

of its smaller charge and because of the greater number of electrons, is larger and hence it is not altogether surprising that the migration of magnesium ion in the "wrong" direction can be forced more readily.

It is extremely probable then that ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$ , which have electronic configurations in the gaseous state like those of the rare gases retain their configurations in solution and that they do not form complex or molecular ions.

### Summary

The nature of complex ions has been reviewed in terms of current theories on molecular structure as related to magnetic properties.

It has been shown that a metallic ion which does not form negative complex ions can show a net migration to the anode. It is to be concluded that the exhibition of such migration is no proof of the formation of complex ions.

A new modification of the Gouy method is described which permits the measurement of relative susceptibilities to be made easily and accurately.

BERKELEY, CALIFORNIA

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE RICE INSTITUTE]

## THE ATOMIC WEIGHT OF VANADIUM

BY ARTHUR F. SCOTT AND CLYDE R. JOHNSON

RECEIVED JANUARY 3, 1930

PUBLISHED JULY 3, 1930

The values now accepted for the atomic weight of vanadium depend upon the determinations of McAdam,<sup>1</sup> and Briscoe and Little.<sup>2</sup> These investigators have reviewed the earlier determinations, and have pointed out serious defects in all of them. Consequently, the earlier work is not given further detailed consideration here.

McAdam, from five measurements of the  $\text{NaVO}_3$ - $\text{NaCl}$  ratio, obtained the average value 50.957 for the atomic weight<sup>3</sup> of vanadium. Briscoe and Little, rejecting two experiments in taking the final mean, derived the value 50.955 from nine measurements of the  $\text{VOCl}_3$ : $3\text{Ag}$  ratio. While these results agree substantially, it may be mentioned that McAdam's investigation was intended only as a preliminary one, and cannot be given the same weight as that of Briscoe and Little. The general agreement between the results of the two series of experiments, however, practically excludes the possibility that the latter investigators, who used a distillation method in the purification of their vanadyl trichloride, were dealing with a constant boiling mixture.

In their determination of the  $\text{VOCl}_3$ : $3\text{Ag}$  ratio, Briscoe and Little em-

<sup>1</sup> McAdam, *THIS JOURNAL*, **32**, 1603 (1910).

<sup>2</sup> Briscoe and Little, *J. Chem. Soc.*, **105**, 1310 (1914).

<sup>3</sup> The antecedent atomic weights used throughout this paper are: O = 16.000; Ag = 107.880; Cl = 35.457; Na = 22.997.

ployed the Richards nephelometric method of titration. They also introduced an entirely new technique for purifying the vanadyl trichloride by fractional distillation. The measurements were carried out with extreme care, and the results indicate that the analytical method may be used to assign a value for the atomic weight of vanadium with an error of only 0.002 or 0.003 unit. Nevertheless, an examination shows that there is a difference of 0.009 unit in the mean values of the atomic weight to be derived from the two fractions (C and D) of the material which Briscoe and Little used in their final analyses. It seems probable that at least one of these fractions contained small amounts of some impurity, possibly air, an impurity which would tend to raise the calculated values of the atomic weight.

This consideration has led us to undertake another determination of the  $\text{VOCl}_3:3\text{Ag}$  ratio, using the method developed by Briscoe and Little, with certain deviations: (1) phosphorus and arsenic were eliminated from the vanadium material prior to the preparation of the vanadyl trichloride; (2) ground-glass connections in the distillation apparatus were avoided, in order to prevent the introduction of air into the material; (3) half of the samples were hydrolyzed in dilute nitric acid, the other half in dilute ammonium hydroxide; (4) considerably larger samples were used for analysis, in the hope of extending the precision of the results.

**Preparation of Vanadyl Trichloride.**—Two pounds of vanadic oxide prepared from Peruvian patronite were obtained from the Vanadium Corporation of America for this work. The analysis of this material stated that it contained 90.75% of  $\text{V}_2\text{O}_5$  and that it was commercially free from arsenic and phosphorus.

