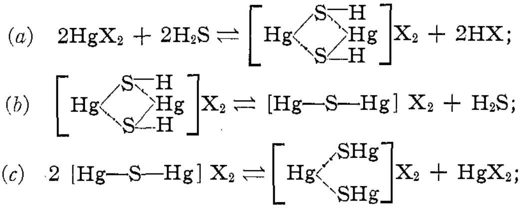
conclude at present, would seem to be that represented by the equations which follow; and there are many indications that salts of other metals, as platinum, lead and cadmium, for example, behave in a more or less analogous manner:[47]



$$(a)\quad 2HgX_2 + 2H_2S \rightleftharpoons \left[Hg\begin{smallmatrix}S-H\\ \\ S-H\end{smallmatrix}Hg\right]X_2 + 2HX;$$

$$(b)\quad \left[Hg\begin{smallmatrix}S-H\\ \\ S-H\end{smallmatrix}Hg\right]X_2 \rightleftharpoons [Hg—S—Hg]\,X_2 + H_2S;$$

$$(c)\quad 2\,[Hg—S—Hg]\,X_2 \rightleftharpoons \left[Hg\begin{smallmatrix}SHg\\ \\ SHg\end{smallmatrix}\right]X_2 + HgX_2;$$

$$(d)\quad [Hg(SHg)_2]X_2 + 2H_2S \rightleftharpoons [Hg(SHg)_2](SH)_2 + 2HX;$$

$$(e)\quad [Hg(SHg)_2](SH)_2 \rightleftharpoons [Hg(SHg)_2]S + H_2S.$$

8. After a careful consideration of the evidence, including that offered in the experimental part, the writers do not hesitate to draw the conclusion that the considerations advanced in this paper give good promise of furnishing a consistent, comprehensive, and truthful interpretation of the interactions of hydrogen sulfide and metallic salt solutions; and that the precipitation of the heavy metals with hydrogen sulfide, both in acid and in alkaline solutions, will eventually be regarded in the light of the coördination theory of Werner, as are already so many of the subjects of chemistry.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF CHARLES UNIVERSITY, PRAGUE]

A REVISION OF THE ATOMIC WEIGHT OF ALUMINUM. II.[1] THE ANALYSIS OF ALUMINUM CHLORIDE

BY HENRY KREPELKA

RECEIVED MARCH 3, 1924

In the table of the International Committee on Atomic Weights for 1921 the value 27.0 for the atomic weight of aluminum was adopted. This new value, replacing the older value of 27.1, which was evidently too high, is based on a preliminary determination by T. W. Richards and H. Krepelka[2] who obtained 26.963 as a mean of four analyses of aluminum bromide, and is rounded for the International Table to 27.0.

In the present investigation upon this subject pure aluminum chloride was prepared and analyzed by comparison with silver. The properties of aluminum chloride are, of course, less suitable both for synthesis and analysis than those of the bromide. Since the chloride does not melt under ordinary conditions, we have to deal with a material obtained by

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[47] Concerning the probable existence of a compound $Mn_8S_4H_2$, analogous to the product in (*d*), see "A Study of the Green Sulfide of Manganese," by Mickwitz and Landesen, *Z. anorg. allgem. Chem.*, **131**, 101–118 (1923).

[1] Presented before the Bohemian Academy of Prague.

[2] Richards and Krepelka, THIS JOURNAL, **42**, 2221 (1920).

repeated sublimation in nitrogen and in a vacuum. On the other hand, the chloride contains twice as much aluminum as the bromide, a property compensating for the above-mentioned disadvantages.

Pure, dry aluminum chloride may be prepared by two methods: first, the direct synthesis from aluminum metal and pure, dry chlorine; and second, the reaction of chlorine upon a mixture of aluminum oxide and sugar charcoal. The reaction of pure, dry hydrogen chloride with metallic aluminum is not suitable because it starts at a rather high temperature.

