"BERYLLIUM"

THESIS.

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by

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General Introduction.

Of all the elements discovered undoubtedly - in proportion to its occurrence on the earth - the least is known about the element beryllium. It has been estimated(1) that from one tenth to one hundredth of one per cent. of the earth's crust is beryllium, comparing this with F.W.Clarke's estimate (1908) of the percentage composition by weight of the earth's crust - which is given below - we see that beryllium is relatively an exceedingly common element, it being somewhere between sulphur and bromine, and yet to the average person it is so little known as to be almost unheard of.

F.W.Clarke's Estimate.

Oxygen	49.78	Carbon	.19
Silicon	26.08	Phosphorus	.11
Aluminium	7.34	Sulphur	.11
Iron	4.11	Barium	.09
Calcium	3.19	Manganese	.07
Sodium	2.33	Strontium	.03
Potassium	2.28	Nitrogen	.02
Magnesium	2.24	Fluorine	.02
Hydrogen	.95	Bromine	.008
Titanium	.37	All other elements	.48
Chlorine	.21		

(Considering the earth's crust one half mile deep and including the ocean and the atmosphere.)

We have available therefore a large store of beryllium, and the minerals which contain it are found in a condition almost free from contamination with other materials. Further, although the exact properties of metallic beryllium are far from being established, yet suficient is known to clearly indicate that there will be great commercial uses for this metal when a cheap method of preparation can be obtained. To quote Dr. J.W.Richards (2) :- "Beryllium is a metal which will well repay extended metallurgical research and minute physical and chemical study of its many unique properties."

Discovery and Name. Although so common it was not until one hundred and twenty five years ago, in 1797, that it was first discovered by L.N.Vauquelin (3) and there is no doubt that the recent date of its discovery is due to the great similarity of the chemical properties of beryllium and aluminium, and more especially to the fact that in the ordinary course of analysis beryllium hydroxide is precipitated with aluminium hydroxide from which it is indistinguishable. Vauquelin undertook to prove the identity of emerald and beryl, he found that a portion of the aluminium hydroxide precipitate was thrown out of solution in potassium hydroxide on boiling, this led to his reporting in "Annales de Chimie" the discovery of a new "earth". Vauquelin did not give it a name but referred to it as "la terre du Beryl" which was translated in German as "Beryllerde", from which was derived the name beryllium

The editors of "Annales de Chimie" suggested the name "glucine" for the oxide, from which was derived the name glucinum; Vauquelin in a subsequent paper adopted the term "glucine ". Both of the names beryllium and glucinum are still in general use.

Occurrence. It is certain that beryllium is a very reactive element - this is to be expected from its place in the periodic table - and so it is always found in nature in combination with other elements, most commonly as silicates, sometimes as phosphates, and occasionally as borates and fluorides. It occurs in such common minerals as beryl ($3BeO.Al_2O_3.6SiO_2$) and chrysoberyl ($BeO.Al_2O_3$), it is also found in many comparatively rare minerals. (4) It is likely that the percentages of alumina reported in mineral analyses - before the discovery of beryllium - contain in many cases beryllia, indeed this is probably true of later analyses.

The only pure beryllium compound on the market today is beryllium nitrate which contains water of crystallization, this is prepared from monazite sand, the preparation being carried out in conjunction with the extraction of the oxides of cerium and thorium. The nitrate is easily converted to the oxide which is used in small amounts in the manufacture of gas mantles.

Preparation of Metallic Beryllium. Two steps are involved, firstly the separation of beryllium oxide (5), and

secondly the preparation from beryllium oxide of the metal. Beryl is unatacked by any acid so it must first be treated with a flux, or it may be heated in an electric furnace [6] to a high enough temperature to volatilize most of the silica. Beryllium compounds are usually separated from those of aluminium by making use of the fact that beryllium hydroxide is soluble in hot ten per cent. sodium bicarbonate solution whereas aluminium hydroxide is not. A basic carbonate of beryllium is finally obtained which can be easily converted if necessary to the oxide.

