THE NATURE OF THE CHANGE FROM VIOLET TO GREEN IN SOLUTIONS OF CHROMIUM SALTS.

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IT is a well-known fact that solutions of certain chromium salts which are violet in color become green on heating. This has been especially noticed in the case of the chrome-alums and of the sulphate, but is also true of the nitrate, chloride, and acetate, in fact, of all the soluble compounds of chromium. A reverse reaction also takes place and all of these solutions made green by heating become violet again on standing, the nitrate, chloride, and acetate very rapidly, the sulphate and alums slowly, and often only after prolonged standing. It is quite reasonable to suppose that these changes are caused by similar reactions in the case of various salts, and that there is one explanation for all.

A large number of explanations have been offered by various investigators. In fact it is surprising to find how many have been drawn to investigate these changes and what an amount of work has been done upon them. Perhaps the difficult nature of the problem has been the great source of attraction. Fischer[1] and Jacquelain[2] have attributed these changes to a separation of the chromium sulphate from the alkaline sulphate; Berzelius[3] and Fremy[4] assigned as the cause of the changes the formation of a basic sulphate; Recoura and Whitney[5] and Dougal[6] have considered the true cause to be the formation of a chrom-sulphuric acid; Schrötter[7] suggested a partial dehydration, and Etard[8] also thought the change due to an alteration in hydration; Roscoe and Schorlemmer[9] regarded the green solutions as containing mixtures of basic and acid salts; Loewel[10] advanced the theory of an isomeric change.

[1] Kastner's *Archiv.*, 14, 164.

[2] *Compt. rend.*, 24, 439.

[3] *Ann. phys. Chem.*, 61, 1.

[4] *Compt. rend.*, 47, 883.

[5] *Ztschr. phys. Chem.*, *1896*, 20, 40.

[6] *J. Chem. Soc.*, Lond., *1896*, 69, 1526.

[7] Pogg. *Ann.*, 53, 513.

[8] *Compt. rend.*, 84, 1090.

[9] Treatise on Chemistry, First Edition, Vol. II, Pt. II, 163.

[10] *J. d. Pharm.* (3), 7, 321.

It is quite manifest that any theory like that of Fischer and Jacquelain, based upon an examination of the alums alone, is quite inadequate. It is further evident that any phenomenon which has aroused so great a variety of speculations as this must be considered very carefully with due weighing of every known fact. These facts are numerous and important.

HOW THE CHANGE MAY BE BROUGHT ABOUT.

Chrome-alum is soluble in six parts of water; the violet solution suffers the alum slowly to crystallize out unchanged by spontaneous evaporation; but if heated to between 50° and 75° it turns green and, according to the extent of decomposition, either deposits on evaporation a brilliant, green, amorphous, difficultly soluble mass, or "yields crystals of sulphate of potash, leaving green sulphate of chromic oxide in solution."[1]

Schrötter says the change takes place at 65°–70°. He further states that the crystals of potassium sulphate separate only from a highly concentrated solution and in small quantity. Sprung has shown, in experiments to be quoted later, that the change begins at a temperature under 30°.

We have repeatedly attempted to secure the separation of crystals of potassium sulphate as described by Fischer and Schrötter, but without success. The exact conditions are clearly difficult to hit upon, if such a separation is at all possible.

Alkaline hydroxides and carbonates, according to van Cleeff,[2] turn violet solutions of the alums green, and Etard[3] has shown that they bring about the same change in solutions of the normal sulphate. Sulphuric acid, phosphorus trichloride, and nitric acid, according to Etard, bring about the same change, but Otto[4] says that sulphuric acid does not turn solutions of the alum green if rise of temperature is prevented. Schrötter says that nitric acid turns green solutions of chromium sulphate blue again.

Our experiments along this line resulted as follows: First as to the action of acids. Hydrochloric acid had no action upon

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[1] Fischer, cited in Gmelin: Handbuch, *1850*, IV. 149.

