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Action of caustic hydroxides upon aluminum

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T 301

THESIS

FOR THE

Degree of Bachelor of Science

IN

Chemistry and Metallurgy.

H. F. ROGERS, 1899.

Action of
Caustic Hydroxides
Upon
Aluminium.

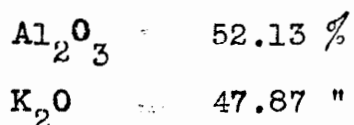
ACTION OF CAUSTIC HYDROXIDES UPON ALUMINIUM.

It is commonly stated, in the text books, that caustic soda and caustic potash dissolve aluminium with the evolution of hydrogen and formation of aluminates.

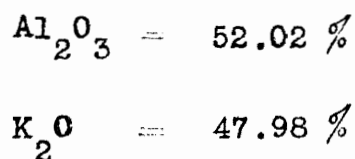
A number of aluminates have been obtained by treating the oxide or hydroxide of aluminium with alkalies either in solution or in the fused state.

Thus Unverdorben # gives an account of the preparation of potassium aluminate by treating aluminium with a solution of caustic potash. He says that the solution saturates itself almost completely, though there always remains some free potash. He separates this from the aluminate by washing with alcohol after evaporating to dryness.

No data were given but he claims the compound contained.



This agrees quite closely with the anhydrous potassium aluminate $\text{K}_2\text{Al}_2\text{O}_4$



Hydrous crystalline aluminate of potassium was first obtained by Fremy ##. He prepared it by treating amorphous alumina, which he obtained by precipitation with ammonium carbonate, with fused caustic potash or a solution of the same.

Poggendorf's Annalen Vol. 7, Page 323 (1826).

An. Ch. Ph. Series III, Vol 12, Page 362 (1844).

In either case he evaporated the solution under an air pump and obtained some hard and brilliant crystals which were very soluble in water but insoluble in alcohol.

Fremy recommends dissolving the salt in a weakly alkaline solution and recrystallizing.

He noticed that it was only partly soluble after heating.

He dried in a vacuum and analysed with the following results:

Name	Analysis of Substance	Calculated for $K_2Al_2O_4 \cdot 3H_2O$.
Al_2O_3	40.60	40.75
K_2O	37.50	37.66
H_2O	21.20	21.59
Total	99.30	100.00

He says that the sodium compound is prepared in a similar manner but crystallizes less readily.

The only account of an attempt to isolate the products formed by the direct action of the alkalies upon metallic aluminium was published by Cavazzi[#].

He found that a solution of sodium carbonate will evolve practically the same amount of hydrogen per gram of aluminium as a solution of sodium hydroxide. He calculated that the first action is between the metal and the water.

He states that 0.665 grams of aluminium were dissolved in a boiling solution of one gram of sodium hydroxide in 20 c.c. of water.

[#] Gazzetta Chimica Ital. N^o. 15, page 202.

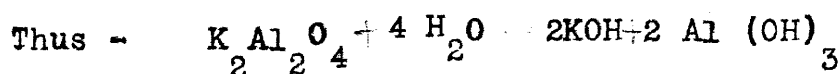
(3)

He then evaporated the solution to dryness and obtained a gummy substance soluble in water, which contained for every 23 parts of sodium 26.11 parts of aluminium instead of 27.1.

An experiment was also tried with a solution of potassium hydroxide. The evaporated solution also gave a gummy substance soluble in water, which for 39.1 parts of potassium contained 26.25 parts of aluminium.

Cavazzi also noticed that the amount of hydrogen evolved in the action of an alcoholic solution of caustic potash on aluminium depended upon the amount of water present. The more water, the more hydrogen will be evolved.

He concluded that the compound formed was $K_2Al_2O_4$, for he claimed that one equivalent of aluminium was dissolved by one equivalent each of potassium or sodium hydroxide, but it was found in the laboratory last year that after the action between aluminium and the alkalies had gone on for some time, a precipitation of $Al(OH)_3$ takes place. This is caused by the hydrolysis of the aluminate.



If this be so, a certain amount of free potash must be found.

