LXII.—*On Glucinum.*

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PART I.—*On the Preparation of Glucina from Beryl.*

VAUQUELIN, who first discovered the presence of a peculiar earth in beryl, pointed out that, unlike alumina, glucina does not form an alum, and took advantage of this fact to effect a preliminary partial separation of the two earths (*Annales de Chemie*, 1798, **26**, 170).

The advantage of effecting this preliminary separation appears to have been subsequently overlooked for a considerable period, as no mention is made of it until Scheffer, in a paper published in 1859 (*Annalen*, **109**, 144), lays stress on its value as a first step in the preparation of pure glucina. Although Scheffer himself does not speak of the method as a novel one, the credit of first suggesting it has been erroneously attributed to him (*Graham-Otto's Lehrbuch der Chemie*, 5te Aufl., 2ter Band III, 697). Since the publication of Scheffer's paper, and of Joy's elaborate review (*Amer. J. Sci.* [2], **36**, 83) of the various methods for effecting the decomposition of beryl, preference has very generally been given to those methods in which the bulk of the aluminium is separated as potassium or ammonium alum as a preliminary step.

During the progress of this investigation all the more important methods hitherto suggested for the decomposition of beryl, and the preparation from it of pure glucina, have been tested; but as almost all of them have been reviewed by Joy, I shall merely state that my experience coincides very closely with his, and that the two methods which he selects as the most satisfactory, namely, fusion with potassium carbonate and fusion with potassium hydrogen fluoride, followed in each case by treatment with strong sulphuric acid and the separation of the bulk of the aluminium as alum, gave in my hands also better results than any of the other methods hitherto described.

In 1864, Wolcott Gibbs, in a paper on the use of potassium hydrogen fluoride in analysis, makes the following statement:—"Glucina may be obtained directly from beryl (as Mr. Newberry has found) by fusing the pulverised mineral with hydrofluoride of potassium, dissolving out the soluble double fluoride of glucinum and potassium, and purifying by crystallisation. As, however, beryl contains only 13 or 14 per cent. of glucinum, this process is not economical" (*Amer. J. Sci.* [2], **37**, 356).

A more important objection to this method lies in the fact that the fused mass is extremely hard, and must be finely ground prior to extraction with water. The labour and loss of time involved in first powdering the beryl itself finely, and then repeating the operation on the fused mass is very considerable, especially in working with large quantities. Having found the use of potassium hydrogen fluoride unsatisfactory, I was led to try the effect of substituting the ammonium for the potassium salt, and some preliminary experiments showed that ammonium hydrogen fluoride effects the complete decomposition of beryl at a relatively low temperature, even when the mineral is only coarsely powdered. The saving of time and labour which this involves will be readily understood, as beryl is an exceedingly hard mineral.

The crude ammonium hydrogen fluoride employed was prepared by neutralising commercial hydrofluoric acid in a leaden dish with solid ammonium carbonate, adding a second quantity of hydrofluoric acid equal to that taken at first, and then concentrating the solution at a gentle heat on a sand-bath. On cooling, the solution set to a mass of crystals of the double fluoride, which, after being drained from the small quantity of mother liquor, was preserved in earthenware jars coated internally with paraffin.

A small portion of coarsely powdered beryl was heated with about 6 parts of ammonium hydrogen fluoride in a platinum basin, at first over a Bunsen burner, and then over the blowpipe. On extracting with water and filtering, a solution was obtained which gave, with ammonia, a white precipitate, and when poured into excess of a strong solution of ordinary ammonium carbonate, a clear solution. No darkening took place on adding ammonium sulphide, either to the white precipitate formed on adding ammonia, or to the solution in ammonium carbonate. The glucinum contained in the aqueous extract was, therefore, apparently free from iron, and if not perfectly free from aluminium, at least, so far free as to give clear solutions in presence of excess of ammonium carbonate. The yield, however, was unsatisfactory.

