ductivity of the galvanometer may be neglected, and if R is changed to obtain a deflection more suitable for reading, the two readings may, without sensible error, be assumed proportional to the two values of R.

Changing R of course changes the sensitiveness of the whole arrangement and this may be done to as great an extent as the coils in R will allow. If it contains coils of one-tenth to twenty ohms the sensitiveness may be varied two hundredfold by a change in plugs, an operation requiring only a few seconds. In the work on heated silicates the resistance varied with the temperature from a comparatively small figure to practical infinity and the method made its determination quite simple, particularly as the same galvanometer was used for determining conductivity and for determining temperature by the thermoelectric method. Alternate readings of temperature and conductivity were taken at intervals of some seconds during the cooling of the materials from a high temperature by the use of a suitably disposed double switch.

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THE COMMERCIAL ANALYSIS OF BAUXITE.

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THE bauxite mined in Georgia and Alabama, constituting practically all of the domestic supply, is used for the manufacture of alum and aluminum, in the proportion of about three-fourths to one-fourth. The analytical methods hitherto employed have been based, to a considerable extent, upon the purposes to which the material was applied.

It is obvious that the easy solubility of the alumina in sulphuric acid is a great desideratum for the manufacturer of alum, and furthermore, that the acidulated mass should filter readily, and be capable of rapid washing.

But it is generally impracticable for the ordinary chemist to base his methods on factory tests, for the reason that these are, for the most part, unknown to him. All that can reasonably be required of him is that his methods should not yield results widely at variance with those obtained on a large scale in actual operations.

Were the question of bauxite analysis one solely of the total amount of alumina, almost any of the methods used for the estimation of this substance in the presence of silica, oxide of iron, and titanic acid could be employed. But the total amount of alumina is of secondary importance as compared with its ready solubility in sulphuric acid, in the manufacture of alum.

Whatever may be said as to the requirements of the manufacturers of aluminum, it is certainly necessary in the manufacture of alum that sulphuric acid should readily dissolve the alumina. One might go a step further and allow that the residue after treating with acid should be of such nature as to permit of rapid and thorough washing. This latter consideration, however, is not of such vital importance in the valuation of bauxite as that the material should dissolve readily in the acid, and that no substance deleterious in alum-making should at the same time go into solution. It seems to us that there are four main points to be considered in valuing bauxite by analysis for alum-making. Ranging them in the order of their relative importance they are as follows :

1. Easy solubility of the alumina in sulphuric acid.

2. Rapid filtration.

3. Rapid washing.

4. Freedom from substances that on going into solution would affect the quality of the alum, or other products.

There may be, of course, a difference of opinion as to the relative importance of the second, third, and fourth considerations but there can be no doubt of the rank of the first.

If the bauxite is ferruginous, the fourth point may come second, but at present and for some time to come the purer bauxite alone will come into the market. There is very little demand for second grade material, and while the percentage of ferric oxide is to be held in view in valuing even the pure bauxite it is not of much importance for the reason that it is generally very small.

The Georgia-Alabama bauxite consists of the trihydrate of alumina, $Al_2(OH)_6$, or $Al_2O_3.3H_2O$, mixed with clay, and what may prove to be a lower hydrate of alumina, possibly $Al_2O_3.2H_2O$.

There are three well recognized hydrates of alumina—the monohydrate (diaspore), $Al_2O_3.H_2O$ or $Al_2O_2(OH)_2$, containing

	Per cent.
Alumina	85.02
Water	14.98

the dihydrate, $Al_2O_3.2H_2O$ or $Al_2O(OH)_4$, with

	Per cent.
Alumina	73.94
Water	26.06

and the trihydrate (Hydrargillite, Gibbsite), with

	Per cent.
Alumina	65.41
Water	34.59

The formula for bauxite, $(AlFe)_2O(OH)_4$, given by Roscoe and Schorlemmer[1] does not seem to apply to the American material. Assuming for the present that the domestic bauxite is a mixture of alumina trihydrate, clay, and possibly a lower hydrate, the methods adopted for its analysis, so far as concerns the alum-maker, should be based upon the estimation of two different things : (1) the amount of alumina existing as trihydrate, and very readily soluble in sulphuric acid, and (2) that existing as some other compound, whether a lower hydrate, or clay, less soluble in the acid, but which in the process of manufacture can be utilized. It would appear that the more easily soluble alumina should have a higher value placed upon it than the other. It costs less to make alum of material easily soluble than of material difficultly soluble, and if there exists in bauxite two or more alumina compounds, differing markedly from each other in solubility, the consumer is entitled to know what are the proportions between them.