The question then arose, why would not more aluminium be dissolved by this caustic potash set free?

In fact experiments showed that several times the theoretical amount of aluminium could be dissolved. The evolution of hydrogen ceased only after the metal had become coated over with a porcelain-like layer of $Al(OH)_3$.

It seems probable that the reaction might be carried on to any length.

Although Cavazzi showed that water took part in the reaction, the remainder of his arguments for the composition of the product seem inconclusive.

The object of my work upon this subject has been to investigate more thoroughly the action of caustic hydroxides upon aluminium.

Composition of the Metal.

The metal used in our experiment was so called c/p. aluminium.

In the analysis of it we followed in general, the methods given by Handy[#].

(1). Determination of Iron.

The method recommended in this journal viz. titrating with a standard $K MnO_4$ solution, was tried and found to yield unsatisfactory results owing to the small amount of iron present in the aluminium.

The $K_2Cr_2O_7$ solormetic method was then tried. In this a standard iron solution was prepared by dissolving 0.1 grams of piano wire in 5 c.c. of concentrated hydrochloric acid, 10 c.c. of water and a pinch of potassium chlorate. The whole being diluted to 200 c.c.

1 c.c. of iron solution = 0.0000499 grams of iron.

1.0024 grams of aluminium were then dissolved in acid and diluted to 50 c.c. and put into a Nessler's tube.

A blank with the same amount of acid as was used in dissolving the aluminium was prepared in another Nessler tube and diluted to 50 c.c.

About 2 c.c. of $K_2Cr_2O_7$ solution was then introduced into each and the number of c.c. of standard iron solution required to give, under the same conditions, the same intensity of color was noted.

[#] Journal of American Chemical Society Vol. 18, Page 766. (1896).

(5)

The blank required 0.2 C.c. of iron Solution.

The Substance " 1.3 c.c. " " "

1.3 - 0.2 = 1.1 c.c. of iron solution corresponds to the amount of iron in 1.0024 grams of aluminium, or 0.054 per cent.

(2) Determination of Silicon.

The method used was that given in the above reference.

The ignited filter paper and residue were treated with hydrofluoric acid and a few drops of concentrated sulphuric acid. The loss equals silicon dioxide.

Analyses.

Number	Wt. of Metal	Wt. of SiO ₂	Wt of Si.	Percent Si.
1	1.0000	0.0089	0.0042	0.416
2#	1.0024	0.0093	0.0043	0.43

(3) Test for Copper.

The aluminium was treated for copper as described in the reference.

The solution of the metal was treated with zinc to precipitate the copper. The residue was dissolved in diluted nitric acid, filtered and evaporated to dryness.

The evaporation was repeated with concentrated H Cl, the residue was taken up with the water and K₄Fe Cu₆ added. Not the slightest trace of coloration appeared.

Analysis made by Dr. Allen.

(6)

(4) Determination of Aluminium in Metallic Aluminium.

Three methods were used.

- 1 Precipitation with NH_4OH .
- 2 Precipitation with NH_4OH^+ (NH_4)₂ S.
- 3 Precipitation by passing carbon dioxide through a caustic hydroxide solution.

In all three methods the aluminium was dissolved in HCl, filtered and the filtrate diluted to 500 c.c.

A portion of this solution was then taken for analyses.

The following results were obtained:-

- 1 By precipitation with NH_4OH .

1.0011 grams Al to 500 c.c. solution.

Number	Amount of Solution taken for analysis	Weight of Metal in Solution	Weight of Al_2O_3	Percent of Al. in metallic Aluminium.
1	50 c.c.	0.10011	0.18802	99.60
2	50 c.c.	0.10011	0.18772	99.43

- 2 By precipitation with NH_4OH^+ (NH_4)₂ S.

One gram of Al. in 500 c. c. of solution.

Number	Amount of solution taken for analysis	Weight of Metal in Solution	Weight of Al_2O_3	Percent of Al. in metallic Aluminium
3	75 c.c.	0.15012	0.28096	99.34

(7)

(3) By precipitation with CO_2 . 1.0008 grams of Aluminium in 500c.c. of solution.