Further experiments showed it to be advantageous to use a larger proportion of hydrogen ammonium fluoride: and it was also found to be necessary to avoid heating too strongly, as this leads not merely to the formation of insoluble fluosilicate, and ultimately of fluoride of aluminium, but also gives rise to insoluble compounds of glucinum. Fluoride and fluosilicate of glucinum, when strongly heated, leave residues entirely, or almost entirely, soluble in water; but in presence of the corresponding compounds of aluminium, it is not always easy to prevent the formation of a large proportion of insoluble compounds of glucinum. Judging from further experiments, it seemed probable that, by a careful regulation of the temperature, it might be possible to effect a satisfactory separation of aluminium and iron from glucinum by means of ammonium hydrogen fluoride alone. The immediate object, however, was to obtain, as rapidly as possible, the glucina from a large stock of beryl, and, accordingly, experiments were made in order to ascertain, in the first instance, the conditions under which coarsely powdered beryl leaves a residue from which the whole of the glucinum may be obtained in solution by simply boiling with water, even though the glucinum be accompanied by some aluminium.

It was always found to be an easy matter to render the greater part of the aluminium fluoride insoluble in water, and thus to effect a preliminary partial separation of the two earths. Satisfactory results

having been obtained, after a series of trials on a small scale, 5 kilos. of coarsely ground beryl were treated, 1 kilo. at a time, with about 6 parts of ammonium hydrogen fluoride.

As the mode of operation was altered in each case, it may be of interest to give a short account of the manner in which each kilo. was worked up.

Working up of the 1st kilo.

The coarsely ground mineral and the ammonium hydrogen fluoride were thoroughly mixed together in a large iron pot, such as is commonly used in cooking, and the whole heated over a coal fire. The mass soon liquefied, and then boiled up, but after some time became thick, and at this stage was well stirred with a wooden stirrer.* After some time, the mass became solid, dense white fumes were given off, and a white sublimate, which proved to be ammonium fluosilicate, formed on the lid of the pot. At this stage, having been allowed to cool, the mass was roughly powdered in a porcelain mortar, after which it was again heated in the iron pot until the evolution of white fumes became very slow. The residue was then boiled in the iron pot with water for several hours, the solution allowed to settle, and the clear liquor poured off. The residue was boiled with a fresh quantity of water, and the extraction repeated until the water in which the residue had been boiled gave no precipitate with ammonia. The whole was then filtered, the filtration being fairly rapid. A current of hydrogen sulphide was passed through the filtrate, contained in glass jars coated internally with paraffin, and ammonia solution was added from time to time, in small portions, without interrupting the current of hydrogen sulphide, until a test portion of the liquid filtered from the black precipitate of ferrous sulphide gave a white precipitate with ammonium sulphide, showing that the iron had been removed from solution. The ferrous sulphide, which contained a little glucinum hydrate, was then filtered off, and the filtrate precipitated by sulphide of ammonium. In order to effect what appeared to be a complete precipitation, it was found necessary not merely to add an enormous excess of ammonium sulphide, but also to dilute very largely with water. The precipitate was washed with hot water, dried, and ignited in a platinum basin.

The glucina thus prepared, when dissolved in sulphuric acid and poured into a solution of pure ammonium sesquicarbonate, gave a clear solution which did not blacken with ammonium sulphide, but was by no means pure. The yield of crude glucina was 100.5 grams.

* An iron pot was used, because in working with such large quantities a very large vessel is necessary, especially as great frothing takes place.

Working up of the 2nd kilo.

The mineral was heated with 6 parts of ammonium hydrogen fluoride until the sublimation of the ammonium fluosilicate became very slow. After about five hours' heating, the residue was extracted with water and filtered, and the filtrate treated as before with hydrogen sulphide and ammonia.

After filtering from the precipitated ferrous sulphide, excess of ammonia was added to the filtrate, and the precipitated hydrate of glucinum filtered off; the filtrate from this was evaporated to dryness, ignited in a platinum basin until the ammonium salts were all driven off, and the residue boiled with water, in which it dissolved almost entirely. The filtered solution was poured into a solution of ammonium sesquicarbonate, to which ammonium sulphide had been added. After filtering from the small, black precipitate produced, the solution was boiled, but no precipitate was produced. On adding a considerable excess of ammonia, a portion of the glucina was precipitated; but the filtrate from this second precipitate of glucinum hydrate, when evaporated to dryness in a platinum basin, still left a residue of fluoride of glucinum weighing about 200 grams. Accordingly the fluoride was heated with excess of strong sulphuric acid, in order to convert the glucinum fluoride into sulphate.