Heretofore the analytical methods adopted, outside of factories, for the valuation of bauxite, have resulted in giving practically all of the alumina, and no efforts have been made, so far as known to us, to discriminate between the alumina compounds present.

The two methods ordinarily used are the Pittsburg, worked out by Mr. Jas. O. Handy, and the Spence method. Both of these agree in evaporating the mixture of sulphuric acid and bauxite to fumes of the so-called sulphuric anhydride and continuing the heat for some minutes. Mr. Handy recommends a mixture of

1 Treatise on Chemistry, 2, [1], 444.

hydrochloric acid of 1.20 sp. gr., nitric acid of 1.42 sp. gr., and sulphuric acid of 1.20 sp. gr., in the respective ratio of 1 : 3 : 6. Mr. Spence uses a mixture of equal parts of strong sulphuric acid and water. In each case the ratio between acid mixture and bauxite is the same ; *viz.*, one gram bauxite and 5 cc. acid. In using either method, taking up the residue in water, boiling, filtering, and washing thoroughly, very little alumina will be found in the residue. From numerous analyses we have found that considerably less than one per cent. of alumina is left in the residue, so that it may be said that practically all of it is dissolved.

More or less objection has been urged by alum-makers, to these methods. They have claimed that for their purposes the yield of alumina is too high, that by carrying the analytical treatment to fumes, whether using the mixture of acids, or sulphuric acid alone, compounds of alumina, which are not suited for the manufacture of alum, are decomposed and dissolved, and consequently the percentage of alumina does not represent what may fairly be considered as soluble alumina.

Aside from manufacturing processes, upon the discussion of which we do not enter, the objections seemed reasonable, and we began a series of investigations on commercial bauxite, not so much with the purpose of studying the exact composition of this material as of ascertaining whether a practical method of discriminating between the several compounds of alumina present in bauxite could be worked out. The results reached are extremely interesting and important alike to the shippers and the consumers, for they seem to indicate that it is perfectly feasible to determine the alumina existing as trihydrate, and therefore readily soluble, and the alumina as clay, or as a lower hydrate, and of less solubility.

From a lot of about 300 pounds of bauxite taken from the loading shed of a company actively engaged in mining and shipping for alum works, five separate samples were taken.

A. A general average of the whole lot, lump and fine.

B. A white, friable material, with no iron stains.

C. A compact, cream-colored variety, with conchoidal fracture and pearly luster.

D. A variety full of nodules considerably stained with iron.

E. A clay, probably halloysite.

A separation of these varieties by elutriation was not possible, as they gave the following specific gravities:

Sp. gr.

B 1.77
C 1.74
D 1.74
E 1.76

Two grams of A, through a sixty-mesh sieve, were treated with ten cc. sulphuric acid of 50° B., in a steam-bath at 100° C., for the time given below, 100 cc. water added, and the contents of the flask heated in the bath for ten minutes. It was then filtered, and washed thoroughly with hot water.

Per cent.

Alumina extracted in two hours 53.37
      "   "   " one hour 53.18
      "   "   " one hour 53.21
      "   "   " one-half hour 51.27

The other samples were similarly treated for one hour. None of the solutions contained titanic acid, and only a small percentage of iron oxide was dissolved.

The insoluble residues were dried at 100° on tared filters, and weighed, then ignited and weighed again, the difference being taken as combined water. The amount of water combined with the alumina dissolved was ascertained in two ways:

1. By deducting the weight of the insoluble residue, dried at 100° from the total weight of substance taken, and, from this result, deducting the sum of the weights of alumina, ferric oxide, and moisture.