The metal was first prepared by "Wohler"[7], he reduced beryllium chloride with potassium, his product was not very pure. Several other investigators have since prepared it by the same method, namely the reduction of a halide using either potassium or sodium, Nilson and Pettersson[8] first obtained 87 per cent. and later 94 per cent., and Humpidge[9] in 1885 obtained a metal of 99.2 per cent. purity. However it remained for Lebeau[10] in 1898 to develop another simpler method for the preparation of the metal, he electrolized the fused double fluoride $BeF_2.NaF$ and obtained a metal 99.8 per cent. pure. The two above methods - Wohler's and Lebeau's - are the only ones that have had any success. A third method, the reduction of beryllium oxide by magnesium[11] is reported by Parsons as being very doubtful.

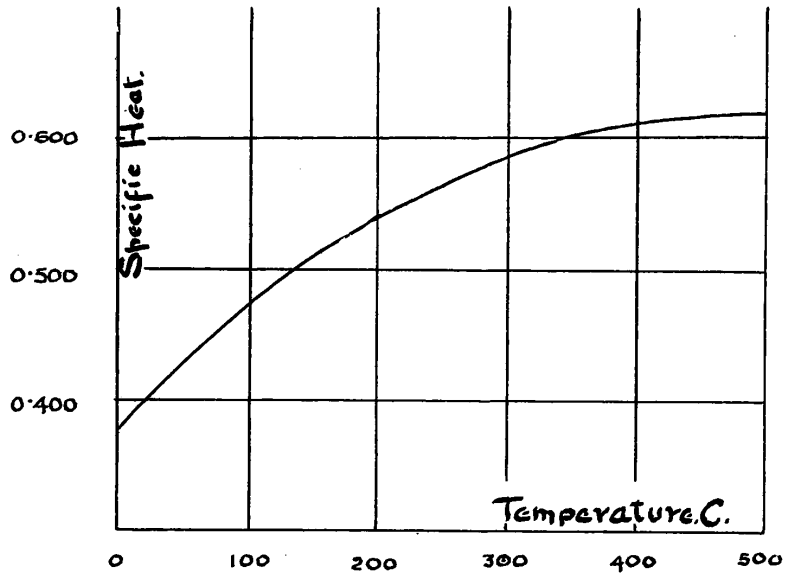
As far as can be deduced from the literature on the

subject, metallic beryllium has never been prepared in sufficiently large quantities, and in a pure enough state, to allow of any exact details of its physical properties being given. Indeed the preparation of the pure metal would seem to be an exceedingly difficult matter.

Physical Properties. Beryllium is a steel grey metal, it is malleable, it can be easily cold rolled, and it will take a high polish; its specific gravity, according to the best results[12] which are not in very good accord, is about 1.7; it will scratch glass, the hardness being between 6 and 7; there is no definite information concerning its electrical conductivity but it is said to be the same as that of silver and therefore greater than that of copper. Nothing is known of its tensile strength or regidity, or about how it might be strengthened by the addition of other metals. The melting point is considered to be about 1100 degrees C. but it has never been determined, as under atmospheric pressure the metal vapourizes before the melting point is reached, this is concluded from the work of Pollok[13] who observed that when heated in an electric arc in an atmosphere of hydrogen, beryllium vapourizes without fusion and condenses to a grey metallic mirror.

One of the most interesting physical properties is the specific heat which has been thoroughly investigated by Humpidge[14] as a result of an attempt to clear up the question of the atomic weight, and - as can be seen from the curve

below - the specific heat, just as in the case of carbon, boron and silicon, at ordinary temperatures has a low value but increases to a maximum, steady, value above 450 degrees C.



Assuming the specific heat to be 0.62, the atomic heat = 9.1 by 0.62 = 5.64; this is in good agreement with Dulong and Petit's Law which states that the atomic heat of an element in the solid state is a constant. It is also interesting to note that the specific heat is the greatest[15] of any metal. The latent heat of fusion is also abnormal, the value being thought to be somewhere about 300 which is an exceedingly high figure.

The spectrum of beryllium has been investigated by several workers, most worthy of mention are the observations of Rowland and Tatnall[16] which are of extreme accuracy.

The atomic weight of beryllium has been determined by many investigators and there seems to be little doubt that the value, as obtained by C.L. Parsons[17] of very nearly 9.1, is highly accurate. Berzelius in 1815 was the first to determine the atomic weight and up to the present day many other determinations[18] have been carried out. Parsons used either the basic acetate, $Be_4O(C_2H_3O_2)_6$, or the acetylacetonate, $Be(C_5H_7O_2)_2$, both of which are very stable and can be obtained in a high degree of purity.