After driving off the excess of sulphuric acid, the glucinum sulphate was dissolved in water. From the solution thus obtained, the glucina was readily precipitated as hydrate by means of ammonia.

Working up of the 3rd kilo.

The heating with ammonium hydrogen fluoride was carried out as with the 2nd kilo., and the residue extracted with water and filtered, the volumes of the united filtrates being about 5 litres. As the previous trials had proved that it was not possible to effect the complete precipitation of glucina by ammonia, or sulphide of ammonium, from the fluoride solution, the aqueous extract was evaporated down to dryness in the iron pot. The residue, consisting chiefly of fluorides and fluosilicates of glucinum and iron, was heated in a platinum basin with excess of strong sulphuric acid. The mixed sulphates were dissolved in water, and the solution treated as before with hydrogen sulphide and ammonia until the iron was completely precipitated. After filtering from the ferrous sulphide, the glucina was precipitated from the filtrate by ammonia. It was then collected on filters, well washed, dried, and ignited. This glucina weighed 108 grams, and was much purer than that obtained from the 1st kilo., the greater yield being accounted for by the more complete precipitation of the glucina from the sulphate solution.

Working up of the 4th kilo.

The coarsely ground mineral was heated with 6 parts of ammonium hydrogen fluoride for seven hours, the residue being then taken out, powdered, and returned to the iron pot, after which the heating was continued for five hours longer. The residue, which was of a rust-red colour and weighed 765 grams, was then extracted with water, and the solution filtered. The insoluble residue, after being washed with water, dried, and ignited, weighed 472 grams. The filtration was very easy and rapid. The filtrate containing the whole of the glucinum was evaporated to dryness and treated, in a large platinum basin, with strong sulphuric acid. After driving off the excess of sulphuric acid, the residual sulphates weighed 640 grams. The sulphates were dissolved in 2.5 litres of water, and the solution divided into two equal portions. The first of these was rapidly poured into 5 litres of a saturated solution of ammonium sesquicarbonate, and as a considerable precipitate remained undissolved, another litre of the ammonium carbonate solution was added, without, however, effecting complete solution. On passing carbonic acid through the mixture, the precipitate seemed to increase. Finally, about 900 c.c. of a strong solution of ammonium sulphide was added, and the solution filtered. The filtrate, which was perfectly clear, and of a fine yellow colour, was boiled in order to decompose the ammonium carbonate, and the precipitated basic carbonate of glucinum was washed, dried, and ignited.

The iron in the second portion of the sulphate solution was peroxidised with nitric acid, and the solution then added gradually, with frequent agitation, to 4.5 litres of a saturated solution of ammonium sesquicarbonate, whereby complete solution of the ferric hydrate as well as of the glucina was effected. To the deep red solution, 900 c.c. of ammonium sulphide was added in portions of about 100 c.c. at a time, and the solution filtered. The filtrate was boiled in order to decompose the ammonium carbonate, and the precipitated basic carbonate of glucinum collected on a filter, washed, dried, and ignited.

In working up both these portions, the bulky precipitates of ferrous sulphide were washed with well boiled water containing a little ammonium sulphide, but the wash waters were not allowed to mix with the main ammonium carbonate solutions, as it was found that they always contained not inconsiderable traces of iron.

The addition of so large an excess of ammonium sulphide was a mistake, as it caused the precipitation of much glucina from the ammonium carbonate solution, so that it was necessary to work up the ferrous sulphide precipitates over again. In order to separate

the glucina contained in these precipitates, they were dissolved in sulphuric acid, and after peroxidation of the iron with nitric acid the solution was poured into a saturated solution of ammonium sesquicarbonate. From the resulting blood-red solution, the bulk of the iron was precipitated by adding an equal volume of boiling water. After filtering from the precipitated ferric hydrate, a small quantity of ammonium sulphide was added to the solution, which was then filtered from the small precipitate of ferrous sulphide. On boiling the solution, now nearly free from iron, a precipitate of basic carbonate of glucinum was obtained which, on ignition, gave a quantity of almost perfectly white glucina. Unfortunately a considerable proportion of the glucina from this kilo. was lost accidentally. This glucina was, however, purer than any obtained previously, and on subsequent examination was found to contain less than 1 per cent. of alumina.