2. By deducting from the total loss on ignition the amount of combined water in the insoluble residue, and moisture.

The first method is probably more nearly correct.

The results of the analyses are as follows:

SOLUBLE PORTION.

	A.	B.	C.	D.	E.
Moisture	0.70	0.38	0.94	0.56	0.45
Ferric oxide	0.93	0.21	0.21	0.96	0.20
Alumina	53.21	58.03	58.94	48.69	3.11
Combined Water (1st method).........	28.28	30.78	31.00	25.77	1.87
" Water (2nd method)........	28.17	31.14	31.31	25.90	1.05
" Water (mean of 1st and 2nd).	28.23	30.96	31.15	25.83	1.46
" Water (calculated)	28.20	30.75	31.26	25.80	1.64

INSOLUBLE PORTION.

Combined Water	1.79	1.10	0.91	2.59	12.83
Alumina	4.15	2.69	2.39	7.48	37.70
Silica	7.28	3.06	2.40	8.85	42.88
Titanium oxide	3.63	3.70	3.08	4.82	1.10

These results point strongly to the formula $Al_2O_3.3H_2O$, or $Al_2(OH)_6$, for the substance dissolved. The iron is probably in the hydrated condition. If so, this would introduce a small correction, which however would be partially compensated by slight action on the clay residue, which will be mentioned later on. The figures for the soluble part have been verified in every case by duplicates, and in some cases by many analyses; as for instance in E, where it becomes very difficult to obtain accurately the per cent. of water, owing to the large amount of insoluble residue.

Little can be said as to the composition of the insoluble residue, but these results and many others which do not properly belong to the present discussion, seem to indicate that it consists chiefly of a halloysite or kaolinite clay ; and that the larger portion of the titanium exists as the hydrated oxide, either titanic or metatitanic acid; that it also contains variable amounts of quartz or silicious sand; and it is not improbable that corundum and rutile are present in minute amounts, though neither have been identified with certainty.

The valuable constituent beyond a doubt is aluminum trihydrate, and the most reasonable settlement of the commercial question, it seems, would be to make this the basis of sales in the future. It might be argued that the alumina yield would be larger in this case than the analysis would indicate, as ordinary treatment will remove some alumina from clay.

To arrive at a fair conclusion in regard to the matter, it would appear to be necessary to further limit and define the word " bauxite" as applied to the Georgia-Alabama mineral. If the results given in this paper prove anything, they certainly show that in the so-called bauxite there is a sharp line of division as regards chemical action under certain conditions.

In outlining this work originally, it was intended to treat samples at various degrees of temperature, with various strengths of acid, the samples also to vary in their state of subdivision.

Other work has however prevented this, but enough has been done to throw some light on the question here involved. Acid of 40° B. dissolves practically the same per cent. of alumina as acid of 50° B. The substance passed through a sixty-mesh sieve gives the same per cent. of soluble alumina, as when all is passed through a 100-mesh sieve.

Some results have already been given showing difference in time of treatment. All results obtained indicate that if any of these variables of time, temperature, strength of acid, or sub-division be taken in regularly increasing increments, the per cent. of alumina dissolved increases rapidly at first and soon becomes fixed, the ratio $Al_2O_3.3H_2O$ being unaffected, and afterwards the per cent. of alumina increases again, the ratio then approaching $Al_2O_3.H2_2O$.

Clearer proof could hardly be desired that bauxite, as we know it, is a mixture, and not a true chemical compound. The same result exactly would be obtained if workmen were directed to mix clay and the mineral, and the chemical methods now in use would not detect the change, at least only partially. They would show a lowering of the per cent. of alumina and increase of silica, but in nothing like the true amount of the addition, while a determination of $Al_2(OH)_6$ would detect it absolutely.

In order to establish the method on a scientific basis it is required to prove (1) that all alumina existing as $Al_2O_3.3H_2O$ is extracted and (2) that it is contaminated by alumina from no other source.