Number	Amount of solution taken for analysis.	Weight of Metal in Solution	Weight of Al_2O_3	Percent of Al. in metallic Alluminium
4	75 c.c.	0.15012	0.28224	99.707
5	75 c.c.	0.15012	0.28146	99.43

Number four was not washed as thoroughly as Number 5. hence it is possible that some potassium salts remained with the aluminium.

Great care was taken to weigh the dehydrated aluminium quickly after removing from the sulphuric acid desiccator, as we found that it absorbs moisture rapidly when exposed to the air.

We also tried the experiment of heating these precipitates in the muffle furnace at 1000 degrees C. They still absorbed moisture rapidly when exposed to the air.

No determinations were made for carbon in the metallic aluminium, on account of insufficient time.

Potassium Aluminate.

Method or preparation. About 2.25 grams of aluminium, cut into small pieces was treated, in a large silver crucible, with a 10 percent solution of caustic potash. About 7 grams of K O H being used.

The whole was heated by a Bunsen Burner. The flame should be kept low.

After the action, which proceeded quite violently at first, had nearly ceased, the whole was filtered into a small evaporating dish and placed in the vacuum desiccator which was then exhausted.

In from two to four day, depending somewhat upon the temperature, crystals of potassium aluminate commenced to separate out. It is better to filter before crystallization, as some alumina, formed by hydrolysis, separates out during the evaporation.

The filtrate was again placed in the vacuum desiccator and in a day or so was evaporated to dryness.

The crystals were next pressed with a filter paper, to absorb any solution remaining upon them, and then transferred to an agate mortar where they were rubbed with absolute alcohol until all the free KOH was removed.

They were then dried between filter papers, then on a porous plate and finally placed in a vacuum desiccator over conc. H_2SO_4 , to dry.

The crystals formed botryoidal aggregates and when the mass was examined under the microscope we found that it appeared to be made up of wart like masses, and these in turn seemed to be composed of a great many translucent plates. They were quite hard and a knife blade had to be used in removing them from the dish. On the other hand they seemed quite brittle and were easily ground to a powder.

Quite a large number of potassium aluminate preparations were made while only a few fairly good analyses were obtained. This is due to the fact that it is extremely difficult to dry them thoroughly, and after they are dry to keep them so while transferring from one dish to another or while weighing.

We found that it would constantly gain weight even in a ground glass stoppered weighing bottle while standing in the balance case.

Another difficulty with which we had to contend was to keep them from carbonating. A very short exposure to the air is sufficient to form enough carbonate to throw off the analyses a few tenths of a percent.

Method of Analysis.

After the aluminate had become thoroughly dry which required about seven days[#], it was quickly transferred to a weighing bottle and a portion weighed out for a water determination, and one for alumina.

For the determination of water a weighed portion was heated in a platinum crucible, for several minutes with a blast lamp, which gave us a temperature of about 850 degrees C. After cooling in a sulphuric acid desiccator it was weighed again. The loss represents water.

The alumina was determined by precipitation with NH_4OH .

The filtrate from the alumina was evaporated to dryness in a platinum dish, over a water bath. The residue was treated with H_2SO_4 and the potassium determined was K_2SO_4 .

[#] This point was determined by making water analyses every few days until the water remained practically constant.

Analyses:

Number	H ₂ O	Al ₂ O ₃	K ₂ O
$K_2Al_2O_4 \cdot 3H_2O$	21.56	40.80	37.63
1	21.82	40.25	37.93 [#]
2	21.57	40.61	37.02

We also tried drying the potassium aluminate, by heating in an atmosphere of hydrogen at 100 degrees to 105 degrees C.

After 5 1/2 hours heating it failed to lose weight but gained a very little.

This was probably due to the formation of a small amount of carbonate although a stream of hydrogen was kept constantly passing through the vessel in which the heating was carried on. After cooling an analysis was made with the following result:

Constituent.	$K_2Al_2O_4 \cdot 3H_2O$	Found.
H ₂ O	21.56	21.49
Al ₂ O ₃	40.80	40.56
K ₂ O	37.63	37.59 [#]

Sodium Aliminate.