Preparation of Materials

Aluminum.—Aluminum of the same origin as that of the metal used for the synthesis of aluminum bromide was treated in the same manner, as fully described in the preliminary paper. The aluminum surface was etched with hydrochloric acid.

Chlorine.—This was prepared by the action of hydrochloric acid on precipitated hydrated manganese dioxide. This method gives chlorine that is free from oxygen. The hydrated manganese dioxide was prepared from twice recrystallized, c. p. manganous sulfate and potassium permanganate.

Nitrogen was prepared by the convenient method described in the first paper and generated in an apparatus which is generally used[2] in the Laboratories of Harvard University.

Phosphorus pentoxide was twice resublimed from a porcelain boat in an electrically heated tube of hard bohemian glass in a current of dry oxygen.

Silver.—Three different samples of standard silver were used for the precipitation of the solutions of aluminum chloride.

1. A sample of silver used in the investigation on the atomic weight of tin,[3] the preparation of which has already been described. It was washed successively in pure ammonium hydroxide, dil. nitric acid, ammonium hydroxide and distilled water. The clean metal was dried in pure air in an electric oven at 250°. This sample of (standard) silver was called Ag-A.

2. Silver newly prepared in the same way as Silver A. The final step in the purification of the precipitated silver was fusion of electrolytic crystals on lime in a current of pure dry hydrogen. All the final operations were carried out according to the usual Harvard methods. This silver was called Ag-B.

3. Silver prepared according to the method of Stas by reduction of silver chloride with glucose. For this pure metal I am greatly indebted to Professor B. Brauner, who kindly gave me the remainder of a lot of material prepared for his investigations on atomic weights. This silver was electrolytically refined and fused in hydrogen in the same manner as was Silver B. This third sample was called Ag-C.

Hydrogen was generated in a glass apparatus from pure, arsenic-free zinc and hydrochloric acid. The gas was passed successively through distilled water, a 20% solution of potassium hydroxide, an alkaline solution of plumbous salt and a tube containing fused potassium hydroxide. The hydrogen, thus partly dried, was passed through a porcelain tube containing pumice stone covered with platinum and copper gauze. This tube was maintained at a red heat. The final drying was effected by means of fused potassium hydroxide.

Sulfuric acid was obtained by the double distillation of ordinary c. p. acid, only the middle fraction in each case being used.

Nitric acid was purified by repeated distillation and carefully tested in the nephelometer to prove the absence of halogen.

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[3] Krepelka, This Journal, **42**, 926 (1920).

Water.—The distilled water for ordinary laboratory use was treated as described in an earlier article.[4]

Apparatus for the Synthesis of Aluminum Chloride

In this investigation pure, dry aluminum chloride was synthesized directly from metallic aluminum and dry chlorine. First, the course of the reaction was studied in two preliminary trial syntheses, from which it appeared that the chief difficulty was the control of the temperature. The reaction started at about 450° and as soon as the first portion of the chloride began to sublime the reaction became violent in consequence of the great heat evolved. In order to prevent the melting of aluminum and eventual cracking of the reaction tube, both the temperature of the heating oven and the flow of the chlorine had to be properly regulated. The melting of aluminum would have retarded the reaction because of the resulting decrease in its surface and this would have favored the formation of silicon tetrachloride in larger quantities.

The apparatus as a whole was very similar to that used for the synthesis of aluminum bromide but was adapted to the higher combining temperature and other special properties of aluminum chloride. The following changes have been made in two main parts of the apparatus.

The reaction tube was made from a special, resistant, hard, Bohemian glass which withstood the high temperature and was very little corroded by chlorine. The reaction tube was connected with the other parts of the apparatus by means of two long, air-tight joints. These had been very carefully ground with fine emery and with rouge and then polished with a paste of pure aluminum oxide and distilled water. Lubricant could not be used for the joints, but aluminum oxide paste with the fine glass rubbed off during grinding proved, when allowed to solidify in the joints, to be sufficiently gas-tight, and did not contaminate the subliming chloride. The whole system could be heated slowly to the temperature of sublimation of aluminum chloride (183°) without perceptible leakage.

