments VI and VII. Since no sulphur trioxide is carried down into precipitation at these fractional points it was considered unnecessary to try an experiment at complete precipitation, inasmuch as the other elements worked with show their greatest "adhesion" activity at these points. Further, since magnesium gives a definite precipitate at the fractional points in absence of sulphur trioxide, it ought to carry down chlorine into precipitation if it exercises the property of "adhesion"; Experiments I, II, and III show no chlorine carried down.

Experiment VIII.—It was determined that magnesium hydroxide precipitated from magnesium chloride by potassium hydroxide in aqueous solution does not redissolve in excess of potassium hydroxide.

Experiment IX.—Twelve different barium sulphate determinations which had been made from solutions containing magnesium chloride, potassium sulphate and hydrochloric acid by addition of barium chloride were treated as follows: fused with sodium carbonate, the alkali washed out with water, the insoluble barium

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[1] Fractional precipitation of chromium chloride by less than three molecules of potassium hydroxide. See "Chromic Hydroxide in Precipitation." *loc. cit.*

carbonate dissolved in hydrochloric acid, reprecipitated by ammonium carbonate to remoe the barium, and the filtrate tested for magnesium by sodium hydrogen phosphate. Not a trace of magnesium was found.

DISCUSSION.

These results may be summarized thus: (1) Magnesium hydroxide does not carry down into precipitation with it either chlorine or sulphur trioxide. (2) Barium sulphate does not carry down into precipitation either magnesium oxide or chloride. (3) More than the theoretical amount of potassium hydroxide is required to completely precipitate magnesium hydroxide from a magnesium chloride solution in water at the concentration and temperature studied. On this last point more work should be done.

MANGANOUS HYDROXIDE.

Method.—The general method used in this investigation was the same as for chromium and iron. The sulphur trioxide was determined directly in "totals" and "filtrates" after the manganese had been removed. This removal was effected in the following manner: Sodium acetate solution was added to the "filtrates" and "totals" and the manganese precipitated as MnO_2 by bromine, the excess of bromine boiled off and the MnO_2 filtered off, well washed, and ignited and weighed as Mn_3O_4. The filtrate from this MnO_2 was concentrated and the SO_3 determined as $BaSO_4$. In the case of the "totals," re-solution of the manganous hydroxide was effected with hydrochloric acid just before the sodium acetate was run in. Occasionally the barium sulphate determinations showed a slight coloration, but the quantity of manganese present was of course negligible. I found this method efficient. Re-solution of these complex precipitates of chromium, iron, manganese, zinc, and aluminum, in hydrochloric or nitric acid has in every case proved sufficient to split them into determinable components.

The chlorine was determined in presence of manganese, a re-solution with nitric acid being first effected, and then all manganese was washed out of the silver chloride by a wash-water containing 25 cc. concentrated nitric acid and 0.1 gram silver nitrate per liter.

Solutions.—*A.* 98.9 grams $MnCl_2 + 4H_2O$ was dissolved in water and made up to 500 cc. at 20° C. This solution was found to contain the equivalent of 0.05186 gram MnO per cubic centimeter. *B*. A solution of potassium hydroxide containing 0.02705 gram KOH per cubic centimeter at 20° C. *C*. A solution of sulphuric acid containing 0.04046 gram per cubic centimeter at 20° C.

Experiments I, II, III, IV, V were made as shown in Table II. Each system contained 50 cc. manganous chloride, Solution *A*; 44.24 cc. sulphuric acid, Solution *C*, neutralized to potassium sulphate by 75.63 cc. of potassium hydroxide, Solution *B*; and varying amounts of potassium hydroxide to cause the precipitation. In every case the potassium sulphate was run into the flask; next the manganous chloride; and finally the potassium hydroxide. Then the system was made up to 500 cc. at 20° C. and well shaken, whereupon four 50 cc. portions were drawn out with a pipette and labeled "totals." The remaining precipitate and solution were thrown upon a dry filter-paper, the filtrate received in a dry flask, and brought back to 20° C. when four 50 cc. portions were drawn off, and labeled "filtrates." Throughout the investigation of chromium, manganese and magnesium, the same pipette was used.

