

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

THE NATURE OF THE CHANGE FROM VIOLET TO GREEN
IN SOLUTIONS OF CHROMIUM SALTS.¹

BY W. R. WHITNEY.

Received October 10, 1899.

AN article entitled "The Nature of the Change from Violet to Green in Solutions of Chromium Salts," was published by Venable and Miller in this volume of the Journal, pages 484-496.

As it does not seem that the conclusions drawn in that article are supported by the experimental evidence presented by them, and as I believe that the statements there made are misleading because of the imperfect presentation and discussion of facts previously known, I desire to call attention again to the subject.

The question under discussion concerns the change in composition taking place when a solution of a violet chromium salt, such as chromic sulphate, is heated, the solution then changing in color to green. The following are some of the facts which have been discovered and published by various investigators as evidence for the belief that the green solution, unlike the violet solution, contains a considerable quantity of free sulphuric acid, a conclusion disputed by Venable and Miller.

1. The green solution is strongly acid to all indicators and is

¹ Read before the Columbus meeting of the American Chemical Society, August 21, 1899.

partially precipitated by barium chloride, giving barium sulphate. These facts together are evidence of the presence of some free sulphuric acid.

2. Distillation of the green solution results in an acid distillate, while the dried salt may be heated above 100° C. without loss of acid.¹

3. Dialysis of the green solution gives a product in the diffusate containing proportionately more SO_4 than was obtained by diffusion of the violet solution.²

4. Sulphuric acid has a retarding action on the change from violet to green taking place when the solution is heated. If sulphuric acid is present in the green solution as one of the products arising from the conversion of the violet salt, its addition should retard the conversion in accordance with the law of mass action.

5. Conversely, alkalis accelerate the change from violet to green (Van Cleeff). On the assumption that free acid is present this also would be acquired by the law of mass action.

6. Alcohol poured in a layer over the green solution takes up acid from that solution.³

7. The heat generated on the addition of various quantities of sodium hydroxide to a quantity of the green solution has been carefully measured and the following results obtained: The addition of sodium hydroxide caused at first a generation of heat for each additional portion, exactly equal to that generated when the sodium hydroxide was added to sulphuric acid alone. This relation ceased when a quantity of alkali had been added equal to one molecule of sodium hydroxide to one of chromic sulphate. When more than one molecule (but not when less than one) has been added, the subsequent addition of sulphuric acid brings about a generation of heat. If the first molecule of sodium hydroxide had caused the formation of a chromium hydroxide instead of sodium sulphate in the solution, the addition of acid would have produced a generation of heat. This indicates that there is one molecule of free sulphuric acid for each two molecules of the original chromic sulphate present.⁴

¹ Recoura : *Compt. rend.*, 112, 1440.

² Van Cleeff : *J. prakt. Chem.*, 23, 58; Dougal : *J. Chem. Soc.*, 69, 1527.

³ Krüger : *Ann. phys. Chem.*, (3), 61, 218.

⁴ Recoura : *Ann. chim. phys.* (7), 4, 494.

8. The electrical conductivity of the violet solution is much less than that of an equally concentrated green solution, the difference being readily explained by the presence of free acid in the green solution, inasmuch as free acids are known to be much better conductors than their neutral salts.¹

9. The electrical conductivity of the green solution is decreased at first by the addition of alkali. This reduction of conductivity ceases as soon as one molecule of sodium hydroxide has been added to each molecule of chromic sulphate of the original solution, while still further addition of the hydroxide causes an increase in the conductivity.¹ This can hardly be explained otherwise than by the assumption that free acid is present and that it is neutralized by the alkali. If no chemical change occurred when sodium hydroxide was added to the green solution the electrical conductivity would, of course, increase. It is hard to see how it could diminish to any considerable extent except in case free acid is present. The hydrogen ions of this acid and the OH ions of the base forming as they do undissociated water molecules and thus ceasing to take part in the electrical conductivity, would, however, account for the considerable reduction in conductivity observed. The above is a fact corresponding perfectly with the discovery of Recoura from his thermochemical measurements, that one free sulphuric acid molecule is present in the green solution of two molecules of chromic sulphate. Sodium hydroxide added to the violet sulphate solution does not produce the above effect except to a very slight extent; the conductivity of the solution increases after a very small addition of the hydroxide.