[2] *J. prakt. Chem.* (2), **23**, 58.

[3] *Compt. rend.*, **84**, 1090.

[4] Graham-Otto, 4 Aufl., 3, 113.

either violet or green solutions, nor does it apparently have any influence upon the change from one to the other on heating. Sulphuric acid brought about no change in either in the cold, but has a retarding influence upon the change on heating. This was so marked in one or two experiments that it was thought the change would be entirely prevented. Nitric acid had no appreciable immediate effect upon either in the cold. On heating with the violet the retarding action was greater than when sulphuric acid was used, and the solution resumed its violet color on cooling. Acetic acid had apparently no influence. As to the action of alkalies, sodium or potassium, or ammonium hydroxide, or the carbonates, readily turned the violet solutions green. They had no action upon green solutions.

CHANGES IN PHYSICAL PROPERTIES.

In the case of chromic sulphate, Sprung[1] has shown that the violet solution with about twenty-four per cent. of the salt has the specific gravity 1.1619, while the green is 1.1486. So too with the alum there is an increase of volume, which has been noticed by Siewert and also by Mohr,[2] and a decrease of volume is observed as the green solution reverts to the violet. Lecoq de Boisbaudran[3] has also observed these changes, noting that they are independent of the concentration of the solution, the presence of crystals, or whether the vessel is open or closed. The changes in density can be reckoned from his dilatometric observations. Dougal[4] has shown that the alteration in density of even a dilute solution of chrome-alum, after boiling, may readily be detected by a specific gravity bottle. In this manner, one, two and a half, and five per cent. solutions were experimented upon. The actual amount of change depended upon the duration of the heating and the length of time which had elapsed since the green solution had been prepared. The violet solutions became specifically lighter when changed to green by boiling. The transformation is accompanied therefore by expansion.

According to Sprung the violet and green solutions show a difference in internal friction or viscosity. The ratios of diffu-

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[1] *N. Arch. ph. nat.*, 53, 112.

[2] *Ber. d. chem. Ges.*, 4, 318.

[3] *Compt. rend.*, 79, 1491.

[4] *J. Chem. Soc.* Lond., *1896*, 69, 1527.

sion out of capillaries at temperatures 10°, 20°, 30°, 40°, 50°, of the green to the violet were as 100 to 60.70 ; to 67.77 ; to 68.74 ; to 70.79 ; to 75.72. From this it is seen that the change begins at less than 30°. From this arises the observation that has been made that the solution of the alum turns somewhat green at ordinary temperatures.

The diffusion of these solutions has also been carefully studied with a view to throwing light upon this puzzling problem.

With regard to the sulphate it has been shown by van Cleeff[1] that green solutions on being dialyzed yield dialysates containing a larger proportion of acids. This has been repeatedly investigated in the case of the alum. Thus van Cleeff has found that in the dialysis of the green solution of the alum, relatively more sulphuric acid goes into the dialysate than when the violet solution is dialyzed. Dougal[2] has also carried out careful experiments along this line. Time, temperature, strength of the dialysate, amount of initial change, amount of retrogression, all affected the results, and little beyond the facts stated above could be deduced from them. The experiments were made upon solutions containing one per cent. of the alum. While the author states that no comparison could justly be made between the experiments, it may be noted that the ratio of increase in acidity was fairly regular and ranged between one-seventh and one-sixth.

A few experiments were undertaken upon the dialysis of the alum before Dougal's experiments were known to us. They were not pushed to completion when these latter became known, especially as there seemed little chance of their throwing much light upon the nature of the change.

CHANGES IN CHEMICAL PROPERTIES.

One of the most singular changes in chemical properties is that noted in the action of the sulphate or alum, before and after heating, upon solutions of barium or lead salts. This was first observed by Loewel[3] and was studied by Favre and Valson.[4] A violet solution on being treated in the cold with a solution of

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[1] *J. prakt. Chem.* (2), **23**, 58.