Working up of the 5th kilo.

The coarsely-powdered mineral was heated as before with 6 parts of ammonium hydrogen fluoride for about seven hours, powdered, and again heated gently in the iron pot for about four hours until the residue was of a straw-yellow colour not so dark as the residue from the 4th kilo. It was then thoroughly extracted with water, the solution filtered, and the insoluble residue well washed and dried.

It weighed 450 grams, and, as in the case of the 4th kilo., the filtration was very easy and rapid. The filtrate was evaporated down to dryness, and the fluorides converted into sulphates by treatment in platinum basins with 1035 grams of strong sulphuric acid. The resulting sulphates, after driving off the excess of sulphuric acid, weighed 1093 grams. The heating was continued so as to produce slight partial decomposition of the ferric sulphate. The mass was then digested for several hours with water, and the solution filtered from the small, dark iron-red residue. The volume of the solution with the wash waters was 2.8 litres. The iron was peroxidised with nitric acid, and the solution then poured into 11 litres of a saturated solution of ammonium sesquicarbonate in small portions at a time, with frequent agitation, whereby a deep blood-red but clear solution was obtained. The bulk of the iron was precipitated from this solution as hydrated sesquioxide by the addition of an equal volume of hot water. The solution was filtered while still warm, the filtration being easy and rapid. To remove the small quantity of iron still in solution, ammonium sulphide was added, and the solution rapidly filtered from the precipitated ferrous sulphide, which was washed with well-boiled water containing a little sulphide

of ammonium. After this treatment, a trace of iron still remained in the filtrate. Lead acetate was therefore added, until the solution contained lead, and then ammonium sulphide in excess, after which the solution was rapidly filtered. The precipitated lead sulphide, on subsequent examination, was found to have carried down with it all but a very minute trace of the iron.

The filtrate from the lead sulphide was boiled so as to decompose the ammonium carbonate, and the precipitated basic carbonate of glucinum collected, washed with hot water, dried, and ignited in a platinum basin.* From the latter filtrate, about 15 grams of oxide of glucinum was obtained by adding to it a large excess of ammonium sulphide, collecting, and igniting the well-washed precipitate. On evaporating this last filtrate down to dryness, and igniting to drive off the ammoniacal salts, a residue was left from which about 4 grams of glucina was obtained. It must always be borne in mind that glucinum hydrate is somewhat soluble in solutions of ammoniacal salts. The bulk of such dissolved glucina may be recovered by the addition of much ammonium sulphide, but in order to obtain the whole it is necessary to evaporate down to dryness and ignite. The total weight of the glucina from this kilo. was 109 grams.

Summary.

The results arrived at may be summarised as follows:—When coarsely-ground beryl is heated in an iron vessel with 6 parts of ammonium hydrogen fluoride to a temperature which should never exceed a dull red, it is not merely completely decomposed, but after 10 or 12 hours' heating, when large quantities are operated upon, a residue is left from which the whole of the glucinum can be extracted as fluoride by simply boiling with water; while, on the other hand, the portion of the residue insoluble in water contains, in the form of insoluble aluminium fluoride, almost all of the aluminium originally present in the beryl, along with much of the iron (as ferric oxide) derived from the action of ammonium hydrogen fluoride on the iron vessel.

In order to separate the aluminium, the heating should be continued (as in the working up of the 4th kilo.) until the residue assumes a rust-red colour and weighs about three-fourths of the weight of the beryl originally taken. From this residue, the whole of the glucinum may then be obtained in solution by simply boiling it with water; a considerable quantity of iron, however, also goes into solution. If the operation has been conducted properly, the

* This glucina was subsequently found to contain a trace of lead.

residue insoluble in water should have about half the weight of the beryl originally taken, when it will contain all but a small trace of the aluminium originally present in the beryl in the form of insoluble aluminium fluoride, but practically no glucinum.

If, as was the case in working up the 5th kilo., the heating is not pushed so far, so that the residue has only a straw-yellow colour, not rust-red, then the whole of the glucinum may be obtained in solution by boiling with water, but it will be accompanied by a larger proportion of iron, and, what is more objectionable, by a not inconsiderable quantity of aluminium.