10. Finally, the green solution inverts cane-sugar solutions and hydrolyzes methyl acetate, and to the same extent as a solution of sulphuric acid containing an amount of acid corresponding to one molecule for two of original chromic sulphate. All investigations previously made have led to the conclusion that this inverting or catalyzing action does not occur with neutral salts and in acid solutions is approximately proportional to the concentration of the hydrogen ions present.² Violet solutions of chromic sulphate do not possess this hydrolyzing power.¹

¹ Whitney : *Ztschr. phys. Chem.*, 20, 40.

² See J. H. Long : This Journal.

These facts Venable and Miller treat in the following manner: "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 explanation." Unfortunately, however, no other explanations are suggested by the authors, nor is the reasoning of other investigators in this field refuted to the slightest degree by them.

The entire experimental work of the authors bearing on this matter, which they apparently consider to outweigh the above evidence showing the presence of free acid, consists of a single experiment, which is as follows: Decinormal ammonia was added to a violet and to an equivalent green chromic sulphate solution until the first appearance of a permanent precipitate was noted, and it was found that the two required, within about four per cent., the same volume of the ammonia solution. They seem to conclude, therefore, that the two contain the same amount of acid, and apparently have overlooked the significance of the fact stated on a preceding page of their article and previously announced by Van Cleeff, "Sodium, potassium, or ammonium hydroxide or the carbonate readily turned the violet solution green." This change in color, moreover, precedes the formation of the permanent precipitate. It seems superfluous to add that if the ammonia changes the violet to a green solution it is an unsuitable reagent to use in attempting thus to distinguish the acidity of the solutions.

NEW EXPERIMENT ON THE FREE ACID.

I have performed the following experiment, which again proves the presence of the stated amount of free acid in the green solution.

In order to separate the free acid from the green solution of the chromium compound, in which it cannot be titrated with alkali owing to the progressive decomposition of the chromium compound, the plan was adopted of passing an electric current through the solution and thus causing a removal of the acid from the chromium into an adjoining solution of a simple salt, owing to the more rapid migration of the hydrogen ions.

In order to avoid stirring and convection currents in the solution, the artifice of gelatinizing the solution as employed by Arrhenius,¹ Oliver Lodge,² and Whetham³ was made use of.

It having been found by Arrhenius that the effect on the velocity of migration of different salts by the solidification of the solution with gelatine was not great, and was practically constant for different substances in the same jelly, Whetham employed the method in obtaining the specific velocities of migration of various ions, finding, for example, that the hydrogen ion moved about five times as fast as the chlorine and three times as fast as the next in order to itself, the hydroxyl ion.

It was on this difference in velocity of migration that it was hoped a method of separation could be based.

The experiment was first carried out as follows: An aqueous solution of 0.5153 gram of $\text{Cr}_2(\text{SO}_4)_3 \cdot 14.8\text{H}_2\text{O}$ was boiled thirty minutes to change the salt completely into the green modification. This was made into a jelly by use of two per cent. of agar-agar. A large quantity of two per cent. agar-agar jelly was also prepared containing a few per cent. of potassium sulphate and some methylorange as indicator. A straight glass tube about forty cm. long and having an internal diameter of about two cm. was corked at one end, placed perpendicularly, and filled nearly half full of the neutral potassium sulphate agar-agar solution, which was then allowed to solidify. The melted agar-agar solution containing the green chromium compound was then poured into the tube and allowed to solidify on top of the first jelly. When this was in turn solid, the tube was filled to the end with more of the potassium sulphate jelly. There was thus obtained a solidified solution of the green compound about three cm. long between similar solutions of neutral salt. The cork having been removed, the ends of the tubes were fitted with glass elbows and the whole arranged horizontally with the elbows turned upwards. In one of these elbows was placed an aqueous solution of zinc sulphate and a zinc electrode, in the other copper sulphate solution and a copper electrode. Thus there could be no acid or alkali produced at the electrodes. The whole apparatus was surrounded by cold water to prevent the liquefaction of the agar-agar due to the

¹ Kongl. Vetenskaps. — Akademiens Fördhandlingar, (1885).

² B. A. Report, 395 (1886).