[2] *J. Chem. Soc.* Lond., *1896*, 69, 1527.

[3] *J. Pharm.* (3), **4**, 32.

[4] *Compt. rend.*, 77, 803.

barium chloride, yields practically all of its sulphuric acid as barium sulphate. A cold green solution forms a precipitate slowly, and even after a number of hours the precipitation is far from complete. On boiling, all of the sulphuric acid will be precipitated. Favre and Valson found that only one-third of the sulphuric acid present in the original chromic sulphate was precipitated in the cold by the barium chloride.

Our own experiments upon this point were as follows: A weighed amount of the pure alum was dissolved and the solution made up to a definite quantity. Two aliquot portions were taken, one of which was heated for half an hour and allowed to cool. Then both portions were precipitated with an excess of barium chloride. It was found impossible to filter these immediately with asbestos felts or the best filter-paper. They were therefore allowed to stand about twenty-four hours. This very long standing probably changed the conditions somewhat, but we were unable to avoid it. Still the results would confirm the observations of Favre and Valson. The prolonged standing also showed that it was not merely a delayed precipitation, but one partially prevented.

	I.	II.
Percentage of SO_3 in alum is 32.06	....	....
Percentage of SO_3 in alum, violet solution precipitated cold	30.44	30.19
Percentage of SO_3 in alum, green solution heated one-half hour	22.78	22.33
Percentage of SO_3 in alum, green solution heated one hour	22.87	21.83

These experiments were upon solutions containing one gram to 100 cc. A solution twice as strong was next taken:

	I.	II.
Percentage in violet solution precipitated cold	28.88	31.80
Percentage in green solution (heated one hour) precipitated cold	19.55	21.47

Again a solution containing 0.5 gram to the 100 cc. was taken.

Percentage in violet solution precipitated cold	28.30
Percentage in green solution (heated one hour) precipitated cold	23.00

The difficulties of washing and filtering barium sulphate precipitated in this manner account in part for the lack of agreement between the analyses, but two things are evident; first, that all of the sulphuric acid is not precipitated from either violet or green solutions in the cold, and, secondly, that a short boiling effects such a change that only two-thirds of the sulphuric acid is precipitated by barium chloride in the cold. The amount not precipitated ranged from 9.06 to 13.51 per cent.

Many observations have been recorded as to the acidity of the violet and green solutions of the alum. Recoura[1] has stated that the vapors coming off from a solution at 100° are acid, while the solid salt at the same temperature does not lose any acid. He further maintains that the green solution, left after the heating, contains a considerable amount of free acid. He made use of the heat of neutralization as a means of measuring the degree of acidity. A known amount of soda was added to the liquid and the heat liberated was measured. In so far as this corresponds with the heat liberated by the neutralization of free sulphuric acid in the same degree of dilution, he concluded that he was dealing with free acid. According to his experiments there was one-half of an equivalent of sulphuric acid for every equivalent of chromium sulphate.

It was Krüger[2] who first attempted to show in 1844 the presence of free sulphuric acid in the green solution. He thought this was proved by the acidity of the layer of alcohol poured over the green solution.

Baubigny and Pechard[3] have shown that the alum has always an acid reaction even after purification by means of alcohol. Further they regarded the following experiment as proving a partial dissociation of the salt. To twenty cc. of a saturated solution of the alum, three-tenths gram of ammonia gas was added, and, after shaking, the liquid was neutral to methyl orange; after some time the liquid which had become green on the addition of the ammonia, yielded violet crystals with strong acid-reaction and the mother-liquor had become acid to methyl orange.

Whitney[4] has also attempted to prove the presence of acid by

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[1] *Compt. rend.*, 112, 1440.

[2] *Ann. phys. Chem.* (3), 61, 218.

[3] *Compt. rend.*, 115, 604.