It is worthy of remark that those properties of which we have exact information, e.g. atomic weight and spectrum, do not necessitate the preparation of the pure metal; concerning all other physical properties - with the possible exception of the specific heat - The information is far from being definite.

Chemical Properties. Beryllium is chemically a metal slightly less basic than magnesium and more basic than aluminium. According to Brauner[19] its chemical nature can be summed up:-

Li: Be = Be:B,

Li: Na = Be:Mg = B: Al,

Li: Mg = Be:Ac = B: Si,

From its place in the periodic table, between lithium and boron, beryllium belongs to the first period, and experience teaches us that the elements of the first period

are not typical of the group to which they belong but rather seem to enjoy characteristic properties of their own. So we expect beryllium to have peculiar properties, and perhaps its most characteristic property might be termed its "elusiveness"; Dr.J.Emerson Reynolds speaks of it as the "chameleon element", and Dr.C.L.Parsons[20] in a paper entitled "The Vagaries of Beryllium" states:- "The literature of Inorganic Chemistry is overburdened with compounds which have no existence------and no branch needs more supervision than the chemistry of beryllium. Its literature is full of errors.------It is recorded that it does and it does not combine with hydrogen, sulphur, selenium and phosphorus; that it is and it is not reduced from its oxide by aluminium and magnesium; that it has been produced (even manufactured) by the electrolysis of its bromide and that its bromide is not a conductor of electricity. In each case the negative is probably true."

Beryllium is unattacked by air or oxygen at ordinary temperatures, however - if in a finely divided state - it combines with oxygen at high temperatures,[21] It is slightely - or not at all - acted upon by water or steam. It combines directly and easily with fluorine, chlorine and bromine[22] and with iodine when heated in iodine vapour.[23] At the temperature of the electric furnace it combines with carbon, boron and silicon.[24] Itis attacked by dilute hydrochloric

acid and dilute sulphuric acid yielding hydrogen, and by concentrated sulphuric acid yielding SO_2, but it is not attacked by dilute or concentrated nitric acid when cold, it is only slightly acted upon by hot concentrated nitric acid. Itis not attacked by ammonia, but it readily dissolves in a caustic potash solution. Its salts are mostly soluble in water and are colourless, these aqueous salt solutions have a characteristic sweet taste.

Beryllium acts upon methyl and ethyl iodides(25) replacing the iodine and forming beryllium methyl and beryllium ethyl, beryllium also replaces mercury from mercury methyl and similar compounds.(26)

The Valence. Previous to 1879 some authorities held the view that beryllium was divalent whilst others thought that it was trivalent, but after Mendeleef(27) pointed out that the only place for beryllium was between lithium and boron research was immediately stimulated and we find at this period many researches carried out with the main object of determining its valence. The first values on the specific heat corresponded to an atomic weight of about 13.6. Considerable light was thrown upon the question by Nilson and Pettersson(28) who conducted a magnificient piece of research on the density of beryllium chloride thus proving that the formula for the chloride was $BeCl_2$ thereby supporting the divalency of beryllium. The divalency of beryllium was soon after

confirmed by the specific heat determinations of Humpidge,[29] and also from the vapour densities found for the bromide, basic acetate and acetylacetonate. So it might be concluded that the divalency has been unquestionably established, but of recent years the question has been again raised by Wyrouboff[30] who argues in favour of trivalency, and Tanatar[31] who claims that the basic acetate can only be explained by assuming the tetravalency of beryllium.

Compounds. In this short introduction it is impossible to give anything like a complete description of the compounds of beryllium. Only such points as seem to be of special interest are included.

The oxide, carbide and halides are the only binary compounds that have any real standing in literature. The most striking property of the halides (except the fluoride) is that they can only exist in the complete absence of water, as water causes them to lose part of their anion as hydracid, and if an aqueous solution is evapourated it loses more and more of the hydracid becoming more and more basic but no precipitation occurs until a very high degree of basicity is reached. Dr.C.L.Parsons says:-[32] "Probably the fact which has the greatest bearing on the chemistry of beryllium and has caused more failures of researches undertaken upon the element than any other one thing, is the great influence which water has upon all of its salts, acting to many of

them as if it were itself a strong hydroxide and in a manner that is hard to understand from our ordinary conceptions of solution and hydrolysis."