DISCUSSION.

For results see Table II; also curves 7 and 8 in the plate. The chemical nature of adhesion is clearly shown here as well as in the case of iron, zinc, chromium and aluminum. Experiment I shows no sulphur trioxide in the precipitate, though the mass of precipitate is a maximum. Experiment II shows that 15.34 per cent. of the total sulphur trioxide is in the precipitate, while the mass of precipitate is some 9 per cent. less than in Experiment I. Experiment III shows 19.3 per cent. of the total sulphur trioxide in precipitation, while the mass of precipitate is still less than in Experiment II. Experiment IV confirms Experiment III, giving the maximum sulphur trioxide carried down. Experiment V shows a falling off in the sulphur trioxide in precipitation, but if we remember how small the amount of precipitated manganous hydroxide is at this point (0.5 molecule KOH) the strength of the action is seen to be considerable.

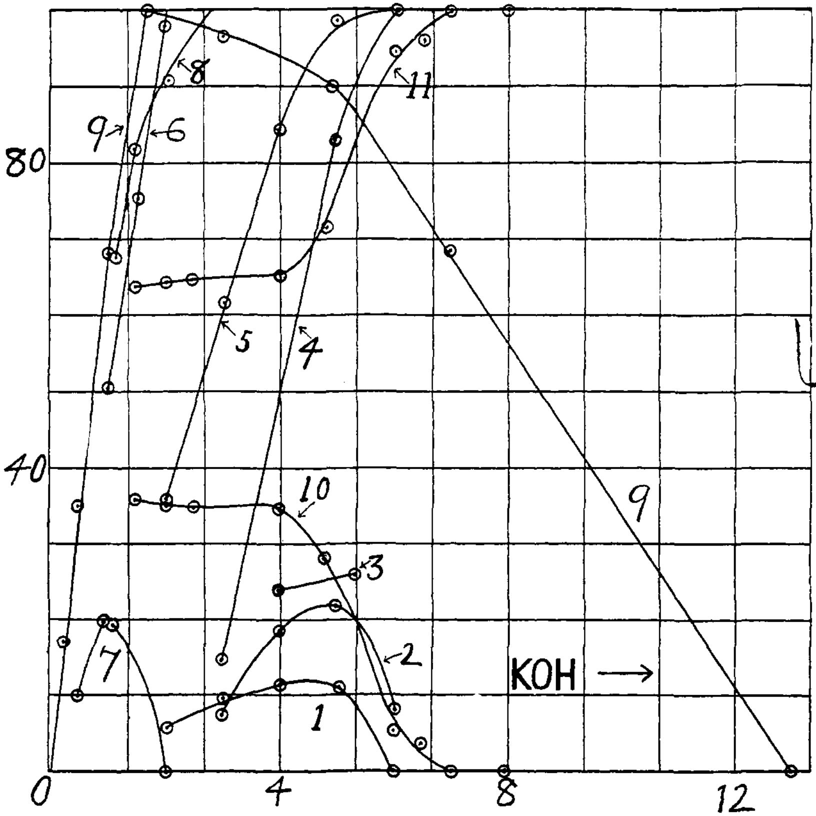
No chlorine was carried down at 1.5 or 1.1 molecules of KOH; hence this "adhesion" is seen to be selective—the sulphur trioxide is taken, and the chlorine left.

TABLE II.