[4] *Ztschr. phys. Chem.*, *1896*, 20, 40.

physical methods. Sodium hydroxide and barium hydroxide respectively were added to the green solution. The addition of a base must lower the conductivity of the solution as long as free sulphuric acid is being neutralized. He found the minimum when he had added one-sixth of an equivalent of sodium hydroxide to the chromium sulphate, or one-third of an equivalent of barium hydroxide. No explanation was given of the variation in the results. He also claimed to have proved the presence of free acid by the catalysis of methyl acetate. Lastly the inverting action of green solutions of chromium chloride, acetate, nitrate, and sulphate was tried upon sugar solutions. He came to the conclusion that in the case of the chloride and nitrate, two-thirds of the acid was set free on boiling; of the acetate more than two-thirds, and of sulphate less than one-third. In our own experiments as to the relative acidity of the violet and green solutions, it was speedily seen that both solutions were acid. We tried a large number of the usual indicators, but the violet and green colors of the solutions interfered too much to give any results with them which could be regarded as at all satisfactory. It was found that fair results could be obtained by using a decinormal solution of ammonia and noting the first appearance of a permanent precipitate.

	Tenth-normal ammonia. cc.
One gram in 100 cc. cold required	27.5
" " " " " boiled one-half hour	27.6
" " " " " " one hour	26.5
" " " " " " two hours	26.5

During the boiling, the water evaporated was repeatedly restored. Unless this was done a little acid was lost, and even with this precaution there was a small loss, and this may explain the acidity of the vapors coming off at 100° as observed by Recoura.

These experiments therefore agree with those of Baubigny and Pechard, but are at variance with the conclusions of the other authors mentioned. We think the experimental data of these authors do not afford sufficient and satisfactory evidence to serve as a basis for their conclusions that free sulphuric acid exists in the solution. The methods adopted are very indirect and the results capable of other explanations.

THE EXISTENCE OF CHROMO-SULPHURIC ACIDS.

Several articles have been published by Recoura[1] upon chromo-sulphuric acids. He claims to have prepared several of these and regards the formation of such bodies as a probable explanation of the change in the green solutions, and others, as Whitney and Dougal, seem to accept his explanation. Recoura thinks there are two isomeric modifications of chromium sulphate; one violet, one green, and also another green sulphate not isomeric, but basic ($2Cr_2O_3.5SO_3$). These he refers to three conditions of chromic hydroxide: $Cr_2(OH)_6$, precipitated by alkalies from violet chromic salts; $Cr_4O(OH)_{10}$, corresponding to the basic sulphate and non-isolable; $Cr_2O(OH)_4$, precipitated by alkalies from green solutions. Solutions of this latter in acids, he says, are not precipitated by solutions of barium salts. This last statement is not strictly true. Such solutions are partially precipitated by barium salts just as all green solutions are. He assigns to the green sulphate the formula $Cr_2O_3.3SO_3.11H_2O$, which he says has quite a different constitution from that of the violet sulphate. Proofs for this statement he does not give. This isomeric green sulphate, he says, possesses neither the characteristics of a sulphate nor of a chromium salt. One molecule can combine with one molecule of either sulphuric acid or a metallic sulphate. Thus we may have $Cr_2(SO_4)_3.H_2SO_4$, or $Cr_2(SO_4)_3.K_2SO_4$. In these compounds all the sulphuric acid is in a non-precipitable form, he maintains. His crucial experiment is as follows:

"Mix a solution containing one molecule of $Cr_2(SO_4)_3$ with a solution containing one molecule of sulphuric acid or a sulphate. Union is immediate, for barium chloride will now give no precipitate and the solution therefore holds no sulphate. The new radical is unstable, for precipitation is immediate on boiling, or in concentrated solutions or in dilute solution on standing one-half hour. *It is necessary to work with very dilute solutions, otherwise the radical containing chromium is decomposed.*"

Of course such reasoning would give us these same strange isomeric metal-sulphuric acids in all sulphates, for if they are diluted enough it will take half an hour or more for the precipitate to form with barium chloride.