To insure complete removal of these impurities, we employed the following procedures, adapted from those described by McAdam.<sup>4</sup> The oxide was dissolved in concentrated sodium hydroxide solution and a black residue was filtered off. The solution of sodium metavanadate was concentrated and allowed to crystallize; the first small crop of crystals was rejected. The sodium metavanadate was acidified with sulfuric acid and the precipitated vanadic oxide washed with distilled water. It was reduced by warming with oxalic acid solution, and converted to the double ammonium oxalate by the addition of a slight excess of ammonium oxalate. The double salt was fractionally crystallized until it gave no test for sulfate with barium chloride. The crystals were dissolved in water and the solution precipitated with an excess of ammonium hydroxide. The precipitate of ammonium vanadite was washed several times, collected on a filter and dried. A portion of the ammonium vanadite was then mixed with recrystallized sodium carbonate and fused. This step was discontinued, however, when it was discovered that a poisonous gas<sup>5</sup> was liberated in the reaction. The bulk of the ammonium vanadite was treated with nitric acid and evaporated to dryness, to drive off the ammonium salts. The resulting vanadic oxide was thoroughly washed with water, dried and fused in platinum. The product was a dark red mass of crystals.

<sup>4</sup> McAdam, THIS JOURNAL, 32, 1606 (1910).

<sup>5</sup> Probably cyanogen resulting from the incomplete removal of the ammonium oxalate. An analogous reaction is:  $\text{NH}_4\text{OOC}-\text{COONH}_4 \xrightarrow{\text{P}_2\text{O}_5} 4\text{H}_2\text{O} + (\text{CN})_2$ .

The preparation of vanadyl trichloride from this material was carried out as follows. The powdered vanadium pentoxide was placed in a pyrex combustion tube contained in an electric furnace and reduced to the trioxide by heating to a dull red in a current of hydrogen. It was noted at this stage that no arsenic appeared in the cooler portions of the tube. After the tube had cooled, the hydrogen was swept out by a current of nitrogen. The nitrogen was displaced by chlorine, which reacted with the trioxide to form vanadyl trichloride when the tube was again heated.

These operations were carried out in an all-glass apparatus, the combustion tube being connected by ground-glass joints. The bulb for condensing the vanadyl trichloride was cooled in an ice-bath, and was connected to the combustion tube only after the reduction of the oxide. Of the gases which were utilized, hydrogen and chlorine were obtained from commercial tanks, while nitrogen was prepared by the reaction of sodium nitrite and ammonium chloride. The gases were washed in towers of glass beads wetted with 1:1 sodium hydroxide solution, and dried in similar towers containing 95% sulfuric acid.

When the formation of vanadyl trichloride had ended, the collection bulb was disconnected temporarily and closed with glass plugs held in place by rubber caps. The vanadic oxide regenerated in the chlorine treatment was again reduced and treated with chlorine, and a second portion of vanadyl trichloride collected in the same bulb as the first. To eliminate some of the excess chlorine in the preparation, mercury was added. The collection bulb was then exhausted by means of a suction pump and sealed off completely from the air. The final product had a red color, probably due to the presence of a small quantity of vanadium tetrachloride.

### Purification of Vanadyl Trichloride

The material from the preparation described above was treated successively with mercury and with sodium in several all-glass systems, without exposure to air. The excess of chlorine in the material at this stage was not markedly decreased by contact with mercury over a period of four months, by continued exposure to sodium wire, or even by a three-hour treatment with molten sodium. The reaction with sodium, however, did remove the red color from the product.

To accomplish the removal of the excess chlorine, the bulb of vanadyl trichloride was heated to about 130° in an oil-bath, and the chlorine was permitted to escape through a small hole punctured in one of the glass capillaries of the system. When the internal pressure of the system was sufficiently reduced, the capillary was again sealed. Under these conditions practically all of the chlorine must have been driven off, while very little moisture, if any, could have entered the system.

The vanadyl trichloride was then distilled in evacuated all-glass apparatus of the type used by Baxter and Fertig<sup>6</sup> in their work on the atomic weight of titanium. The general procedure of distillation which was followed differed in no respect from that described by these investigators.