The magnetic valve described in the previous paper was also modified. The Richards-Craig[5] modification was first applied, using a rather strong electromagnet for breaking the fine inner tube. This delicate operation was never easy and always risky. When a weak magnetic field was generated to actuate a bar of soft iron enclosed in a glass tube the impact against the capillary was not strong enough to break it; on the other hand, increase of magnetization increased the risk of breakage of the outer tube of the magnetic valve, an accident that occurred once and caused the loss of material at a late stage in one analysis. The method of breaking was therefore modified as follows.

[4] Brauner and Krepelka, This Journal, **42,** 923 (1920).

[5] Richards, Craig and Sameshima, *ibid.*, **41,** 131 (1919). Richards and Craig, **45,** *ibid.*, 1159, 1160 (1923).

The electromagnet was replaced by a solenoid S (Fig. 1). When an almost instantaneous current was sent through this solenoid, the iron bar was driven out and withdrawn again, gaining sufficient momentum to break the previously scratched capillary but never reaching the opposite glasswall. This method of breaking the valve was found to be very satisfactory.

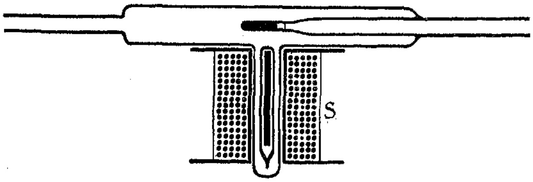

Fig. 1.

The entire apparatus used for all operations of synthesis and for the preparation of nitrogen and chlorine was made of glass and sealed together. In the presence of aluminum chloride only magnetic valves were used instead of stopcocks. Vacuum stopcocks lubricated with sirupy phosphoric acid were used where necessary in the gas trains. The caps of these vacuum stopcocks were sealed above with paraffin wax which was melted before they were operated.

The collecting bulbs were of the type used and fully described in a preceding paper. They are shown in cross section in Fig. 2.

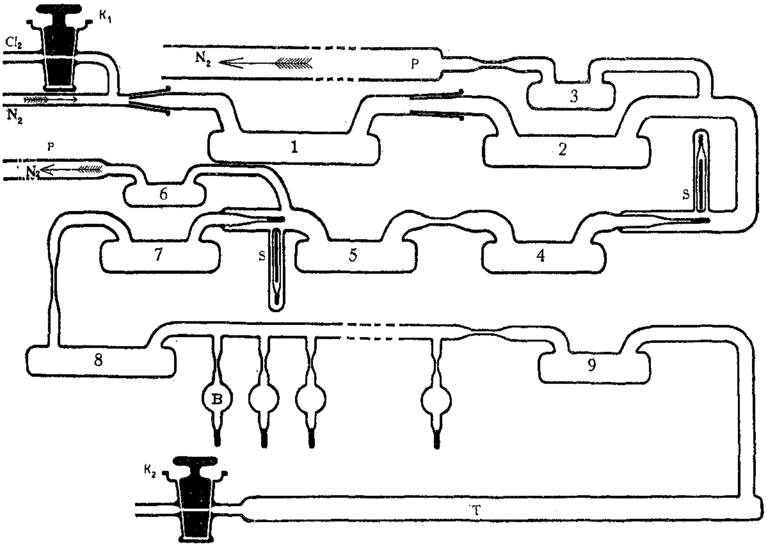

Fig. 2.

Preparation of Aluminum Chloride

About 80 g. of aluminum was cautiously introduced into Tube 1 and the latter joined to the apparatus in the manner described. The whole apparatus was then thoroughly dried by heating in a current of dry nitrogen which passed through a drying system comprising a long tube with phosphorus pentoxide and a wash bottle containing distilled sulfuric acid. Pure dry nitrogen was then passed for two hours through the first part of the apparatus, namely, Tubes 1, 2 and 3, Reaction Tube 1 being electrically heated to 100°. When this system was completely filled with nitrogen the temperature of Tube 1 was gradually raised, the current of nitrogen temporarily stopped and pure dry chlorine was introduced through the stopcock K_1. The dry halogen attacked the aluminum perceptibly at about 500° and the chloride formed sublimed into Tube 2. Owing to the high heat of reaction the temperature of the reaction tube rose very rapidly and had to be regulated to prevent violent combustion.