Beryllium hydroxide is well known and is very similar to aluminium hydroxide.

Only the normal salts of the non-volatile acids, e.g. sulphate, selenate and oxalate have been prepared from aqueous solutions. Normal salts of more volatile acids, such as nitrite, carbonate, etc., have never been prepared, or if so only in the absence of water, e.g. the sulphite has been prepared from absolute alcohol, and the halides from the direct combination of the elements. Solutions of these normal salts act like acids, they attack metals, liberate CO_2, and redden litmus even after several equivalents of beryllium oxide have been added; notwithstanding this it has been shown by Ley[33] and also Brunner[34] - using the sugar inversion method - that the sulphate, chloride and nitrate of beryllium are less hydrolized than the corresponding salts of aluminium and iron. These so-called "basic solutions" of normal salts exhibit many other peculiar properties and C.L.Parsons[35] has put forward the possible explanation that we have a case of the simple solution of a substance (beryllium hydroxide) in a mixed solvent (water and normal salt) in one of which alone (water) it is insoluble.

Solutions of acids can hold in solution abnormally

large quantities of beryllium hydroxide (or oxide), thus acetic acid can take up 6 equivalents of beryllium hydroxide, hydrochloric acid 4 equivalents, etc., and still the solutions exhibit acid properties, turn litmus red etc., These solutions when diluted with water throw down basic precipitates and the filtrate on evapouration gives a gummy basic mass. These facts have caused the presence in the literature of beryllium of a large number of so-called basic compounds which have no real existence.

The action of water is very much modified in the case of the double salts of beryllium - as is also the case with the salts of aluminium and magnesium - and some of these salts e.g. the carbonates, chlorides, iodides, nitrities and sulphites are readily obtainable in definite, crystalline, forms from aqueous solutions. Very little work has been done on the double salts.

Lastly mention must be made of the truly basic beryllium compounds, discovered in Urbain's laboratory by Lacombe.[36] They are produced only in contact with anhydrous acids. These very interesting volatile basic compounds have only been produced from acids of the fatty series. Amongst those described are the formate, acetate, propionate and several others.

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EXPERIMENTAL WORK.

Object. The chemistry of the element beryllium is at present in its infancy, and on reviewing the work of previous investigators it is at once perceived that future work must follow along the two following main lines. First it is necessary to prepare by any method whatever a sufficiently large specimen of the pure metal so that the physical properties - which indicate to what uses the metal may be put - may be accurately determined. These determinations would supply exact information as to the possible commercial value of the metal.

If the metal should prove of commercial value - and all of the results of previous workers seem to point to this - the second problem would then be an attempt to discover some cheap process for the manufacture of beryllium metal.

The object of this work was therefore to prepare some pure beryllium, make a minute examination of its physical properties, and lastly, to ascertain whether a commercial process of manufacture could be devised.

Starting Material. When the work was begun it was considered best to use beryl as the material from which to start. One hundred pounds of beryl of about 100 mesh was obtained from the Foote Mineral Company. Afterwards Dr. Johnson (under whose direction the author is working) was informed by Dr. C.L. Parsons that hydrated beryllium nitrate,

which is a far better material to start with, could be obtained at a very moderate price from the Welsbach Light Company. One pound was immediately ordered and later an additional three pounds. The author also takes much pleasure in mentioning the kindness of the National Drug and Chemical Company of Montreal which has donated four pounds of beryllium nitrate to the chemical department of McGill University. Hence there is available a considerable quantity of beryllium nitrate which is sufficent for present needs.

Experiments on Beryl.

The proceedure which it seemed best to follow with beryl was first to determine its composition and then to separate the beryllium in the form of beryllium oxide, this oxide could then be used in attempting to prepare the pure metal. In the course of the work several experiments were carried out on beryl in order to obtain if possible a more convenient method for the preparation of beryllium oxide.