The essential details of the distillations proper are given in Table I. This table does not include several partial distillations which were not very effective because of the presence of excess chlorine in the material. The capital letters in Table I refer to glass bulbs of 200 to 50-cc. capacity, in which the main portion of the material was handled. The combined numerals and letters refer to the small bulbs (5 cc.) in which samples were removed for analysis. These symbols are arranged in the table in the order

<sup>6</sup> Baxter and Fertig, *THIS JOURNAL*, **45**, 1230 (1923).

in which the corresponding bulbs were sealed off from the main system. The terms "head" and "tail" are used to designate more and less volatile fractions removed during the distillation. In order to indicate the composition of different fractions of the material, we have included in the table the values for the atomic weight obtained by analysis of various samples. Volhard's method was used to determine the chlorine content of Samples A1 and B3; the method applied to the other samples is described in the following section of this report.

TABLE I  
DISTILLATION OF VANADYL TRICHLORIDE

System no.	Fraction of VOCl <sub>3</sub>	Estimated wt., g.	Type of fraction	At. wt. of vanadium		
1	A1	5.5	Head	50.7		
	A2	6.0	Head			
	B	167.5	Main			
	A, A3, A4	13.0	Tail			
2	C	150.5	Main	51.1		
	B, B1, B2	10.5	Tail			
	B3	6.5	Tail			
3	D1-D4	4.5	Head	50.949		
	E	132.0	Main			
	C, D, D5, D6	14.0	Tail			
4	F1, F2, F3	17.0	Head	50.955		
	F4	8.0	Head			
	G	77.5	Main			
	F5	7.5	Tail			
	F6	7.0	Tail			
	E, F, F7, F8	15.0	Tail			
	5	G1	8.0		Head	50.936
		G2	8.0		↓	50.950
G3		9.0	50.938			
G4		8.5	50.950			
H		4.5				
G5		6.5	50.941			
G6		7.5				
G7		8.0	50.947			
G8		7.5	↓	50.951		
G	10.0	Tail				

The samples included in Table I were all condensed with carbon dioxide-alcohol mixtures; liquid air was used in some of the earlier distillations. The temperature of the paraffin oil-bath used in distilling the material was adjusted to maintain proper refluxing in the Hempel column. This temperature, which was about 120° in the first distillation, dropped abruptly to about 50° in the third distillation, and remained the same in the final distillations. The sudden fall was quite marked, and may be taken to indicate the removal of the last traces of chlorine and air. The amounts of chlorine and air present in even the first and second distillations, how-

ever, must have been quite small, since we experienced no difficulty in condensing samples in these distillations. As further evidence of the complete removal of air from the material, we may mention that the hydrolysis of the contents of the systems remaining after the second, third and fourth distillations gave only negligible amounts of residual gas.

One further observation bearing upon the purification of vanadyl trichloride may be noted here. The original preparation, containing mercury and excess chlorine, was frequently exposed to bright sunlight over a period of four months, and showed no marked changes. However, during the second distillation, when, judging from the above indications, most of the excess chlorine had been removed, a faint red discoloration appeared on the glass walls of the distillation apparatus. That this effect resulted from the action of light was demonstrated by the fact that sample D3, on exposure to sunlight, darkened markedly, and on long exposure became quite brown. Accordingly, we took precautions to guard our pure material against photochemical decomposition and carried out the two final distillations and the weighings of the sample bulbs in very dim yellow light.

### The Analyses

The vanadyl trichloride samples for analysis were contained in sealed glass bulbs having a capacity of about 5 cc. The vanadyl trichloride was hydrolyzed, and titrated against silver nephelometrically. Standard methods,<sup>7</sup> adapted from various representative atomic weight determinations, were employed in the analyses. Only the details which indicate our adaptation of the standard procedures are described below.

**Weighings.**—A No. 10 Troemner balance, sensitive to about 0.02 mg. with a load of 50 g., was used for the weighings. The weights, which were of the best grade of lacquered brass, were calibrated just before, during and after use in this work. None of the weights used in the analyses showed any changes greater than 0.01 mg. except one 2.0-g. weight, for which it was necessary to increase the correction by 0.05 mg., in all of the gravimetric analyses. Weighings were made by the method of substitution, with precautions to avoid errors greater than 0.02 mg. Suitable counterpoises were used whenever possible. In the analysis of the "G" samples weighings were made in duplicate.

Vacuum corrections were calculated from the usual formula,<sup>8</sup> the air density being determined for every weighing by measurement of the temperature, pressure and relative humidity. Calibrated instruments were used.

The densities used in calculating the vacuum corrections were: silver, 10.5; silver chloride, 5.56; glass, 2.48; sodium chloride, 2.16; brass, 8.4.