In the course of 10 hours the necessary amount of chloride was deposited in Tube 2. The least volatile portion of this sublimate which accumulated in the part adjacent to Tube 1 was yellowish,[6] due to a trace of iron present in the original aluminum. This color gradually faded in the direction of sublimation. After the completion of the reaction the aluminum chloride and the uncombined metal were cooled in a very slow stream of nitrogen. During the cooling process a bright green phosphorescence appeared surrounding the small pieces of corroded, uncombined metal. This phenomenon was probably caused by the presence of a trace of activated nitrogen, its activation having been effected by the violent reaction of the chlorine left in the tube with the metallic aluminum.[7]

The contents of Tube 2 were digested for one hour at 100° in nitrogen, and thereupon without interruption of the current the most volatile portion was sublimed at 150° into Receptacle 3 which was kept cool with ice water. Tube 3 was then sealed off at the connecting capillary. The first magnetic valve was opened, and nitrogen was passed through Tubes 1, 2, 4, 5, 6 and the drying system, while Vessel 2 was heated to about 180° by means of an adjustment which permitted the volatilization of only the white sublimate deposited in the farther part of Tube 2, the remaining yellowish first part having been cooled and insulated from the electric oven by an asbestos board. In this manner the white sublimate, freed from traces of iron was deposited in the cooled receptacle No 4. This method of purification was, of course, accompanied by a considerable loss of material, about one-half of the contents of Tube 2 being discarded. The capillary tube of the magnetic valve greatly assisted in the separation of ferric chloride from the aluminum chloride, the narrow opening probably effecting a fractionation by diffusion. A second sublimation into Vessel 5 continued the fractional purification, a fraction of residue having been left in each case.

The contents of Receptacle 5 were digested in a slow current of nitrogen

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[6] When, later on, 10 g. of the yellowish sublimate was dissolved in 50 cc. of water, only a reddish coloration was observed upon addition of a fresh solution of thiocyanate.

[7] Nature, July 28, **1923**, No. 2804.

for one hour at 100° and again for 20 minutes at 120°. The most volatile impurities, if there were such, were then sublimed in nitrogen at 160° into Vessel 6, and this and the drying system were then removed by being sealed off in the same manner as was Tube 3. Thereupon Vessels 4 and 5 were disconnected by sealing off the heavy capillary tube joining them. Before the connecting valve between Vessels 5 and 7 was opened, the system including Tubes 7, 8, etc., was repeatedly evacuated through the phosphorus pentoxide tube T. During that operation this portion of the apparatus was heated to ensure perfect dryness.

Next, the second magnetic valve was broken and the residual nitrogen was completely exhausted through Stopcock K_2. By heating Vessel 5 to about 140° the aluminum chloride was sublimed in a vacuum into Vessel 7, again leaving a residue of about one-quarter of the whole. A faintly yellowish residue that deposited in the capillary of the second valve gave no positive reaction for ferric ions with a fresh thiocyanate solution; this shows, incidentally, the marked intensity of color produced by dry ferric chloride.

The accepted product was then pure white; any trace of iron that might have remained was eliminated by a second sublimation in a vacuum into Vessel 8, which again left behind about one-quarter of the original substance. During this sublimation the capillary of the magnetic valve was plugged with aluminum chloride by a suitable adjustment of temperature in order to prevent the escape of any of the substance into Tube 5. Vessel 7 was then sealed off at the connecting capillary and removed.