Exp.	KOH + ½K_2SO_4	MnO "total."	MnO "filtrate."	MnO "prec."	SO_3 "total."	SO_3 "filt."		SO_3 "prec."	Cl "total."	Cl "filt."	Cl "prec."	Total % SO_3 in "prec."	Total % MnO in "prec."
I	2	0.2593	0.0146	0.2347	0.1381	0.1379 0.1368		0.0000	.....	.....	.....	....	90.51
II	1½	0.2593	0.04371	0.2122	0.1382	0.1186 0.1154	0.1170	0.0212	0.3307	0.3335 0.3321	0.0000	15.34	81.83
III	1$^1/_{10}$	0.2593	0.0833	0.1760	0.1376	0.1110 0.1111	0.1110	0.0266	0.3298	0.3302 0.3340	0.0000	19.33	67.86
IV	1	0.2593	.....	.....	0 1384	0.1103 0.1106	0.1114	0.0270	.....	.....	.....	19.50	....
V	½	0.2593	.....	.....	0.1378	0.1244 0.1247	0.1245	0.0133	.....	.....	.....	9.65	....

I think it probable that in absence of sulphur trioxide the chlorine would be carried down, since ferric hydroxide shows this same selective action and does carry down chlorine in absence of sulphur trioxide.

Since in the case of iron, potassium appears in the precipitate only at 8 molecules of potassium hydroxide, and in the case of chromium, potassium does not appear at all up to 8 molecules of potassium hydroxide, it was considered unnecessary to determine potassium in the present investigation.



In the plate, I have plotted curves which show the per cent. of oxide and of sulphur trioxide in the precipitates obtained by adding various amounts of potassium hydroxide to the chloride. Ordinates are in per cent. of constituent; abscissas, in molecules of potassium hydroxide required to produce the precipitate. Curve

1 is the per cent. of total sulphur trioxide in the precipitate of ferric hydroxide; curve 2, the same for chromic hydroxide; curve 3, the same for ferric hydroxide (produced from a solution of ferric chloride having twice the concentration of that used for curve 1).[1] Curve 7 is the same for manganous hydroxide. Curve 4 gives the per cent. of total chromium trioxide precipitated by varying amounts of potassium hydroxide in presence of a fixed amount of potassium sulphate. Curve 5 is the same for ferric oxide. Curve 6, the same for magnesium oxide—presence or absence of potassium sulphate has no effect on the trend of the curve. Curve 8, the same for manganese oxide. Curve 9, the same for zinc oxide.[2] Curve 10 is the per cent. of total sulphur trioxide in the precipitate whose remaining constituent is aluminum trioxide, the per cent. of which is given in curve 11.[3]

My results as plotted in curve 7 show that the action of manganous hydroxide in carrying down sulphur trioxide into precipitation is truly chemical in nature, since the maximum carrying-down effect is observed far short of the maximum quantity of manganous hydroxide, as may be seen by reference to curve 8. The carrying down of chlorine and of potassium oxide remains to be investigated.[4] The results show, too, that the standard equations for the reaction between manganese chloride and potassium hydroxide, and between magnesium chloride and potassium hydroxide in aqueous solution do not represent the facts (see curves 6 and 8; likewise, 9 and 11). The distribution of the constituents of these systems is dependent upon temperature, concentration, and the relative masses of the constituents. Further, the composition of the precipitates as given in the tables and curves considers the precipitate as anhydrous; unquestionably much water is combined in the gelatinous precipitates here studied, but owing to the lack of a method of getting at it quantitatively it has purposely been left unconsidered.

This work has a bearing on the subject of colloidal solution. Reference to a former paper will show that it is possible to form a

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[1] Curves 1, 3, and 5 are taken from the thesis of V. J. Hall, *loc. cit.*

[2] C. E. Linebarger: This Journal, 17, 358 (1895).

[3] Taken from Table VI. A. V. E. Young, *loc. cit.*

[4] This work was done in 1896 and I have kept it back, hoping to make the data more complete; however, circumstances have not permitted of it, and do not at present. These results are of interest to those working on precipitation and solution, so I do not feel justified in withholding them longer.

colloidal solution containing chromium chloride, potassium chloride and potassium hydroxide all combined with each other and with water so that the equation,

$$2CrCl_3 + 3KOH = CrCl_3 + Cr(OH)_3 + 3KCl,$$

does not represent the true state of the system. If any soluble sulphate be added, this colloidal solution gelatinizes. A nitrate or chloride will not produce this effect. It seems to me that this reaction disposes of the idea which had been advanced that *any electrolyte* will precipitate a colloid.[1] Here certainly the colloid seems to have a decided preference for sulphates.