Samples A and E were used for this purpose, the alumina being first extracted in the usual way using two grams of substance and fifteen cc. of 50° B. sulphuric acid at 100° C. for one hour, the residues washed free of alumina and dried at 100°, retreated in the same way, etc.

	Percentage of soluble alumina.	
	A.	E.
First extraction	53.18	3.21
Second "	0.22	1.20
Third "	....	1.08

Certainly no considerable amount of $Al_2O_3.3H_2O$, could have remained or it would have appeared in the second extraction of A, but it seems that the reagent decomposes clay slowly as is shown

by E and it is probable that the additional alumina in A comes from the clay of the residue. It is intended at some time in the future to ascertain the minimum strength of acid which will extract at 100° C. in one hour all $Al_2O_3.3H_2O$, and it is possible that the action on clay may become very slight and a correction be determined and applied.

Results are quite close enough for commercial purposes, and, while it is possible that they may vary three- or four-tenths or even five-tenths of one per cent. from the true figure for alumina existing as $Al_2O_3.3H_2O$, the error is always in the same direction, and when the process is carried out in exactly the same way each time, results are remarkably concordant.

As illustrating this the following results are given ; they were made as checks on per cent. of soluble alumina.

	A.	B.	D.	E.	D.
1	53.21	58.03	58.94	48.69	3.11
2	53.18	58.00	59.05	48.80	3.12
3	53.14	58.10	59.00	....	3.08
4	53.26	....	....	....	....

It should be noticed that the error of the determination will depend upon the amount of the residue. A bauxite of average composition would give about twenty per cent. of insoluble residue, and the soluble alumina would probably be 0.25 per cent. too high, and the calculated $Al_2(OH)_6$ about 0.35 per cent. too high.

We beg, therefore, to recommend that, instead of carrying the analytical treatment to fumes of so-called sulphur trioxide, there be substituted the treatment with 50° B. sulphuric acid at 100° C. for one hour. We give at the conclusion of this paper our method of analysis. It may be of interest here to give some comparative results by the different methods.

A bauxite, containing by the Pittsburg method 59.20 per cent. of soluble alumina, was found by our method to contain 57.22 per cent. Another sample with 56.26 per cent. of soluble alumina by the Pittsburg method gave by our method 53.38 per cent.

A sample with sixty per cent. soluble alumina by the Pittsburg method gave us fifty-nine per cent., another with 54.87 per cent. gave us fifty-three per cent. Speaking generally we have found

that the difference between the Pittsburg method, or the Spence, and our method is less the purer the bauxite.   This result may be anticipated, for the purer the bauxite the more of the alumina does it contain as the trihydrate.

Under the proposed change in the method of valuing bauxite it would be necessary to fix upon some name for the alumina dissolved at 100° by sulphuric acid of 50° B., and for that dissolved at fumes.   We suggest the term " free alumina" for the alumina dissolved at 100° C. and " combined alumina" for the difference between this and the alumina dissolved at fumes, the sum of the two to be known as " available alumina."   For instance, if a bauxite contained fifty-four per cent. of alumina soluble in 50° B. acid in one hour at 100° C. it would contain fifty-four per cent. of free alumina.   If by the Pittsburg or the Spence method there was found fifty-eight per cent. " soluble alumina," we would now call this fifty-eight per cent. of " available alumina," and there would be four per cent. of " combined alumina."

There is an objection to this system of nomenclature in that the free alumina is really combined, just as much so as the additional alumina extracted by fuming acid.   It being combined with water in the form of the trihydrate, the exact meaning of the term should be that the free alumina is the alumina from the trihydrate, and easily soluble in sulphuric acid.   This much may be taken as proved.   We can not state, at present, in what form the alumina exists that we propose to call " combined alumina."   It may be as clay, as a lower hydrate, or as a form of Al_2O_3 itself, insoluble except in fuming acid.   It does not greatly matter in what form it exists, the chief thing to be considered being that it is not soluble in 50° B. sulphuric acid at 100° C., but is soluble in acid brought to fumes.