Composition of Beryl. Analyses were made by the method of Parsons and Barnes(1) which briefly is as follows. The proceedure is very similar to an ordinary rock analysis. The sample for analysis is fused with sodium carbonate and the silica determined in the usual way. Aluminium, iron and beryllium hydroxides are thrown down in the ammonia precipitate. The beryllium hydroxide is separated by treatment with hot, ten per cent., sodium bicarbonate solution in which it is

soluble.

The analysis takes up a very considerable amount of time but the results were in good agreement, the mean result was:-

Analysis of Beryl.

SiO_2,	67.60%
Al_2O_3 (containing a trace of iron)	17.84%
BeO,	10.74%
Other Material,	3.82%
	100.00%

Preparation of Beryllium Oxide from Beryl. The most convenient method seemed to be that of Parsons and Barnes.(2) But the difficulty of removing the contents of the nickel crucible was so great that this method had to be abandoned. Finally a modification of the method of Parsons and Barnes was used, an outline follows. Beryl is mixed with sodium carbonate in a platinum crucible and fused. The silica is removed in the usual way by treatment of the fused mass with hydrochloric acid and evapourating to dryness. The aluminium, beryllium and iron are precipitated as hydroxides, filtered off and the precipitate dissolved in hydrochloric acid. The solution, which contains only salts of aluminium, beryllium and iron, is neutralized with ammonia and enough sodium bicarbonate (solid) added to make a ten per cent. solution. The solution is heated to about 55 degrees C. and kept stirred at this temperature for 24 hours, and then filtered. The filtrate contains almost all of the beryllium and no aluminium

or iron. The beryllium can be easily obtained in the form of an easily filterable basic carbonate by diluting with water and then passing live steam into the solution. This basic carbonate can then be filtered off and washed. If it is desired to remove any adhering salts the basic beryllium carbonate can be dissolved in hydrochloric acid and precipitated as beryllium hydroxide by ammonium hydroxide. This process can be repeated until the desired degree of purity is reached. On heating either the basic carbonate or the hydroxide of beryllium the oxide is produced.

By this method a 60 per cent. yield of beryllium oxide was obtained, but the process is very long and tedious owing to the use of small platinum crucibles and the bulkiness of the precipitate obtained. As soon as the first pound of beryllium nitrate was obtained from the Welsbach Light Company this method of preparation was abandoned.

Miscellaneous Experiments with Beryl. With the main idea of obtaining a simpler method for the preparation of beryllium oxide the following experiments with beryl were undertaken.

1. Sodium chloride and beryl were mixed and the mixture heated until the sodium chloride melted. There was no evidence of the beryl being in any way affected.

2. Powered beryl was treated in a silver dish with a 50 per cent. solution of sodium hydroxide for from 24 to 48

hours at a temperature just short of boiling. (Glass could not be used as any kind of glass is readily attacked under these conditions.) As a result of sevsral analyses it was shown that from 20 to 30 per cent. of the beryl was dissolved, but that there was no selective solution, that is to say, the percentage composition of the dissolved portion was approximately the same as that of the original sample. Hence to separate the beryllium oxide after treatment with sodium hydroxide solution would be an exactly similar process to the preparation given before. This treatment does not therefore simplify the preparation of beryllium oxide. However it is interesting to remark that the fact that beryl is attacked by a solution of sodium hydroxide is not mentioned in any literature on the subject.

3. An intimate mixture of beryl and sugar charcoal was placed in a hard glass tube. The tube was heated until red hot and a stream of dry chlorine passed over the mixture. Not more than 7 per cent. of the beryl was lost after 4 hours treatment, and there was no indication of any beryllium chloride being formed on the cooler parts of the tube. Some slight amount of a volatile substance sublimed onto the quite cold parts of the tube but its composition was not ascertained as it was most certainly not beryllium chloride.

An Attempt to Dehydrate Beryllium Nitrate.

If the dehydration of beryllium nitrate could be successfully accomplished, it is probable that the anhydrous nitrate

could be dissolved in some solvent - say alcohol - and if this solution would conduct an electric current it might be possible to get an electrolytic deposition of metallic beryllium from the solution. The essential point is an entire absence of water in order to prevent hydrolysis of the beryllium nitrate.

Dehydration can not be accomplished by heating since decomposition of the nitrate with the formation of beryllium oxide and nitric anhydride occurs. Hence it was decided to see if the problem could be solved by placing hydrated beryllium nitrate in a vacuum desiccator over phosphorus pentoxide.