This very pure substance was digested for 30 minutes at 80° while the sampling bulbs were heated to about 180°, and Vessel 9 was cooled with ice water. The temperature of the sampling bulbs was then raised to about 250° and the aluminum chloride again fractionated, the first portion of the sublimate being collected and sealed off in Receptacle 9 at the connecting capillary.

About 50 g. of the aluminum chloride left in Vessel 8, representing the purest halide, was then fractionally sublimed into the single bulbs, in the same manner as in the case of aluminum bromide.[2] Thus 13 samples were obtained in such an order that the first fraction was allowed to condense in the bulb farthest from Vessel 8.

Method of Analysis

Each bulb furnished material for a single analysis. To correct the results to the vacuum standard[8] the exterior volume of each bulb separately was determined by weighing in water and subtracting this weight from the weight in air, the temperature and pressure being noted. The pre-

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[8] The specific gravities of silver, glass and brass were taken as 10.5, 2.56 and 8.4, respectively.

viously scratched bulb was carefully cleaned with alcohol and distilled water, and wiped dry with a chemically clean, lintless cloth. The bulb thus prepared, after standing for several hours in a desiccator, was ready for precise weighing by substitution. All weights were carefully standardized by the substitution method of Richards.[9]

As in the case of aluminum bromide,[2] the salt was dissolved in water with great care to avoid loss of hydrogen chloride, by the same satisfactory method. To the solution was added a few drops of nitric acid and it was then filtered very carefully through a weighed Gooch-Munroe platinum crucible into a large glass-stoppered precipitating flask. The crucible with the glass fragments after drying in an air-bath was again weighed and the weight of the empty bulb thus ascertained. From the weight of aluminum chloride the necessary amount of silver to combine with the chlorine was computed and this quantity of standard silver was weighed out and dissolved in nitric acid. After dilution until the concentration was about 0.1 *N* the silver solution was slowly added to the chloride and the mixture was thoroughly shaken and allowed to stand for several days in the dark room during which time it was occasionally shaken. To prevent the hydrolysis of the aluminum nitrate formed, 2 or 3 cc. of nitric acid was added. After cooling the precipitating flask and its contents for several hours in an ice-bath the point of exact equivalence between chlorine and silver was ascertained in a nephelometer.

Twelve samples were analyzed, and in each case the ratio $AlCl_3:3Ag$ was determined. Bulb 3 cracked while being prepared for weighing and therefore its contents were not analyzed. Sample 13 was analyzed but

TABLE I

DATA FOR THE ANALYSIS OF BULB 1

	G.	
Wt. of Bulb 1 in air	4.53474	
Correction for vacuum (d., 1.34)	+0.00345	
Bulb 1 in a vacuum	4.53819	4.53819
Glass of Bulb 1 in air	2.82690	
Correction for vacuum (d., 2.56)	+0.00093	
Glass in a vacuum	2.82783	2.82783
Aluminum chloride (in a vacuum)		1.71036
Silver A in air	4.15165	
Correction for vacuum (d., 10.49)	−0.00013	
Silver (in a vacuum)	4.15152	
Nephelometric test	−0.00025	
Total amount of silver (in a vacuum)	4.15127	4.15127

The atomic weight of chlorine was taken as 35.458; that of silver, 107.88. $AlCl_3:3Ag = 0.412009$. At. weight of Al = 26.969.

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[9] Richards, THIS JOURNAL, **22**, 144 (1900); *Z. physik. Chem.*, **33**, 605 (1900).

the result of this analysis was omitted as improbable, since the value obtained was Al = 26.989, a figure perceptibly higher than any of the others. This discordance might have been due either to some error during the analysis or to some unrecognized difference in the method of obtaining the sample.[10]

The data of the first of the analyses are given in full in order to make clear the corrections applied.

The results are summarized in Table II.