In working up the 1st kilo., the heating was not continued nearly long enough, and accordingly the glucina precipitated from the aqueous solution was mixed with much alumina, oxide of iron, and silica.

Almost the whole of the iron may be removed by saturating the aqueous fluoride solution with hydrogen sulphide, and then adding ammonia, in small portions at a time, until the filtrate from a small test portion no longer gives a black or greenish precipitate on adding ammonium sulphide. But, as the working up of the 1st and 2nd kilos. showed, it is very difficult to obtain anything like a complete precipitation of the glucina directly from the filtrate.

A large proportion of the glucina may indeed be precipitated by adding a large excess of ammonium sulphide, after the removal of the iron, but it is necessary to add an enormous excess of this reagent in order to produce an approximately complete precipitation; and, for this reason, it is far better, before separating the iron, to evaporate the filtrate to dryness in the iron pot, and then treat the residue in a platinum basin with an excess of strong sulphuric acid.

In order to completely remove the fluorine and silicon, the heating should be continued until the ferric sulphate has begun to decompose. In order to effect the separation of the glucinum from the bulk of the iron, the mixed sulphates should be dissolved in water, the iron peroxidised with nitric acid, and the filtered solution poured gradually, with constant agitation, into a large excess of a concentrated solution of ammonium sesquicarbonate. It is advisable, in order to effect a rapid and complete separation, to take care that the locally-formed precipitate redissolves completely after each addition of the sulphate solution before adding a fresh portion. With a little care, it is easy to obtain a clear solution, which, however, becomes turbid on standing.

The bulk of the iron is precipitated on adding an equal volume of hot water to the ammonium carbonate solution, and the precipitate can be rapidly filtered and washed, its behaviour in this respect being very different from that of ferric hydrate precipitated by am-

monia from acid solutions. After removing the ferric hydrate by filtration, very nearly the whole of the small quantity of iron which still remains in solution may be precipitated by ammonium sulphide, but it is not possible to remove every trace of iron from the solution, even by repeated treatments with this reagent. In presence, however, of a large excess of a soluble salt of lead, the precipitation of the lead as sulphide by ammonium sulphide effects, by mass action, the complete precipitation of the iron from the solution. After the iron has thus been removed, the solution contains traces of lead, and these are, in part, precipitated, along with the basic carbonate of glucinum, when the solution is boiled. On dissolving the basic carbonate of glucinum in sulphuric or hydrochloric acid, the bulk of this lead remains undissolved as sulphide, and the traces which pass into solution may be easily removed by treatment with hydrogen sulphide. Subsequent experiments have shown that mercuric chloride may, with advantage, be substituted for lead acetate in this separation, as the traces of mercury which escape precipitation by ammonium sulphide are still more easily got rid of by simply igniting the basic carbonate of glucinum strongly—an operation which is necessary in any case, as the precipitated basic carbonate of glucinum invariably contains ammonium, not removable by washing with water, and is, moreover, of variable composition.

In this manner I prepared, several years ago, a large quantity of glucina, which was pure white, and gave a colourless solution when dissolved in strong hydrochloric acid.

The chief advantages of this method are: that it is easily worked on a large scale; that it is not necessary to grind the beryl to a fine powder; that the whole of the glucinum is obtained in solution nearly free from aluminium after one easy filtration; that the tedious filtrations from large quantities of silicic acid and of aluminium hydrate are avoided; and that the complete decomposition of the beryl is effected at a relatively low temperature.

As stated already, the glucina prepared by this method always contains a little alumina. It was only after a series of prolonged and tedious investigations that a method for the removal of the last traces of this impurity was arrived at. By none of the older methods can large quantities of equally pure glucina be obtained so easily, or in so short a time.

Supplementary Critical Investigation.

The following analyses were carried out long after the work described in this paper, but they are inserted here, as they afford definite proof of the complete extraction of the glucina from the beryl.

The analysis of a sample of the beryl from Limoges, used in this investigation, was made for me by Mr. W. W. Taylor. The analysis of the residue insoluble in water obtained from the 4th kilo. was made by Mr. Theodore Rettie, B.Sc. I have much pleasure in thanking these gentlemen for the careful manner in which they carried out these very troublesome analyses. The method used in estimating accurately the quantity of glucinum contained in such substances will be described in a subsequent communication.