The sodium aluminate was prepared in a very similar manner to that of the Potassium aluminate.

Two preparations were made and the product in each case was to all appearance identical.

In the first we treated 1.12 grams of aluminium with five grams of NaOH in a 10 percent solution, while in the second we used 2.71 grams of

[#] By difference.

aluminium and 4.0 grams of NaOH in 50 c.c. of water.

After about three quarters of an hour the aluminium was nearly all used up, but hydrolysis had thrown down a considerable quantity of crystalline $\text{Al}(\text{OH})_3$.

This was filtered off and the filtrate placed in the vacuum desiccator over weight. A thick, transparent, highly refracting liquid was obtained. This was filtered into a watch glass and allowed to remain in the vacuum desiccator until nothing but a gummy mass remained. It was then transferred to a mortar where it was repeatedly washed with absolute alcohol, at the same time being mixed about with the pestle.

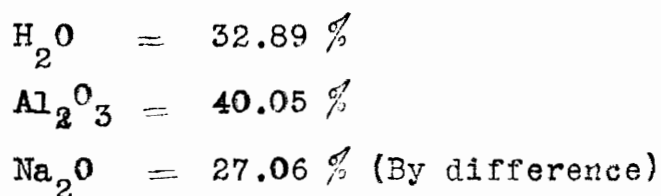
In a short time it became whiter and looked very much like taffy candy.

We then placed it in the vacuum desiccator and concentrated H_2SO_4 and P_2O_5 .

An analysis was made of the first preparation, about two weeks after it had been placed in the desiccator to dry.

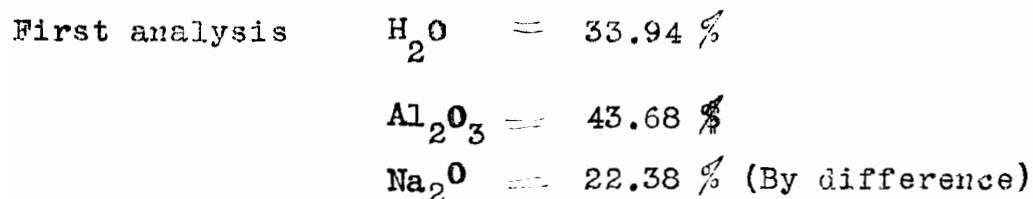
The mass was still quite gummy when the analysis was made.

The following results were obtained:



The second preparation was analyzed after drying ten days over concentrated sulphuric acid in the vacuum desiccator, and also again after remaining over P_2O_5 until a portion had become somewhat brittle.

The following results were obtained:



Second Analysis

$$\text{H}_2\text{O} = 31.54 \%$$

$$\text{Al}_2\text{O}_3 = 40.46 \%$$

$$\text{Na}_2\text{O} = 28.00 \% \text{ (By difference)}$$

A third analysis was made for water after one month's drying giving $\text{H}_2\text{O} = 32.16 \%$

Calculating the ratio of Al_2O_3 to Na_2O in both preparations we find:

$$(1) \text{Al}_2\text{O}_3 : \text{Na}_2\text{O} :: 3.9 : 4.8 \quad 1 : 1.23$$

$$(2) \text{Al}_2\text{O}_3 : \text{Na}_2\text{O} :: 3.9 : 5 \quad 1 : 1.26$$

In both cases it is nearly 1:1 with the soda in slight excess.

This shows that the formula is most probably $\text{Na}_2\text{Al}_2\text{O}_4 \cdot \text{X H}_2\text{O}$

Lithium Aluminate.

The lithium hydroxide used, in the preparation of the aluminate was freed from any carbonate by boiling with calcium oxide and filtering.

Two grams of aluminium, cut into small pieces, was treated with four grams of lithium hydroxide in 70 c.c. of water.

The action is quite violent and as soon as it has nearly ceased, or when the solution becomes saturated with lithium aluminate, the liquid is filtered into a porcelain dish and placed in the vacuum desiccator.

In fifteen or twenty minutes all of the lithium aluminate will separate out as a pure white, soapy looking mass.