BARIUM SULPHATE.

To examine further this "adhesion" phenomenon, samples of barium sulphate were prepared in two ways: (1) Precipitated with sulphuric acid from barium chloride dissolved in water, and the washed barium sulphate boiled for several hours with the aqueous solution of some metallic chloride. (2) Precipitated with sulphuric acid from an aqueous solution of barium chloride containing the same metallic chloride used in Method (1).

These samples enable one to decide whether the coloration of barium sulphate which is observed in samples precipitated in presence of salts of iron, manganese, chromium, etc., is necessarily enclosed when the crystal forms.

In this way I prepared samples of barium sulphate containing nickel, cobalt, manganese, chromium, iron and copper, and examined them under a high-power microscope. The crystals were measured by a stage and eye-piece combination micrometer, and averaged 0.00005 to 0.000125 inch in diameter.

No difference in shade could be detected between barium sulphate crystals prepared by Method (1) and those obtained by Method (2) with any of the metals used. The coloration was well marked and was compared with that of freshly prepared pure barium sulphate on the same glass side.

These results indicate that the metals given can penetrate barium sulphate crystals after they are formed and find lodgment there. But once these metals are in the barium sulphate crystal it is, as every analyst knows, no easy matter to get them out. From this we might, without doing violence, argue for chemical combination between the barium sulphate and the metal (or its salt or oxide). Further, chromic chloride in aqueous solution is

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[1] "Chromic Hydroxide in Precipitation." *loc. cit.*

known to dissolve barium sulphate crystals in appreciable amount. This shows that we have here a case of mutual action, the barium sulphate dissolving the chromium (in some form) and the chromium chloride in water dissolving the barium sulphate. As the barium sulphate remains solid, we have another case of a solid solution and a liquid solution coming into equilibrium in such a way as to give ground for believing that solid solution and liquid solution are of the same order, and to be classed as chemical combinations of solvent with solute.

I wish to thank Professor A. V. E. Young, of Northwestern University, for many helpful suggestions given me during the progress of this work.

CHEMICAL LABORATORY, UNIVERSITY OF WISCONSIN,
MADISON, November 26, 1902.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 65.]

THE GRAVIMETRIC DETERMINATION OF MERCURY AND ITS SEPARATION FROM ARSENIC, ANTIMONY, AND COPPER.

BY CHARLES J. PRETZFELD.

Received December 8, 1902.

HISTORICAL.

Mercury Weighed as Chloride.—For the determination of mercury in this form, the following reducing agents have been proposed: formic acid,[1] ferrous sulphate,[2] phosphorous acid,[3] glucose,[4] potassium hypophosphite,[5] a mixture of hypophosphorous acid and peroxide of hydrogen,[6] and hydrazine sulphate.[7]

Mercury Weighed as Oxide.—The determination of mercury in this form is unimportant, the only method known being that of Marignac.[8]

Mercury Weighed as Metal.—Under this heading, the history of mercury determination can be subdivided into three classes:

(*A*) By application of reducing agents in the cold.

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[1] Bonsdorff : *Ann. Chem. Phys.*, **33**, 78.

[2] Hempel : *Ann. Chem. Pharm.*, **110**, 176.

[3] Rose : *Jsb. d. Chem.*, **13**, 665.

[4] Hager : *Ztschr. anal. Chem.*, **17**, 380.

[5] Thompson : *J. Soc. Chem. Ind.*, **16**, 263.

[6] Vanino and Treubert : *Ber. d. chem. Ges.*, **30**, 2808-2809.

[7] Jannasch and Durselen : Doctor's Dissertation at Heidelberg, 1899.

[8] *Jsb. d. Chem.*, (1849), p. 594.