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[1] *Compt. rend.*, 113, 1037; 114, 477; 116, 1367.

On such slender basis Recoura builds up a series of salts of a hypothetical chromo-sulphuric acid $(Cr_2.4SO_4)H_2$. He has also prepared a chromo-disulphuric acid, chromo-trisulphuric acid, etc., by evaporating solutions of chromium sulphate with two, three, etc., molecules of sulphuric acid, and then heating to 110°-120°. Calvert and Ewart[1] have shown that, on dialyzing these, they all leave a colloidal $Cr_2(SO_4)_3.H_2SO_4$ upon the septum, the liquid passing through free of chromium. The behavior of these solutions makes it appear probable that the chromo-sulphuric acids do not exist in them as such, but are hydrolyzed, forming a colloidal substance, $Cr_2(SO_4)_3.H_2SO_4$, and free sulphuric acid. Our repeated experiments have failed to show the presence of this colloidal body in the ordinary green solutions of the alum or sulphate. A boiled solution of either, even though very concentrated, will pass entirely through an unglazed porcelain suction filter, such as Calvert and Ewart made use of. There seems to be no colloidal body present.

We cannot regard the experiments of Recoura as advancing the knowledge of the subject in any degree. As an explanation of the changes it is by no means satisfactory. Dougal's formula for the reaction causing the change, is even more remarkable and baseless :

$$2[Cr_2(SO_4)_3.K_2SO_4] + H_2O = [Cr_4O(SO_4)_4]SO_4 + 2K_2SO_4 + H_2SO_4.$$

This is not based upon Dougal's own experiments but is offered as an explanation deduced from the work of Recoura, Whitney, Favre, and Valson.

THE ACTION OF ALCOHOL.

There have been several investigations of the action of alcohol, both upon the sulphate and the alum, with the hope of throwing some light upon the changes under consideration. Traube[2] states that the solid salt is unaffected by boiling alcohol. Schrötter has observed[3] that solutions covered with a layer of alcohol became gradually green and the concentrated green solution is not dissolved by alcohol. Of course the first obser-

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[1] *Chem. News*, 74, 121.

[2] *Ann. Chem.* (Liebig), 66, 168.

[3] Pogg. *Ann.*, 53, 513.

vation does not necessarily connect the alcohol with the change. Alcohol in large amounts precipitates from violet solutions of the sulphate a pale violet colored, crystalline powder, and decolorizes the liquid.[1] This can be used as a mode of purifying the alum.[2] Siewert[3] states that, when the violet sulphate is dissolved in a small amount of water and boiled with alcohol until the crystals formed are again taken up and then precipitated with ether, a green syrup is gotten which consists of $5Cr_2O_3 12SO_3.xH_2O$ and the mother-liquor contains sulphuric acid in a condition in which it is not precipitated by barium chloride. Krüger[4] states that alcohol precipitates from a green solution of the alum a green oil which solidifies and which contains only two-thirds of the sulphuric acid. Siewert confirms this and says that this substance has approximately the composition $6K_2O.5Cr_2O_3.18SO_3.H_2O$. Krüger mentioned the acidity of the alcohol used in precipitating the green oily liquid and evidently regarded it as withdrawing sulphuric acid from the original salt. He also mentioned the formation of a basic salt, by heating the green solution until it becomes rose-red, which contains half as much acid as the neutral salt and is insoluble in water.

After a careful consideration of the results obtained by others by means of alcohol, it seemed to us quite possible that these might afford a clue to the explanation we were in search of. It was necessary to examine with care the action upon both the violet and the green solutions. Our experiments are therefore given in detail, and it will be seen that they agree in part only with the observations just quoted.