This was filtered and washed repeated with cold water. It was then washed with alcohol, dried between filter papers, then on a porous plate and finally allowed to stand in the vacuum desiccator until it was ^{completely} ~~dehydrated~~ ^{dehydrated}.

When examined under the microscope it appears as wart-like aggregations of very small crystals.

An experiment was made in which I tried recrystallizing from a 5 percent solution of LiOH but no crystals separated out after standing for nearly a day in the vacuum desiccator.

This shows how difficultly soluble the lithium aluminate is in a lithium hydroxide solution.

Six different preparations were made but no good results were obtained owing to the extreme difficulty in drying them and at the same time keeping the carbon dioxide, in the air, from converting the partially into lithium carbonate.

The first and second preparations were all used up in making water analyses, to determine when the substance was dry.

The water in the third preparation decreased from 41.40% to 40.98% after standing six days in the vacuum desiccator.

Further analyses of this compound were prevented by an accident but the last water determination corresponds rather closely# with the water in $\text{Li}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$.

The fourth preparation turned brown while drying. This was probably caused by a little lithium hydrate which was not completely washed out and which colored the alcohol in washing.

The fifth preparation was heated in an atmosphere of hydrogen for eight hours, after which it gained slightly.

Examination showed that some carbonate had formed during the heating.

The sixth preparation was dried over conc. H_2SO_4 and P_2O_5 for five days.

Analyses gave the following results which show that some free alumina must have been present.

H_2O	=	37.48%	
Al_2O_3	=	59.62%	
Li_2O	=	2.90%	(By difference)

40.98 % instead of 40.45%.

Barium Aluminate.

The barium aluminate was prepared by dissolving 12 grams of $\text{Ba(OH)}_2 \cdot 8 \text{H}_2\text{O}$ in 30 c.c. of hot water.

This was filtered into a 250 c.c. round bottom flask.

About 2 grams of aluminium was then added, a few pieces at a time, waiting each time until the action had nearly ceased before introducing any more.

The flask was heated over a water bath and a stream of hydrogen passed through it to prevent the carbon dioxide, in the air, from entering and forming barium carbonate.

After about two hours a considerable quantity, of a granular, transparent, crystalline substance formed adhering to the glass vessel and to the strips of aluminium.

The liquid was decanted and the crystals washed into a filter where the pieces of aluminium were separated out, the crystalline layer of barium aluminate being broken off.

The crystals after being washed with water several times were transferred to a large watch glass where they were treated with water, the lighter portions, including silicon and carbon being washed away.

After drying between filter papers and on the porous plate the crystals were placed in a calcium chloride desiccator to dry.

The barium aluminate has a high specific gravity, is insoluble in water and is very easily carbonated when exposed to the air for any length of time.

When examined under the microscope the crystals appeared as small rectangular, transparent plates.

The following results were obtained upon analyzing the crystals:

Preparation I.

This was allowed to remain over CaCl_2 for 12 days and the water decreased from 14.56 % to 13.12%.

No analyses were made for BaO or Al_2O_3 .

Preparation II.

$$\text{H}_2\text{O} = 15.23\%$$

$$\text{BaO} = 60.40\%$$

$$\text{Al}_2\text{O}_3 = 21.69\%$$

Preparation III

$$\text{H}_2\text{O} = 14.54\%$$

$$\text{BaO} = 59.30\%$$

$$\text{Al}_2\text{O}_3 = 24.03\%$$

Another preparation was made in which the flask was heated by the direct flame just hot enough to keep the solution in gentle ebullition.

After about four hours the liquid was diluted with hot water, filtered and washed.

A large yield of a very fine powdery substance was obtained which after heating, in an atmosphere of hydrogen, till its weight remained practically constant, analyzed with the following results:

$$\text{H}_2\text{O} = 33.40\%$$

$$\text{BaO} = 6.29\%$$

$$\text{Al}_2\text{O}_3 = 60.31\% \text{ (By difference)}$$

This shows that there was probably some Al_2O_3 set free during the preparation.

The analytical results obtained in this study seems quite incommensurate with the large amount of time put on the work, but the difficulties encountered in preparing pure substances were so great that much had

to be done before proper methods of preparation were discovered.