³ *Phil. Mag.*, 392 (1894).

heat of the electric current. The current from a 110-volt circuit was passed through a thirty-two candle-power lamp and this apparatus in series, the copper pole being made the cathode. The current resulting was probably not far from three-quarters of an ampere. The jelly adjoining the green zone towards the cathode immediately began to redden and the resulting red zone augmented slowly towards the cathode, as the methyl orange was effected by the advancing acid. After four and a half hours, when the methyl orange had been reddened for a distance of 16.5 cm. the current was interrupted and the jelly pressed out of the tube. The reddened portion was cut out and divided into two parts. One constituting the end towards the cathode had a length of 14 cm. and the other adjoining the chromium compound a length of 2.50 cm. These portions were extracted with cold water until the jelly contained no more acid and the resulting extracts titrated. The larger portion required 12.95 cc. of sodium hydroxide (0.0504 normal) solution, the smaller 0.63 cc. of the same solution, showing that the migrating acid was principally in the forward part of the moving reddened zone. The total quantity of sulphuric acid thus found was 0.0355 gram, while a calculation on the basis of Recoura's hypothesis, *i. e.*, one molecule of free acid for two of original chromic sulphate, requires 0.0379 gram. In other words, 88.4 per cent. of the acid hypothetically present had been obtained. Owing to the long period necessary for this migration it was certain that the green compound reverted somewhat to the violet, thus reducing the quantity of free acid, and in fact the movement of a narrow violet zone due to the chromium ions was plainly visible between the green and reddened portions of the jelly, the green color having moved no more than to the small extent attributable to ordinary diffusion.

The above experiment was repeated with chrome alum under improved conditions. This time the jelly was removed after being in use between two and three hours. It was separated into its differently colored parts, and that containing chromium was this time reheated to reconvert any violet chromium sulphate into the green modification. It was then returned to the tube as before, together with fresh portions of the neutral potassium sulphate jelly. On the passage of the current a faint red zone was produced, but not nearly so marked as before, and

it was soon evident that the acid had all been separated from the chromium compound. The total quantity of acid obtained on extraction of the reddened portions of jelly was titrated as before.

In this case 0.8125 gram of chrome alum had been used, corresponding theoretically to 0.0399 gram of free sulphuric acid. There were 16.3 cc. of the alkali solution used to neutralize the free acid, which corresponds to 0.0402 gram of sulphuric acid instead of 0.0399. This is as close an agreement as the process could be expected to give. Experiment showed that no measurable action of free acid on the agar-agar takes place under the conditions of the above process.

It was now desirable to perform a similar experiment with the violet solution. On making the jelly containing the alum as before, it was found that the return of the violet color which was changed to green by the melting of the agar-agar solution, required at least weeks for its completion, and therefore for this purpose the solution of the alum in the hot melted agar-agar had to be abandoned. It was found, however, that on placing the solid powdered alum between two pieces cut from a jelly cast in the tube above described, the substance dissolved quite readily, and rapidly diffused throughout the pieces of jelly. Such a plug of the jelly, containing two-tenths gram of alum, was placed in the center of the tube with the neutral potassium sulphate jelly as before and the current passed through the whole for an hour. It failed to yield sufficient acid to affect the indicator, though the relatively slow migration of the chromium ions was evident. These experiments therefore show the presence of the free acid in the green sulphate solutions and determine that its amount corresponds to the hypothesis of Recoura.

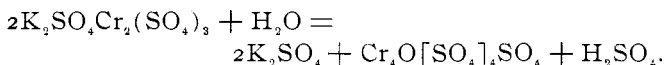
THE NON-PRECIPITABLE SULPHATE.

Favre and Valson¹ fractionally precipitated the green chrome alum solution by adding to it successively portions of barium chloride solution equivalent to one-quarter of the quantity theoretically necessary to precipitate all the SO_4 present. The first and second quarters were immediately and completely used up in precipitating barium sulphate, while the third quarter produced a very slowly appearing cloudiness, which became an

¹ *Compt. rend.*, 74, 1032.

actual precipitate only after the expiration of a considerable time. The heat generated in this reaction was likewise measured. For the first, second, and third quarters of barium chloride added, 4104, 4102, and 146 calories, respectively, were generated. Thus, these authors were led to conclude that only half of the sulphuric acid actually present is immediately precipitable.

Recoura¹ simply states that he has confirmed this conclusion, and advances the following reaction and formulas as representing the compounds actually in the green solution :



In this case, the SO_4 in the brackets assumed to be a part of a positive radical attached to a single SO_4 , and forming one-half of the total SO_4 present would be the non-precipitable portion. Venable and Miller also attempted to investigate the point quantitatively. As they were unable to filter the precipitated sulphate, because of its finely divided condition, until after the lapse of about twenty-four hours, it is not surprising that they obtained in the precipitates about ninety per cent. of the total SO_4 present. To obtain a satisfactory separation of the immediately precipitable sulphate, it is necessary that the barium sulphate at first thrown down should be filtered at once, for the remainder of the SO_4 present will be slowly precipitated, as described by Favre and Valson, owing to the gradual return of the green to the violet compound.