<sup>7</sup> See, for example, Richards and Wells, *THIS JOURNAL*, **27**, 502 (1905); Briscoe and Little, *J. Chem. Soc.*, **105**, 1327 (1914); Baxter and Scott, *Proc. Am. Acad. Arts Sci.*, **59**, 33 (1923).

<sup>8</sup> Landolt-Börnstein's "Tabellen," 2d ed., p. 15.

**Hydrolysis of the Vanadyl Trichloride.**—Each sample bulb was broken in 500 cc. of solution in a heavy-walled two-liter pyrex Erlenmeyer flask, cooled in ice to 0°. For half of the samples, selected alternately from the distillation series, the solution contained 30 cc. of 15.6 *M* nitric acid. For the other samples, the solution was approximately 0.3 *M* ammonium hydroxide, freshly prepared by distilling concentrated aqua ammonia (sp. gr. 0.90) into water, in an all-glass apparatus.

After the bulb was broken, the flask was cooled for at least eight hours, opened, closed and cooled for another four hours, before the solution was filtered.

**Separation and Collection of the Glass Fragments.**—The solutions from the hydrolysis were filtered into glass-stoppered 3-liter pyrex Erlenmeyer flasks or 4-liter pyrex bottles, as follows. (a) The clear yellow liquid from the hydrolysis in acid was decanted through a low-ash<sup>9</sup> filter. The glass fragments of the bulb and the filter were washed with 500 cc. of water containing 20 cc. of 15.6 *M* nitric acid, in 50-cc. portions. (b) The ammoniacal liquid from the hydrolysis in alkaline solution was decanted through a low-ash filter. The precipitate in the flask was washed twice to remove most of the chloride, and dissolved in 60 cc. of 7.8 *M* nitric acid. The solution was poured through the filter. The glass fragments of the bulb and the filter were then washed with 500 cc. of water containing 20 cc. of 15.6 *M* nitric acid. In each case the final volume of the solution before precipitation was 1100 cc.

The glass fragments of the bulb were collected in the manner which we have previously described.<sup>10</sup>

**Precipitation of Silver Chloride.**—The solutions were precipitated with almost the theoretical amount of silver, weighed out and made up to 750 cc. in a solution containing 50 cc. of 15.6 *M* nitric acid. The partially diluted solution of silver nitrate was warmed to remove nitrous acid.

The silver solution was added to the chloride solution at the rate of about 4 cc. a minute. The final volume was in each case made up to 2250 cc. Subsequent titration showed the acid concentration to be 0.57 to 0.59 *M* in the solutions containing ammonium ion, and 0.65 *M* in the solutions containing no ammonium ion.

**Determination of the End-Point.**—After precipitation of the silver chloride, the stoppered flasks were first cautiously shaken by rotation, then violently shaken twice each day for twelve days. Two or three tests of the supernatant liquid from each analysis were made at this time. After four months another series of tests was made. The changes taking place

<sup>9</sup> Ten weighings of the ash of thoroughly washed individual filters gave values varying from 0.01 to 0.07 mg. In the correction for the ash there is thus an uncertainty of about 0.03 mg.

<sup>10</sup> Scott and Johnson, *J. Phys. Chem.*, **33**, 1980 (1929).

during the interval were negligible. The maximum change in the average nephelometric ratio for any analysis was 0.09 units, which corresponds to  $-0.00010$  g. of silver in the total volume of solution. At the completion of these tests the solutions were adjusted to the final end-point.

The procedure used in the above-mentioned tests and in the determination of the end-point was the same as that which we have previously described,<sup>11</sup> with this deviation: the 1-cc. portions of silver nitrate and sodium chloride standard solutions were added to the 20-cc. samples of the supernatant liquid, with identical stirring; the nephelometric observations took place between thirty and sixty minutes later.

The actual adjustment to the final end-point was continued until three independent series of 20 readings each, made over a period of a week, gave an average value within 0.05 unit of 1.00 for the ratio of the exposed lengths of the nephelometer tubes. The average deviation of the mean of each series from the final mean was about 0.02 unit. In most cases the end-point was "crossed." The correction to make the ratio 1.00 exactly, which was never more than 0.06 mg., was calculated and is included in the value for the total silver added or subtracted in solution, in Table II.