It is not in the province of this paper to assign exact commercial values to the free and the combined alumina, or to the free and the available alumina, as this should be left to the decision of the miners and the consumers.   In the fertilizer trade it has not been found difficult to agree upon the price of water-soluble phosphoric acid, and available phosphoric acid, this latter being the sum of the soluble and the reverted.   Acid phosphate

is now offered in bulk at so many cents per unit of available phosphoric acid, and the higher the percentage of the available acid the higher the price per unit.

We propose to introduce into the alum trade a system which has been used for many years in the fertilizer trade, and which has been found to be extremely useful. In bauxite the difference between the easily soluble trihydrate, and the difficultly soluble alumina in the residue, should be considered.

We are convinced that the changes proposed would be for the benefit of all concerned. Take for instance the case of a shipper who is sending out bauxite containing clay, such as E, and we beg to say again that E was taken from a lot of bauxite ready for shipment. If the prepared bauxite should contain an undue proportion of E, with only 3.11 per cent. of free (or easily soluble) alumina, it goes without saying that its value for alum-making would be seriously impaired. Comparing E with C (and both varieties came from the same bag) E has 3.11 per cent. of free alumina, and C has 58.94 per cent ; in the insoluble portion E had 37.70 per cent. of alumina, and C had 2.39 per cent. In other words the free alumina in E was 7.62 per cent. of the total alumina, and in C it was 96.10 per cent.

Take another instance. With the very best bauxite there occurs a white clay which, when the material is ready for shipment, can not be distinguished from the bauxite itself. It may be mixed with the bauxite in considerable proportions and yet fail of recognition, because its physical qualities so nearly approximate those of pure bauxite. In the pits the lines of separation between bauxite and clay are perceptible indeed to the trained eye, but it is practically impossible to prevent the miners from overrunning the line. This is both theoretically and practically true. The situation at the mines renders it theoretically impossible to keep the clay out of the bauxite, and samples of clay picked out of the bauxite already mined show that it does occur in it. In pure bauxite the proportion of clay is at the minimum when the mine is operated from the middle of a big pocket of bauxite, but as the mining nears the sides of the pocket and approaches a bed of clay, the danger of admixture of clay increases, and when the pocket is almost exhausted and the mining is carried on close to the clay, more or less of this sub-

stance is sure to get in.   The quality of the Georgia-Alabama bauxite is sufficiently high, as proved by the low silica and high free alumina, to preclude the possibility of there being much clay in it, but some clay is always present so far as our observation goes, covering several years.

We have ourselves obtained samples of these clays from the bauxite mines.   One of them came from immediately next to a pure bauxite.   It contained 41.80 per cent. of total alumina, of which 2.08 per cent. was free, 37.75 per cent. combined, and 1.97 per cent. insoluble.   Of the total alumina 4.97 per cent. was free and easily soluble, 90.31 per cent. was 'combined' and difficultly soluble, and 4.72 per cent. was insoluble in fuming acid.

Another sample gave 43.00 per cent. of total alumina, of which 3.00 per cent. was ' free,' 37.40 per cent. ' combined,' and 2.60 per cent. insoluble.   Of the total alumina 6.97 per cent. was 'free,' 86.98 per cent. was 'combined,' and 6.05 per cent. was insoluble.

Compare these results with those obtained from sample E, remembering that these two were clay taken from the mines, and E is clay taken from bauxite already mined.   For convenience of reference we will call the two clays F and G, and put the comparative results in a table.

TABLE I.—CLAYS.

Sample.	Free alumina.	Combined alumina.	Available alumina.	Insoluble alumina.	Total alumina.	Total alumina = 100.			
						Free.	Combined.	Available.	Insoluble.
E.	3.11	35.45	38.56	2.25	40.81	7.62	86.86	94.48	5.52
F.	2.08	37.75	39.83	1.97	41.80	4.97	90.31	95.28	4.72
G.	3.00	37.40	40.40	2.60	43.00	6.97	86.98	93.95	6.05

Now take three good bauxites :

TABLE II.—BAUXITES.