Analysis of Beryl from Limoges.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	GlO.	CaO.	MgO.	H ₂ O.*	Total.
66.60	21.13	0.19	0.51	10.54	trace	0.09	1.36	99.88

Analysis of Residue from 4th kilo.

GlO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	PbO.	SnO ₂ .	CaO.	F ₂ -O.	SiO ₂ .
0.22†	29.02	44.54	2.38	0.23	0.42	17.49‡	2.35
		P ₂ O ₅ .	SO ₃ .	H ₂ O.	Total.		
		2.01	0.43	0.74	99.83.§		

The residue from the 5th kilo. was also examined, and found to contain only 0.10 per cent of glucina.

In order to throw further light on the course of the reaction between beryl and ammonium hydrogen fluoride, the following trial on a small scale was made:—4.91 grams of beryl was heated in a platinum basin for two hours over a steam-bath with 30 grams of ammonium hydrogen fluoride, the mass being occasionally moistened with water. After this, it was boiled with water, and the insoluble residue allowed to settle. A small test portion of the clear, supernatant liquid, when evaporated to dryness, left practically no residue, showing that, at the temperature of the steam-bath, beryl is not decomposed by ammonium hydrogen fluoride. The whole was, therefore, evaporated to dryness with constant stirring, and, when solid, removed from the steam-bath and heated very cautiously over the naked flame, when it rapidly became liquid and appeared to boil

* Loss on ignition.

† Corresponding to 0.10 per cent. of the beryl originally taken.

‡ Corresponding to 26.12 per cent. Al₂O₃.

A dualistic statement of analytical results has in many cases great advantages, but can only be consistently carried out by the aid of some such device as that adopted in the text where the percentage of halogen, in this case fluorine, is not given directly, but after deduction of the equivalent quantity of oxygen, so that CaF₂ is represented as CaO, F₂ - O and 2AlF₃ as Al₂O₃, 3(F₂ - O). The author believes that this method of stating analytical results was first adopted by the late Professor Dittmar.

up, dense white fumes being given off. In a few minutes the mass again became solid, and the heating was then stopped before the temperature of the residue had risen even locally to redness. The residue was boiled with water, the aqueous solution evaporated to dryness, the ammoniacal salts driven off by gentle ignition, and the now considerable residue treated with strong sulphuric acid. The resulting sulphates were dissolved by prolonged boiling in water containing hydrochloric acid, and the clear yellow solution, which evidently contained iron, was poured into a solution of ammonium carbonate in small portions at a time. Ultimately, an almost perfectly clear solution was obtained, which, however, on standing for 10 minutes, became turbid, and deposited a considerable precipitate, consisting principally of aluminium hydrate, which was collected, washed, ignited, and weighed. The glucina in the filtrate from the aluminium hydrate was precipitated as basic carbonate, and also ignited and weighed. The main residue insoluble in water, when dried at 100°, weighed 2.956 grams. It was mixed with 13 grams of ammonium hydrogen fluoride, and again heated for a few minutes as before. The aluminium and glucinum rendered soluble in water by this second treatment were determined. This time, the residue insoluble in water weighed 1.340 grams. It was mixed with 5 grams of ammonium hydrogen fluoride, and the process repeated. After extraction with water, the residue insoluble in water was now found to weigh 0.754 gram. The aluminium and glucinum rendered soluble in water by this third treatment were determined as before, and the residue insoluble in water was heated with ammonium hydrogen fluoride for a fourth time. After extraction with water, 0.511 gram was left undissolved, and as the quantity of crude glucina obtained from the aqueous extract weighed only 0.013 gram, it seemed probable that the insoluble residue now consisted of aluminium fluoride only. In order to make certain of this, however, the insoluble residue was fused with potassium hydrogen sulphate in a platinum crucible. On boiling the fused mass with water and filtering, the insoluble residue dried at 100° was found to weigh 0.508 gram, as against 0.511 before fusion. Thus the very intractable aluminium fluoride had resisted the action of the potassium hydrogen sulphate.

The numerical results are given in the table on p. 921.