The sodium and potassium compound are very easily decomposed by water and all are sensitive to the action of carbonic acid. Besides, the compounds lose their hygroscopic moisture slowly so that much time was consumed before they were ready for analysis.

New Method for the Determination of Aluminium.

The old method for the determination of aluminium, that is by precipitation with NH_4OH affords considerable difficulty for the reason that the alumina comes down as a colloidal precipitate which soon fills the pores of the filter paper, thus causing considerable loss of time in washing out the soluble salt, and if the precipitate be large it is almost an impossibility to wash it through without some loss.

For this reasons experiments were made upon the precipitation of alumina from an alkaine solution, by means of carbon dioxide.

Very satisfactory results were obtained as all of the aluminium can be precipitated and it comes down as crystalline $\text{Al}(\text{OH})_3$ which can be filtered quickly and consequently washes through in a short time.

This method can only be used in the absence of metals of the fourth groupe, including Lithium, ~~that is~~ i.e. in the absence of all metals which will form insoluble carbonates.

The substances in which the aluminium is to be determined, should be dissolved in acid, preferably hydrochloric acid, care being taken not to add a large excess.

Now dilute about 200 c.c. and gradually add to this solution of KOH until the precipitated alumina redissolves.

The steam of carbon dioxide is now passed through the cold solution until aluminium is precipitated.

Remove and wash thoroughly the glass tube through which the carbon dioxide was lead into the solution.

Place the beaker with both solution and precipitate over a Bunsen burner and heat nearly to boiling, allow to settle, decant through a filter paper and wash once by decantation, using from 150 c.c. to 200 c.c. of boiling water, filter and wash the $\text{Al}(\text{OH})_3$ remaining on the filter several times with hot water:

Dry and ignite, in a weighted platinum crucible, at a white heat.

Allow to cool in a sulphuric acid desiccator and weigh as Al_2O_3 .

The following tables give a few results showing the degree of accuracy which can be obtained by this method.

The substance analyzed was Ammonium alum, (C p)

Number	Weight of Ammonium alum	Time of Precipitation	Weight of Al_2O_3	Aluminium in Ammonium Alum	Found
1	0.3068	30 min.	0.03392	5.978 %	5.860
2	0.5034	60 min.	0.05792	5.978 %	6.101
3	0.7622	45 min.	0.08742	5.978 %	6.082
4	1.9389	60 min.	0.21822	5.978 %	5.96.

A few other experiments were made in which I tried this method of precipitation from a nearly saturated solution of potassium sulphate and also from solution containing lithium salts.

In each case 200c.c. of solution was used. In which Number 6 and 7 $\text{Li}(\text{OH})_2$ was first dissolved in hydrochloric acid and then added to the solution.

Number	Weight of Ammonium alum	Weight of Foreign Salt added	Time of Precipitation.	Weight of Al_2O_3	Aluminium in Ammonium alum	Found.
5	.7245	16 gr. K_2SO_4	60 min.	0.0786	5.97%	5.75
6	.2593	0.4" $\text{Li}(\text{OH})_2$	1 1/4 hr.	0.03522	5.97%	7.16
7	.6384	0.6" $\text{Li}(\text{OH})_2$	1 1/4 "	0.08252	5.97%	6.84

The above results shows that it is possible to use this method in the presence of sulphates, while by the old method the results are always too high. It being necessary, in such cases, to dissolve the precipitated alumina in HCl and reprecipitate with NH_4OH .

We thought for a while that this method could be used in the presence of lithium salts as the carbonates, especially the acid carbonates# are somewhat soluble in cold water, but analysis 6 and 7 show that too high results are obtained although the precipitate was washed thoroughly with both hot and cold water.

In each of the above cases the filtrate was tested for aluminium with NH_4OH and $(\text{NH}_4)_2\text{S}$ but in no case was the slightest precipitate obtained.

One hundred parts of water dissolve 1.48 parts of Li_2CO_3 at 15 degrees.

100 parts of water dissolve 5.5 parts of LiHCO_3 at 13 degrees.