Sample.	Free alumina.	Combined alumina.	Available alumina.	Insoluble alumina.	Total alumina.	Free.	Combined.	Available.	Insoluble.
A	53.21	3.55	56.76	0.60	57.36	92.76	6.19	98.95	1.05
B.	58.03	2.29	60.32	0.40	60.72	95.57	3.77	99.34	0.66
C.	58.94	2.04	60.98	0.35	61.33	96.10	3.32	99.42	0.58

The analyses show very clearly that treatment with sulphuric acid to fumes dissolves alumina from such clays as occur with

and in bauxite, and that treatment with acid at 100° C. does not dissolve this alumina. As regards bauxite itself the treatment at 100° C. serves to discriminate between the alumina of the tri-hydrate and the alumina of clay, or of a lower hydration.

As to calcining the bauxite before shipment in order to remove the water of hydration, we do not think it advisable. In well arranged bauxite plants the material is now heated in revolving cylinders to remove hygroscopic water, but the temperature should not be great enough to cause loss of combined water. In order to test the effect of loss of combined water on the solubility of the alumina at 100° C. we selected a very pure variety of bauxite, and deprived it, by careful heating, of various percent-ages of its combined water, and then extracted the alumina with 50° B. sulphuric acid at 100°.

The results are in Table III.

The sample contained 60 per cent. of alumina.

EFFECT OF CALCINING ON SOLUBILITY.

TABLE III.

	Soluble alumina. Per cent.
Dried at 100° C. not calcined	59.00
Loss on calcining, 12.55 per cent	57.60
" " 18.55 " "	57.10
" " 26.60 " "	53.10
" " 32.15 " "	20.40

Calcination certainly tends to decrease the solubility of the alumina, but does not constitute a serious menace until about 80 per cent. of the total combined water is removed. With a loss of about 38 per cent. of the water there is a loss of 1.40 per cent. soluble alumina; with a loss of about 58 per cent. of the com-bined water the loss of soluble alumina is 1.9 per cent. ; with a loss of about 82 per cent. of the combined water there is a much greater loss of soluble alumina; *viz.*, 5.9 per cent. while the loss of soluble alumina rises to 38.60 per cent., when the material is thoroughly calcined. These results would seem to indicate that the material could be calcined until something more than half of its combined water was removed, without seriously affecting the solubility of the alumina, but the practical difficulties in the way of maintaining a uniform calcination at this point would cer-tainly have to be considered. Unless the saving in freight would

more than counterbalance the loss in soluble alumina, there would appear to be no good reason for calcining. The percentage of available alumina (*i. e.*, the alumina dissolved by carrying the treatment with acid to fumes of so-called sulphur trioxide) is decreased by thoroughly calcining the bauxite, but the loss is not serious. In one experiment the 'available' alumina in the sample, dried at 100° C., was 57.20 per cent. and in the thoroughly calcined material 56.40 per cent.; in another sample 55.30 per cent. and 54.54 per cent. In one sample the loss was more considerable, the percentages being 54.87 per cent. and 49.50 per cent.

On the whole we can not recommend that the analytical sample be calcined previous to treatment with acid, whether by the old or the proposed new method, as a serious loss of dissolved alumina *may* be the result.

ANALYTICAL METHOD RECOMMENDED.

The analytical sample is to be passed through a sieve of 100 meshes per linear inch.

Moisture.—Two grams to constant weight at 100° C.

Available Alumina.—Two grams bauxite, ten cc. cold sulphuric acid of 50° B.

Heat gradually in a casserole until fumes of the so-called sulphuric anhydride appear, stirring the while to break up any small pieces ; cover with a watch-glass and heat for ten minutes. Cool, add 100 cc. hot water, and boil for five minutes. Filter, and wash free of acid and alum with hot water. Cool filtrate, make up to 200 cc., and take out fifty cc. (equal to five-tenths gram) for alumina, ferric oxide, and titanium dioxide, and fifty cc. for titanium dioxide and ferric oxide, TiO_2 and Fe_2O_3.