The apparatus - see figure 1 - was evacuated to a pressure of one tenth of a millimeter of mercury and maintained at this pressure for 4 days. The appearance of the hydrated beryllium nitrate changed considerably. When the experiment was started the sample was a crystalline white solid. Under treatment it became a colourless viscid liquid and bubbles could be seen slowly rising (slow because of the high viscosity) to the surface. The mercury in the pump was attacked showing that some gas was being given off other than water vapour, and on removing the cover of the desiccator brown fumes of N_2O_4 were at once seen showing that some decomposition had occurred, this was further verified by the following analyses:-

Original Sample before Treatment.

$Be(NO_3)_2$, by nitrometer method----------65.2%

$Be(NO_3)_2$, by weighing as BeO----------74.8%

Difference---------- 9.6%

After Removal from the Vacuum.

$Be(NO_3)_2$, by nitrometer method----------70.3%

$Be(NO_3)_2$, by weighing as BeO----------87.0%

Difference----------16.7%

To determine the percentage of beryllium nitrate by weighing as BeO it is only necessary to weigh out a sample and heat in a crucible until there remains only BeO, from the weight of the BeO the percentage of $Be(NO_3)_2$ in the sample can be calculated assuming that all of the BeO was derived from $Be(NO_3)_2$. If this assumption is correct the value so found should agree with the nitrometer determination.

The above analyses point out two facts. Firstly that some of the beryllium must have been present in some other form than nitrate, probably as beryllium hydroxide. Secondly that after keeping in a vacuum the ratio of $Be(NO_3)_2$: $Be(OH)_2$ decreases, thus proving that the $Be(NO_3)_2$ was partly decomposed. Hence dehydration can not be carried out by this process. It has also been shown by other investigators that the hydrated sulphate of beryllium can not be hydrated in this manner. Perhaps better results could be obtained at very low temperatures.

An Attempt to Reduce Beryllium Oxide.

It seemed probable that under suitable conditions beryllium oxide could be reduced to the metal by heating in contact with carbon. First it is necessary to decide what conditions would be best. Air must be excluded, so the mixture should be placed in either a vacuum or in an atmosphere of an inert gas.

If a reaction does take place, such as is represented by the following equation:-

$$BeO + C = Be + CO,$$

the equilibrium point may be arrived at with a very slight concentration of CO present. Hence in order to make the reaction go in the direction left to right it would be necessary to keep the concentration of the CO below its equilibrium value. This could be accomplished by keeping the reaction mixture in a highly evacuated receptacle. A vacuum furnace is accordingly necessary.

An ingenious vacuum furnace - shown in figure 2 - was devised by Dr.Johnson, It consists of two alundum crucibles fitting one within the other, the inner one being wound with nicrome wire and the intervening space between the two crucibles lagged with powdered magnesia. The mixture to be heated is placed in the inner crucible. The crucibles are encased in a large inverted tube, sealed at one end, and closed at the other end by a three-holed rubber stopper. The stoppered

end is immersed in a trough of mercury in order to obtain a mercury seal. Through two holes of the rubber stopper glass tubes pass containing silver wires which close the electric circuit, these two glass tubes are closed with sealing wax. Through the third hole of the rubber stopper passes a third glass tube which connects with a Toepler vacuum pump. A continuous stream of cold water flows over the outer large tube into the trough of mercury from which it overflows. The water keeps the tube cool thus preventing it from being cracked by the heat. A maximum temperature of about 1200 degrees C. is obtainable.

The carbon used was prepared from sugar. The sugar was heated at a not very high temperature until it had charred. Then the residual charcoal was placed in a crucible with a cover (to prevent too free contact with the air) and heated in a muffle furnace at a bright red heat. This treatment was found necessary in order to remove hydrocarbons absorbed by the charcoal.

The beryllium oxide was prepared in the usual way by heating the hydrated beryllium nitrate.