The following quantitative evidence on this point has been obtained :

Two solutions were made by dissolving 0.5982 and 0.4605 gram of recrystallized chrome alum, each in about 100 cc. of water at 0°C . An excess of a four per cent. barium chloride solution, also at 0°C ., was slowly added to each from a burette, the solutions being constantly stirred. The precipitates of barium sulphate were filtered and washed immediately. They were perfectly white and on ignition weighed 0.5508 and 0.4249 gram, respectively. This corresponds in each case to 98.7 per cent. of the SO_4 theoretically present in the alum. The filtrates

¹ *Ann. chim. phys.* (7), 4, 502.

yielded no further precipitates on being boiled. This shows that the SO_4 can be precipitated immediately from the ordinary violet solution of chrome alum at 0°C .

The green solutions to be precipitated were made by dissolving known weights of the alum in water and boiling for half an hour. After being cooled to 0°C . these were precipitated as above, more of the precipitant being added in each case than would be necessary to throw down all the sulphuric acid present in whatever form. The resulting precipitates collected on double filter-papers were of different shades of green and evidently contained varying quantities of the chromium compound. After thoroughly washing these precipitates they were digested with boiling dilute hydrochloric acid, the acid evaporated almost to dryness, and the precipitates, after being digested with boiling water, were filtered. These were then fused with sodium carbonate and the sulphate in the filtered and acidified solution of the fusion, reprecipitated. The following table contains the results :

Alum.	Total BaSO_4 calculated.	<i>a.</i>	BaSO_4 found. <i>b.</i>	<i>c.</i>	Precipitated SO_4 . Per cent.
0.8064	0.7531	0.4336	0.4129	54.9
0.7255	0.6776	0.3787	0.3397	50.1
0.5062	0.4728	0.2557	0.2515	53.2
0.6470	0.6042	0.3490	0.3409	56.4
0.8235	0.7690	0.4102	0.4042	52.5
0.9160	0.8554	0.4564	0.4489	52.4

The values under *a* give the weights of the greenish precipitates at first obtained, so far as they were determined. All of these precipitates yielded considerable quantities of chromium and of sulphuric acid to the hydrochloric acid used in their purification. Under *b* are the weights of the precipitates after the hydrochloric acid treatment, and under *c* the weights of barium sulphate after fusion with the sodium carbonate and reprecipitation. These latter were used in the calculation of the percentages of precipitable sulphuric acid which appear in the last column.

When the difficulties connected with this determination are taken into account, it is probable that exactly one-half of the sulphuric acid of a green solution of chrome alum is present in a form which does not readily yield the SO_4 ion. The fact

that the filtrates from the above precipitates remained perfectly clear for periods of from thirty to ninety minutes, varying with the temperature at which they were kept, is worthy of note.

It is therefore clear that all experimental evidence thus far points to the correctness of Recoura's peculiar symbols representing chromium compounds, for here in the case of the chrome alum solution, the free acid, as well as the directly ionizable sulphuric acid radicals, has been shown to correspond in quantity with the requirements of the symbol,



i. e., one-half of the SO_4 exists as ordinary sulphate, including one-eighth as free acid, and the other half in a condition of considerable stability and non-precipitable, at ordinary temperatures.

LABORATORY OF THE MASSACHUSETTS
INSTITUTE OF TECHNOLOGY.

THE DETERMINATION OF THE BROMINE ABSORPTION OF OILS.

BY PARKER C. MCILHINEY.

Received September 22, 1899.

SOME time ago the writer suggested a method of fat analysis, having the same end in view as the Hübl process; *viz.*, the determination of the unsaturated constituents of fats and oils.¹ Since then Hehner² has called attention to the fact that Allen³ had previously described a similar method of analysis for shale oils. This fact had escaped the writer's attention and his apologies are due to Mr. Allen for the omission of credit where it belonged.

Further experience with the method has confirmed the belief that its results are more valuable than those given by the Hübl process, and recently it has been found possible to so modify its details that it can be carried out more easily and expeditiously. The method consists briefly in adding to a weighed portion of the fat or resin in a stoppered bottle, an excess of standard solution of bromine in carbon tetrachloride, and, after the reaction between them has taken place, determining the excess of bromine

¹ This Journal, 16, 275.

² Analyst, 20, 40 (1895).

³ Commercial Organic Analysis, second edition, 2, 353.