Estimation of Available Alumina.—The fifty cc. (equal to five-tenths gram) is diluted to 300 cc., two cc. hydrochloric acid added, heated to boiling, and ammonia added slowly to slight excess. The contents of the beaker are kept boiling for five minutes, filtered hot, and thoroughly washed with hot water. The precipitate is dried, ignited, and weighed as Al_2O_3, Fe_2O_3, TiO_2. The Al_2O_3 is given by subtracting the Fe_2O_3 and TiO_2, obtained in other operations.

Estimation of Titanium Dioxide.—Fifty cc. (equal to five-tenths gram) of the main solution are carefully neutralized with ammonia, the ammonia being added until there is a slight permanent precipitate. This precipitate is dissolved in sulphuric acid, added carefully so that there shall be but a slight excess ; the volume is then made up to 350 to 400 cc. and boiled for one hour. If much iron is present, shown by the color of the main solution, it is best to deoxidize with sulphur dioxide, led into the boiling solution in which the titanium dioxide is being precipitated, but if there is only a small amount of iron present sulphurous acid may be used. In either case, however, it is well to maintain the volume of the boiling solution at about the same point, by addition of fresh portions of water, and to be sure that it smells of sulphur dioxide during the boiling. By observing these precautions the titanium dioxide is completely precipitated practically free of iron. Filter hot, through double filters, and wash thoroughly with hot water, dry, ignite, and weigh as titanium dioxide.

Estimation of Ferric Oxide.—This is best determined in the filtrate from titanium dioxide, by reduction with zinc and titration with permanganate.

The weight of $TiO_2 + Fe_2O_3$ subtracted from the weight of $Fe_2O_3 + Al_2O_3 + TiO_2$ gives the Al_2O_3, and this is the " available alumina."

Estimation of "Free Alumina."—Two grams bauxite, ten cc. 50° B. sulphuric acid, in a four-ounce Erlenmeyer flask, provided with a perforated stopper. Heat for one hour in a water-bath at a temperature of 95° to 100° C. with frequent shaking. Add 100 cc. hot water and keep in bath for ten minutes. Filter, wash thoroughly with hot water, and for the estimation of alumina proceed as before, with this difference, however, that the titanium dioxide does not have to be determined, since none of it goes into solution. In the solution we have merely the free alumina, and a small amount of ferric oxide, which can be estimated in the usual manner and its weight subtracted from the weight of the $Al_2O_3 + Fe_2O_3$.

Combined Alumina.—The difference between the available alumina and the free alumina is the combined alumina.

We do not at this time wish to give an opinion as to the form in which this alumina exists. It may be as clay, as a lower hydrate, or a mixture of these and other alumina compounds. We have thus far disregarded the insoluble residue, whether from the acid carried to fumes, or from the treatment at 100° C.

In case it is desired to determine the total alumina, the total titanic acid, the total ferric oxide, and the silica, the insoluble residue from the treatment to fumes may be folded up in the paper, and ignited.   When the paper is consumed, fuse the residue with potassium bisulphate, and allow to stand in cold water containing at least five per cent. of strong sulphuric acid several hours, or until completely decomposed.   Filter off the silica, which should be perfectly white, wash thoroughly with cold water, and ignite the silica.   In the filtrate the alumina, titanium dioxide and ferric oxide are determined as in the filtrate containing the available alumina.   Adding these several amounts to those found in the estimation of the available alumina gives, of course, the totals.

We can not advise the determination of silica in the insoluble residue by treatment with hydrofluoric acid and sulphuric acid, as we have found that some of the titanium dioxide is also volatilized, and the loss is $SiO_2 + TiO_2$.

So far as we are aware Riley was the first to point out the volatilization of titanium dioxide as fluoride.   It may be that some if not all of what is volatilized goes off as hydrogen titanofluoride, as Roscoe and Schorlemmer[1] state, that when titanium dioxide is dissolved in hydrofluoric acid, a sirupy liquid is obtained which is probably hydrogen titanofluoride, H_2TiF_6.   Crookes,[2] in speaking of the estimation of titanium dioxide in silicious residues, says that on treating them with hydrofluoric acid "a titanium fluoride is formed at the same time, which can not be heated without the larger portion going off."   He quotes an experiment of Riley's in which 2.235 grams of titanium dioxide were dissolved in hydrofluoric acid, evaporated and ignited, and the residue weighed only 0.99 gram, a loss of 1.245 grams or 55.70 per cent. of the original weight.