It should be observed that the weights of glucina given in this table represent crude, not pure, glucina. The above-described separation of aluminium from glucinum by ammonium carbonate is very far from perfect. Had the crude glucina been subjected to a process of purification, the weights of glucina would have been considerably diminished, and the weights of alumina correspondingly increased. It was

Substance treated with ammonium hydrogen fluoride.	Weight in grams.				$\text{Al}_2\text{O}_3 \times 100$ 4·913	$\text{GfO} \times 100$ 4·913
	Sub- stance taken.	Residue insoluble in water after treat- ment.	Al_2O_3 from aqueous extract.	GfO from aqueous extract.		
Beryl in fine powder	4·913	2·956	0·250	0·412	5·09	8·39
1st insoluble residue	2·956	1·340	0·292	0·145	5·94	2·95
2nd „ „	1·340	0·754	0·136	0·059	2·76	1·20
3rd „ „	0·754	0·511	0·041	0·013	0·83	0·26

not considered necessary to do this, the object of the above-described operations being simply to ascertain roughly the lowest temperature at which ammonium hydrogen fluoride effects the complete decomposition of beryl, and in what time. For this reason, also, no attempt was made to separate the small quantity of iron present.

This trial brings out the following points which are of practical importance.

1. That beryl is very rapidly and completely decomposed by the action of ammonium hydrogen fluoride at a temperature which is much below a red heat, but considerably higher than that obtainable by heating on a steam-bath.

2. That at this low temperature the greater part, if not all, of the aluminium, as well as all the glucinum, is rendered soluble in water. The small quantity of insoluble fluoride of aluminium formed is probably to be accounted for by the difficulty of avoiding local over-heating when using a naked flame.

After these points had been ascertained, a number of attempts were made to effect the perfect separation of aluminium and iron from glucinum by simply heating the mixed fluorides, but, contrary to expectation, these attempts, which involved much time and labour, were unsuccessful, and therefore it would serve no useful purpose to give a detailed account of them. Glucina which contained only small traces of alumina and still smaller traces of oxide of iron was repeatedly obtained, but I never succeeded in preparing pure glucina in this manner, although the conditions were greatly varied. One point was, however, ascertained which suggests an improvement in the method for preparing crude glucina from beryl. It was found that when the mixed fluorides of iron, glucinum, and ammonium are heated together in the presence of air, a large part of the iron fluoride is converted into ferric oxide; and, further, that if care be taken to

peroxidise the iron previous to heating the mixed fluorides, almost every trace of the iron may be thus rendered insoluble in water without difficulty. I have not tried this method of separating the iron on a large scale, and cannot therefore say definitely that it is to be preferred to the easy separation effected by diluting the ammonium carbonate solution with hot water, as described on p. 917. In any case, the great difficulty lies in the removal of the last small traces of iron, and this separation is best effected by the mass action of mercuric sulphide in the manner already described.

One further point deserves mention. It was found that the presence of fluosilicate is very prejudicial to the separation of the mixed fluorides, as it gives rise on heating to the formation of compounds of glucinum insoluble in water.

Deville (*Ann. Chim. Phys.* [3], **61**), in an interesting paper, points out that when alumina is boiled with a solution containing aluminium fluosilicate, silica is precipitated, and ultimately a solution of a soluble fluoride of aluminium free from silicon is obtained. He supposes this soluble modification of aluminium fluoride to be an aluminium salt of a hydrofluoaluminic acid. It occurred to me that it might be possible to effect the perfect separation of glucinum from aluminium, by first boiling the aqueous solution of the mixed fluorides with alumina, so as to remove all silicon from solution, and then simply evaporating the solution to dryness, and igniting the mixed fluorides. In the course of experiments made in this direction, Deville's observation was fully confirmed, and it was also found that hydrated oxide of iron behaves similarly to alumina, and removes almost every trace of silicon from the fluoride solution. After removal of the silicon in this manner, a much better and, indeed, almost perfect separation of aluminium from glucinum was repeatedly effected by simply igniting the mixed fluorides. This behaviour of ferric hydrate may not improbably contribute to the success of the method of working on a large scale described in the first part of this paper.

A method for removing the last traces of aluminium from glucinum will be described in a subsequent communication.