Action on the Violet Solutions.—When alcohol was added to the violet solution of the alum, fine violet crystals were precipitated, which gave on analysis the following results:

	Calculated for $K_2Cr_2(SO_4)_4\ 12H_2O$.	Found.	
		I.	II.
Cr	13.32	13.68	13.36
K	9.99	9.80	....
SO_4	49.99	48.85	....

This may be an old observation that on crystallizing from alcohol the crystals contain only half the usual amount of water,

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[1] Gmelin's Handbuch. IV, 127.

[2] Baubigny and Pechard: *Loc. cit.*

[3] *Ann. Chem.* (Liebig). 126. 97.

[4] *Ann. phys. Chem.*, 61, 218.

but we have not met with it anywhere. The fact that this very considerable change of hydration effects no change in color nor in the precipitating power of barium chloride, argues against the partial dehydration theory of Schrötter and Etard. It should be added that the precipitation was carried out with absolute alcohol upon concentrated solutions of the alum, was rapid, and the precipitate was immediately removed. There seemed to be two layers of crystals, one of violet crystals, and the other (upper) one of a fine heliotrope power. Analysis showed that the composition of both was the same and that the difference was probably one of subdivision. The precipitation is almost complete, as the alcohol shows very little color. From this it is evident that alcohol itself does not materially affect the violet solutions.

Action on the Green Solutions.—Green solutions of the alum were first experimented with. When absolute alcohol is added to concentrated solutions of chrome alum, which have been boiled until fully green and allowed to cool, a dark green gummy mass separates out after a short time. If the boiling is not sufficiently prolonged there will form afterwards a few violet crystals. The alcohol retains something in solution, as is shown by the green color. This amount retained may be considerable if much water is present. It would seem then, that alcohol precipitates out the body formed by the boiling and makes it available for analysis and examination. If a portion of this green, gummy mass is taken and dissolved in water, it exhibits the same behavior towards barium chloride as has been observed in the green solutions. In one or two cases it was observed that the part remaining dissolved in the alcohol yielded practically all of its sulphuric acid to barium chloride in the cold. The green mass was thoroughly washed with alcohol and dried over sulphuric acid. It also dries to a brittle mass if exposed in thin layers to the atmosphere. It is quite insoluble in alcohol, but soluble in water. A number of preparations of this substance were made and analyzed and the results are in such agreement that one is inclined to believe that the substance is a definite compound.

Fifteen grams of chrome alum were dissolved in 100 cc. water and boiled for one hour to a concentration of fifty cc. This was cooled and precipitated by the addition of 100 cc. of absolute alcohol. The green mass obtained on drying weighed about eight grams. This was carefully analyzed :

	Calculated for $7K_2SO_4.5Cr_2(SO_4)_3.Cr_2(OH)_6.4H_2O$.	Found.			
		I.	II.	III.	IV.
Cr	18.07	18.23	18.32	18.02	17.76
K	15.88	15.18	15.63	15.78	....
SO_4	61.08	60.55	60.73	....	60.79

Analysis III and IV were from other preparations, made, however, in a similar manner to that just described. This substance appears to have quite a complicated constitution, and it is not easy to see the part played by the potassium sulphate. It does not seem to be a matter of accidental occurrence, however. The important feature is that the salt is a basic one. Siewert gives, as the result of his analysis, $6K_2O.5Cr_2O_3.18SO_3.H_2O$, for which the following percentages would be required: Cr, 18.7 ; K, 16.8 ; SO_4, 61.9. While these percentages differ somewhat from those obtained by us, the agreement is sufficiently close to show that the substances examined were practically the same.

On concentrating the liquid poured off from the green gum, it was repeatedly observed that more of the gum was obtained. For instance, in the experiment described where the green mass from fifteen grams weighed about eight grams, a further portion weighing 0.3915 gram was gotten. The analysis of this yielded the following percentages: Cr, 13.66 ; K, 8.57 ; and SO_4, 55.45. We could only regard this as a mixture consisting in part of the green basic mass which had not completely separated out. The small amount of material left in solution (less than one-half gram) consisted of a little chromium with sulphuric acid in the ratio of about five to one.