TABLE II

RESULTS

Ratio, $AlCl_3:3Ag$

Sample	Sample Ag	Wt. of $AlCl_3$ in a vacuum G.	Wt. of Ag in a vacuum G.	$AlCl_3:3Ag$	At. weight of aluminum
1	A	1.71036	4.15127	0.412009	26.969
2	B	2.59733	6.30438	.411988	26.962
3	..	.....	.....	......	....
4	B	1.98148	4.80897	.412038	26.978
5	B	2.73108	6.62852	.412019	26.972
6	C	3.18750	7.73663	.412001	26.966
7	B	1.37059	3.32652	.412019	26.972
8	A	2.99900	7.27846	.412038	26.978
9	C	3.77259	9.15600	.412035	26.977
10	A	2.88939	7.01296	.412007	26.968
11	B	2.22557	5.40157	.412023	26.973
12	C	1.88892	4.58440	.412032	26.976
13	..	.....	.....	......	....
				Av. 0.412019	26.972 ± 0.001

This value is only 0.009 higher than that obtained in the preliminary analysis. The slight increase falls within the experimental error and so cannot be accounted for by a possible trace of iron impurity, since during the process of fractional purification the chloride of even Vessel 5 failed to show any analytical test for iron. On the other hand, silicon, if present, would tend to lower the atomic weight. The possibility of these two impurities compensating each other is excluded by the negative test for iron.

The agreement of all of the eleven analyses is a good indication of the purity and chemical identity of both the various fractions and the three samples of silver.

We are thus justified in accepting the mean value of 26.963 (obtained by Richards and Krepelka) and 26.972 (found in the present analyses), namely, 26.97 as the most probable figure for the atomic weight of aluminum.

This result is also of theoretical interest. According to Aston[11] alumi-

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[10] All the residues from the connecting tube and the necks of the bulbs were in this case collected into Bulb 13 by sublimation at 160°.

[11] Aston, *Nature*, **1922.**

num is a pure element (that is, contains no isotopes), its atomic mass being 27. From the standpoint of the nuclear structure it belongs to the type having the nucleus composed according to the scheme $4n + 3$. The results reported here confirm the previously accepted value of slightly less than the sum of the nuclear masses of helium (4.00) and hydrogen (1.008), and although the three hydrogen nuclei are here satellites, the new value suggests that this loss of mass might be due to a disturbing effect of electromagnetic forces within the nuclear system.

I take pleasure in acknowledging my indebtedness to the Bohemian Academy of Prague for financial support in this investigation.

Summary

This paper records the synthesis and analysis of pure aluminum chloride.[12] The substance was prepared from very pure chlorine and the purest obtainable metallic aluminum. Eleven different fractions of the chloride, digested and repeatedly sublimed in nitrogen and in a vacuum, were analyzed. The ratio $AlCl_3:3Ag$ was determined, using three different samples of standard silver. The mean of these eleven determinations is Al = 26.972 (±0.001), when silver is taken as 107.88, and chlorine as 35.458.

PRAGUE, CZECHOSLOVAKIA

[CONTRIBUTION FROM THE SIR DONALD CURRIE LABORATORIES, THE QUEEN'S UNIVERSITY OF BELFAST]

THE EMISSION SPECTRA OF ORGANIC COMPOUNDS

BY WILLIAM HAMILTON MCVICKER, JOSEPH KENNETH MARSH
AND ALFRED WALTER STEWART

RECEIVED MARCH 5, 1924

Introductory

Owing to the disruptive effect of the ordinary spark discharge upon the vapors of organic compounds, it has hitherto been impossible to obtain characteristic emission spectra from the majority of carbon derivatives; for, as a general rule, only the spectra of carbon, its oxides, or cyanogen, are observed, which result from the decomposition of the compound under examination.

Wiedemann and Schmidt,[1] by selecting some specially stable polynuclear compounds, were able to produce characteristic spectra in the case of ten substances; but as they were unable to extend the field and as, further, their investigations were confined to the visible region of the spectrum, their results contributed very little to our knowledge.

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[12] During this work a new synthesis of aluminum chloride from pure aluminum oxide, sugar charcoal and chlorine has been commenced.

[1] Wiedemann and Schmidt, *Ann. Physik*, **56**, 20 (1895).