By seven successive treatments of titanium dioxide with

[1] Treatise on Chemistry, 2, [II], 262.
[2] Select Methods in Chemical Analysis, Second Edition, p. 193.

hydrofluoric acid we found the following losses on 0.0700 gram ;
viz.:

	Per cent.
0.0025	3.57
0.0240	34.28
0.0135	19.29
0.0058	8.29
0.0032	4.57
0.0015	2.14
0.0001	0.14
0.0506	72.28

While there is a gain in time by treating the insoluble residue
with hydrofluoric acid and sulphuric acid and taking the loss as
silica, and while the error introduced is, perhaps, of no conse-
quence commercially, yet the fusion with potassium bisulphate is
to be preferred.   But unless the silica, and the total alumina,
titanium dioxide and iron are required, it is not necessary to
make a fusion, the data obtained by the two separate treatments
with acid being, in most cases, entirely sufficient for the valua-
tion of bauxite.

So far as our observation goes, and we analyzed many different
kinds of bauxite, titanium dioxide is always present, and in
some bauxites may rise to four per cent.   The clay immediately
next to the bauxite may contain one per cent. of titanium dioxide,
as we have found eight-tenths per cent.   In other clays associ-
ated with bauxite we have found mere traces, and in the near-
by soils it rarely exceeds five-tenths per cent.   The concentra-
tion of the titanium dioxide in the bauxite is a very interesting
phenomenon, and worthy of more extended investigation.

The titanium dioxide in bauxite is partly soluble in sulphuric
acid brought to fumes.   By using the Pittsburg method in bauxite
acid analysis, or sulphuric acid alone to fumes, varying amounts
of titanium dioxide are dissolved, as the following results show :

Total titanium dioxide.	Soluble titanium dioxide.	Per cent. soluble.
4.00	3.30	82.50
3.00	2.60	93.33
4.00	2.50	62.50

The percentage of soluble titanium dioxide, calculated on the
total amount present, may fall as low as fifty per cent., but for the

most part appears to be about seventy-five per cent. No titanium dioxide seems to be dissolved by the acid at 100° C. during one hour, but as the temperature rises the solubility increases, and when brought to fumes considerably more than half is dissolved. The variations in the amount dissolved may be due to variations of the form in which the titanium dioxide is present, but on this point we have no definite information. In summing up the chief points in this paper, we desire to call attention to the following :

    1. The importance of discriminating in the analysis of bauxite between the trihydrate of alumina, easily soluble in sulphuric acid, and the other compounds of alumina, difficultly soluble.

    2. A change in the basis of valuation, by which the trihydrate of alumina is to be given a higher value than the alumina present in some other form.

    3. The adoption of a new nomenclature, calling the alumina soluble in 50° B. sulphuric acid at 100° C. during one hour " free alumina," and that soluble in sulphuric acid to fumes "available alumina," the difference between them to be known as " combined alumina."

    4. The adoption of a standard method of analysis binding alike on the producer, the broker, and the consumer of bauxite for alum-making.

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UPON THE SALTS OF HYDRONITRIC ACID.

By L. M. DENNIS AND C. H. BENEDICT, with Crystallographic Notes by A. C. GILL.

IN the year 1890 Th. Curtius announced[1] his successful preparation of hydronitric acid (HN_3), and briefly described the trinitrides of barium (BaN_6), silver (AgN_3), and mercury (Hg_2N_6). He mentioned also the existence of trinitrides of copper, iron, sodium, and ammonium. Since that time no further work upon the inorganic compounds of this most interesting acid was published until last year when thallous trinitride (TlN_3) and thallous thallic trinitride ($TlN_3.TlN_9$) were added to the list.[2] Having a large amount of the acid on hand, we have entered upon the systematic study of the compounds of hydroni-

1 *Ber. d. chem. Ges.*, 23, 3023.
2 Dennis and Doan : this Journal, 18, 970.