Next the action on chromium sulphate was examined. The chromium sulphate used was in the form of small violet scales or crystals. It was a commercial product and the method of its preparation was unknown to us. An analysis of it gave :

Cr	22.10
SO_4	44.20

It is therefore a basic chromate, but we have seen no such body described in the books. It dissolved in water with a green color. Fifteen grams of this dissolved in 100 cc. of water, boiled to a concentration of 50 cc. and precipitated with 100 cc. of alcohol, yielded about ten grams of the green, gummy mass, very similar in appearance to that obtained from the alum, but more soluble in alcohol. In a second experiment twelve grams were taken and treated in the same way, and yielded about eight grams. The analysis showed these to be identical.

	Calculated for		Found.	
	$Cr_2(SO_4)_3.Cr_2(OH)_6.15H_2O$.	I.	II.	III.
Cr	24.06	22.41	22.40	22.69
SO_4	33.17	34.64	34.73	34.43
Water	43.77	....	....	....

The agreement is far from satisfactory, but the body is evidently a basic salt.

On evaporating the liquid portions other masses were obtained. These were also analyzed:

	Calculated for		Found.	
	$2Cr_2(SO_4)_3.Cr_2(OH)_6.20H_2O$.	I.	II.	III.
Cr	22.70	22.93	22.71	22.98
SO_4	42.72	43.71	42.32	43.46
Water	34.57	....	....	....

This is less basic than the previous compound. As the alcohol left is decidedly acid, it must contain either free acid or an acid sulphate.

It did not seem to be necessary to prepare other chromium sulphates, as these experiments were in accord with those obtained with the alum, and lack of time made it necessary to bring the experiments to an end.

CONCLUSIONS.

On weighing the experimental evidence which has been brought to bear upon these changes, it is an easy matter to exclude some of the explanations offered. Thus the dissociation of the alum into chromium and potassium sulphates and similar theories which will not cover the cases of the nitrates, chlorides, etc., must of course be dropped. The formation of chromosulphuric acid, as suggested by Recoura, is not tenable in the light of the experiments performed. The theory of the change of hydration is not satisfactory, since it has been seen that a loss of one-half the water did not bring about the change of color.

The theory of Berzelius, however, of the formation of basic salts of chromium which would naturally be green and uncrystallizable, offers a full and sufficient explanation of the changes, and is in accord with the observations so far as they have been verified by us. It accounts quite plausibly for the partial withholding of the sulphuric acid from precipitation by barium chloride in the cold, and is strongly confirmed by the experiments with alcohol. This theory is also in accord with the facts that the green coloration may be brought about by the addition of alkaline substances, and that it is retarded by the addition of sulphuric or nitric acid. It is also easy to apply this explanation to the cases of the nitrate, chloride, acetate, and other soluble compounds of chromium. When we have opportunity we propose examining the action of alcohol upon these other compounds.

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A METHOD FOR THE DIFFERENTIATION OF ORGANIC MATTER IN WATER.

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AT present one of the least satisfactory determinations made in the usual course of a sanitary water analysis is that of the so-called "oxygen-consumed" or carbonaceous matter. Various methods have been proposed for estimating the organic matter in water to replace the difficult and tedious combustion process of Frankland. Probably the one most generally used is some modification of the Forchammer potassium permanganate process. The objections to this process may be briefly summarized as follows: (1) The results obtained by means of it are only comparative and do not indicate in any degree the absolute amount of carbonaceous matter present; (2) these comparative results are of value only when the organic matter in the various samples compared is practically identical in composition. As a matter of fact, this latter condition is one that is very seldom realized in natural waters from different sources. The readiness with which the organic matter is oxidized by potassium permanganate varies not only with its character and the conditions under which it is found in the water, but also with the manner in which the determination is conducted.