In order to check the standard solutions employed, and the nephelometric procedure, nine saturated solutions of pure silver chloride containing varying amounts of nitric acid were tested at various times during the nephelometric observations. The average value found for the ratio of the exposed lengths of the tubes was 1.01, with an average deviation of 0.03 unit, the individual values varying from 0.94 to 1.05.

The analytical reagents used in this investigation were carefully purified, by methods<sup>12</sup> which we have previously outlined. Only one preparation of silver was used in the analyses. In the analysis of samples G1 to G8, inclusive, 20-cc. portions of liquids covering all of the ammonia, nitric acid and water added to the analytical solutions were tested nephelometrically for silver and chlorine. Only when the concentration of chloride was between the concentration of silver and the concentration of chloride in a solution containing sodium chloride equivalent to 0.02 mg. of silver per liter, was the liquid used in the analysis.

## Results

Table II gives the results of all of the nephelometric analyses. The supernatant liquid from the analysis of sample G6, when first tested, showed a large excess of silver. The analysis was completed gravimetrically, giving the value 51.63 for the atomic weight of vanadium. This result is evidently due to some error, which a careful examination has failed to reveal.

<sup>11</sup> Scott and Johnson, *J. Phys. Chem.*, **33**, 1981 (1929).

<sup>12</sup> Scott and Johnson, *ibid.*, **33**, 1978 (1929).

TABLE II  
 ATOMIC WEIGHT OF VANADIUM.  $\text{VOCl}_3 \cdot 3\text{Ag}$   
 $\text{Ag} = 107.880$ ;  $\text{Cl} = 35.457$ ;  $\text{O} = 16.000$

Sample of $\text{VOCl}_3$	$\text{VOCl}_3$ in vacuum, g.	Ag in vacuum, g.	Ag added or subtracted in soln., g.	Corr. wt. of Ag in vacuum, g.	Ratio $\text{VOCl}_3:3\text{Ag}$	Atomic weight of vanadium
F4	7.75120	14.47351	+0.00033	14.47384	0.535532	50.949
F5	7.62984	14.24619	+ .00047	14.24666	.535553	50.955
F6	7.01143	13.09200	+ .00018	13.09218	.535543	50.952
G1	7.88453	14.72254	+ .00132	14.72386	.535493	50.936
G2	8.15697	15.23166	- .00023	15.23143	.535535	50.950
G3	9.19783	17.17479	+ .00135	17.17614	.535500	50.938
G4	8.29538	15.48965	+ .00021	15.48986	.535536	50.950
G5	6.69572	12.50289	+ .00055	12.50344	.535510	50.941
G7	8.04970	15.03074	+ .00062	15.03136	.535527	50.947
G8	7.60527	14.20116	- .00005	14.20111	.535541	50.951
				Mean	.535527	50.947

The values of the atomic weight from Table II are arranged below according to the decreasing volatility of the samples, and the nature of the solutions used in their hydrolysis.

Ammoniacal hydrolysis		Acid hydrolysis	
Sample	Atomic weight $\text{VOCl}_3:3\text{Ag}$	Sample	Atomic weight $\text{VOCl}_3:3\text{Ag}$
F4	50.949	G2	50.950
G1	50.936	G4	50.950
G3	50.938	G8	50.951
G5	50.941	F6	50.952
G7	50.947		
F5	50.955		
Mean	50.945		50.951
Average deviation	0.006		0.001

There is no trend in the "acid" series. In the "ammonia" series the values of the atomic weight, with one exception, are lower than the values in the "acid" series, and show a regular increase with decreasing volatility of the samples, particularly apparent in the fractions from the last distillation.

Two observations which were made at the conclusion of the fourth distillation seemed to establish the uniformity of our material at this stage of the purification. Analysis of more and less volatile samples gave essentially the same values for the atomic weight. The hydrolysis of the residual vapor in the apparatus from the fourth distillation, carried out soon after the completion of the distillation, yielded only a negligible amount of residual gas.

Subsequent observations, however, suggest that the variations noted above were caused by the presence of chlorine in the samples. A faint chlorine-like odor was detected during the filtration of the solutions from the "acid" hydrolysis of samples G2, G4, G6 and G8. The hydrolysis of



the material remaining in the 400-cc. all-glass system from the fifth distillation gave about 3 cc. of residual gas, mostly chlorine. This system contained 10 g. of the extreme *tail* fraction of the vanadyl trichloride, which had been standing for five months in a dark cupboard. It showed no discoloration which would indicate a leak.

It may be noted that if chlorine were present in the samples as an impurity, it would tend to make the mean value 50.945 derived from the "ammonia" series too low, and the value 50.951 from the "acid" series a little too high. Under the circumstances, the close agreement between the mean values of the atomic weight derived from the "acid" and "ammonia" series, and the small range, 0.019 unit, covered by the entire nephelometric series, shows that only extremely small amounts of chlorine could have been present. Since chlorine is the only impurity whose presence there is any occasion to suspect, it seems reasonable to conclude that the atomic weight of vanadium lies between the above limits, and cannot be far from the mean value, 50.947, obtained from all of the nephelometric analyses.

As a means of confirming this conclusion, we have extended the experiments to take into account two possible sources of constant error in the analytical method. If the coagulating actions of equivalent amounts of silver nitrate and sodium chloride, added in excess according to the usual procedure, are not equally affected by the presence of vanadic acid, the nephelometric end-point may not correspond to the stoichiometrical point. To investigate this possibility, the supernatant liquids from the analyses of the "G" samples, after adjustment to the end-point, were analyzed for their silver and chloride content. The measurements were made in the usual way by direct nephelometric comparison against standard silver and chloride solutions. In these comparisons, in order to eliminate any disturbing action of the vanadic acid, the same precipitating ions were present in excess (in equal amounts) in the "standard" and "unknown" tubes, and the concentrations of vanadic acid, ammonium ion and nitric acid in the two tubes did not differ by more than 1%. Similar measurements were also made upon four saturated solutions of silver chloride in 0.65 *M* nitric acid.

In these experiments two effects were found which may be attributed to the presence of vanadic acid. Every one of the supernatant liquids from the seven analyses contained more silver than chloride ion. The (approximate) "solubility product" of silver chloride was greater in the analytical solutions than in the saturated solutions of silver chloride. It may be noted that the observed deviations are only a little greater than the analytical error. Thus, on the assumption that the excess of silver found in each solution is real, the mean atomic weight calculated<sup>13</sup> from the seven ex-

<sup>13</sup> When the apparent excess of silver is taken into account the average  $\text{VOCl}_3:3\text{Ag}$  ratio from the seven analyses is  $0.535536 = 0.000011$ .

periments is 50.950 instead of 50.945. While the results of these experiments can obviously be regarded only as provisional, they indicate that any error due to the effect of vanadic acid on the nephelometric end-point is small.

The possibility of a serious error due to the contamination of the precipitate has also been investigated. In three analyses from each of the "acid" and "ammonia" series the precipitated silver chloride was collected and weighed. The usual gravimetric procedures<sup>14</sup> were followed in collecting the silver chloride and in determining the silver chloride in the wash liquors. The results of these gravimetric analyses are given in Table III.

TABLE III  
SUMMARY OF RESULTS.  $\text{VOCl}_3:3\text{AgCl}$

Sample of $\text{VOCl}_3$	AgCl in vacuum, g.	Loss on fusion, g.	AgCl removed in supernatant liquid, g.	AgCl dissolved in washings, g.	Corr. wt. of AgCl in vacuum, g.	$\text{VOCl}_3:3\text{AgCl}$ Ratio	Atomic weight of vanadium
G1	19.55896	0.00035	0.00220	0.00137	19.56218	0.403050	50.945
G2	20.23316	.00041	.00117	.00127	20.23483 <sup>a</sup>	.403115	50.973
G3	22.81668	.00037	.00214	.00079	22.81924	.403073	50.955
G4	20.57677	.00021	.00140	.00076	20.57872	.403105	50.969
G7	19.96741	.00031	.00183	.00083	19.96976	.403094	50.964
G8	18.86606	.00031	.00136	.00059	18.86755 <sup>a</sup>	.403087	50.961
					Mean	.403087	50.961
						$\pm 0.000006$	

<sup>a</sup> Corrected for *total* chloride added in the nephelometric analysis.

The loss on fusion of the silver chloride is the value found after an initial heating of about sixteen hours in an electric furnace at 300°. Part of the data for the estimation of the chloride removed in test portions of the supernatant liquid was obtained in the experiments described above; another part, in additional experiments of the same nature.

The many tests made upon the supernatant liquids limit to a considerable extent the precision of the gravimetric analyses. Nevertheless, the results of these analyses do show that there is no serious contamination of the precipitated silver chloride. In fact, the mean value  $1.32855 \pm 0.000012$  for the  $\text{AgCl}:\text{Ag}$  ratio calculated for the six analyses completed gravimetrically, is low rather than too high. Further evidence of the absence of coprecipitation of vanadium is the fact that the fused silver chloride was always white. One milligram of vanadic oxide in twenty grams of fused silver chloride gives a distinct color to the mixture.

We are indebted to the Vanadium Corporation of America for the gift of the vanadic oxide used in this work.

### Summary

The analysis of vanadyl trichloride has yielded for the  $\text{VOCl}_3:3\text{Ag}$  ratio

<sup>14</sup> See, for example, Baxter and Moore, *THIS JOURNAL*, **34**, 1651 (1912).

the value  $0.535527 \pm 0.000004$ , from which the atomic weight of vanadium is found to be 50.947.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]  
**ELECTRICAL CONDUCTANCE OF COBALT SULFATE SOLUTIONS<sup>1</sup>**

BY R. C. CANTELO AND ALFRED J. BERGER

RECEIVED JANUARY 20, 1930

PUBLISHED JULY 3, 1930

This paper records the results of an investigation of the conductances of cobalt sulfate solutions, and is the first of a series dealing with the properties of solutions of cobalt salts.

The conductivities of cobalt sulfate solutions have been determined previously by Jones and Jacobson<sup>2</sup> for concentrations varying between  $N$  and  $N/1024$  at 0, 10, 25 and 35°. This was part of an investigation of the influence of temperature upon the dissociation of thirty-four electrolytes. For reasons to be discussed later, we felt that it was necessary to repeat the measurements of the conductances of cobalt sulfate solutions.

### Materials

**Conductivity Water.**—The conductivity water was prepared by the usual method of redistilling distilled water with alkaline potassium permanganate and condensing the vapor in a block-tin condenser. The water was kept in a six-liter pyrex flask fitted with a siphon and a soda lime tube. All the water used had a conductivity between  $1.2 \times 10^{-6}$  and  $2.0 \times 10^{-6}$  mhos.

**Cobalt Sulfate.**—Chloropurpureocobalt chloride  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  was prepared by the method of Sørensen<sup>3</sup> and was converted to the carbonate and eventually to the sulfate. The cobalt sulfate was precipitated by means of absolute alcohol, and was then twice recrystallized from conductivity water.

**Cobalt Sulfate Solutions.**—A solution of cobalt sulfate, approximately 0.5  $N$ , was prepared and this was standardized by an electrolytic determination of its cobalt content. The exact amount of conductivity water needed to make the solution exactly 0.5  $N$  was added from a calibrated buret, and from this stock solution was prepared the 0.2  $N$  by diluting 100 cc. of the 0.5  $N$  to a volume of 250 cc. Similarly the 0.1  $N$  solution was prepared by diluting 100 cc. of the 0.5  $N$  to 500 cc. The third "standard" solution 0.05  $N$  was prepared in a similar manner.

In this way three solutions were prepared from the 0.5  $N$  solution. Also duplicate solutions were made by dilution in different ratio, for example, the 0.1  $N$  from the 0.2  $N$ , etc.

The above method was followed for the preparation of the more dilute solutions. In every case at least 100 cc. of a "standard" solution was used in the dilution.

### Experimental Method

The conductivity was measured by the Kohlrausch bridge method using two Washburn cells,<sup>4</sup> Types A and B. A new Leeds and Northrup Stu-

<sup>1</sup> This paper is an abstract of a part of the doctorate thesis of Alfred J. Berger.

<sup>2</sup> H. C. Jones and C. A. Jacobson, *Am. Chem. J.*, **40**, 355 (1908).

<sup>3</sup> Sørensen, *Z. anorg. Chem.*, **5**, 369 (1894).

<sup>4</sup> Washburn, *THIS JOURNAL*, **38**, 2449 (1916).