Four experiments were carried out, the proportion of carbon to beryllium oxide being varied. The required quantities of sugar charcoal and beryllium oxide were weighed and mixed by grinding together in an agate mortar, and then placed in the vacuum furnace. The temperature was keept just short of

the fusing point of the nicrome wire, which would be about 1200 degrees C. In one case in order to get a very intimate mixture the beryllium oxide was added to the sugar before the charring took place. Always at high temperatures it was possible to pump off some gas, and this gas on ignition burnt producing moisture. It was concluded that the gas was evolved by the charcoal. In no case was there any indication of a reduction of the beryllium oxide.

In conclusion it may be remarked that although the reaction might proceed at high temperatures, it is not very likely as Lebeau[3] has shown that at quite high temperatures only the carbide of beryllium is formed from a mixture of beryllium oxide and sugar charcoal.

An Attempt at the Reduction of Beryllium Chloride.

R.Edson and D.McIntosh[4] have shown that pure vanadium can be deposited from the vapour of vanadyl chloride onto a white hot platinum wire placed in an atmosphere of hydrogen. It therefore seemed probable that some similar method for the preparation of beryllium could be obtained.

The basis of the process has to be a volatile salt of beryllium and the salt chosen as being the most likely to succeed was the chlorides which is easily volatile. Lebeau[5] found the melting point of the chloride to be about 440 degrees C, and Nilson and Pettersson found the boiling point to be about 520 degrees C. The preparation and handling of the

chloride are however by no means easy, it being essential to exclude the slightest trace of moisture. After several unsucessful attempts the following method - based on that of Pollok's[6] - for the preparation of beryllium chloride was used.

See figure 3 - Beryllium and sugar charcoal are intimately mixed and the mixture placed in the pyrex glass tube FG. The asbestos plugs H, K keep the mixture M in position. F and G are rubber stoppers. The tube is placed in an electric furnace PQ and heated to about 800 degrees C. Tap C is closed and a stream of dry chlorine is passed through the open taps A, B and E. The stream of chlorine is allowed to pass for about 3 hours. The beryllium chloride condenses in the cooler part L of the tube. It was found necessary to first heat the sugar charcoal and the asbestos in a stream of chlorine in exactly the same way as in the experiment itself in order to remove any volatile chlorides that might be formed from impurities in these materials.

Tap B is now closed and taps D and C are opened. This allows tube FG to be cooled whilst a stream of dry CO_2 is being passed through it. As soon as the apparatus is cool, rubber stopper G is removed and the beryllium chloride quickly raked into the quartz tube shown in figure 4, and the stopper of the quartz tube with its attachments is immediately placed in position.

In this second apparatus - figure 4 - the large quartz

test tube is closed by a two-holed rubber stopper. Through one hole passes a glass tube which is closed at both ends and which contains the wires that complete the circuit with the loup of tungsten wire. Through the other hole a stream of dry hydrogen is passed, the pressure being regulated by a suction pump. The tungsten wire is kept red hot by the passage of a small current and the beryllium chloride is volatilized by heating the outside of the quartz tube with a Bunsen burner.

After continuing the experiment for half an hour there was no apparent reduction of the beryllium chloride. The pressure of the hydrogen was varied and also the temperature of the tungsten wire but in no case was the experiment successful.

Electrolysis of the Double Fluoride.

The electrolysis of the double fluoride, $BeF_2.2NaF$, to obtain beryllium metal has been successfully carried out by Lebeau.(7) Later, in 1913, Fichter and Jabloczynski(8) claimed to have obtained better results by using the double fluoride, $2BeF_2.NaF$, None of these investigators however seemed to have obtained sufficient of the metal to thoroughly examine its physical properties, it must be concluded therefore that they only obtained minute quantities.

IT was decided to try and obtain sufficient of the metal for our purposes by using the method of Fichter and Jabloczynski. The following are the details of this work.

Twelve grammes of $2BeF_2.NaF$ were prepared by dissolving the required amount of BeO in hydrofluoric acid and the calculated amount of $NaHCO_3$ added. The hydrofluoric acid was evapourated off and the residue fused in a platinum crucible. The double fluoride was kept molten by heating with a Bunsen burner and a current of 0.5 amps at 20 volts was run through the melt for 5 hours, a platinum wire being used as cathode and a graphite rod as anode. Carbon seems to be the only material that can possibly be used for the anode, as all metals - even platinum - would be readily attacked and would therefore contaminate the beryllium metal.

The result was disapointing in that there was no adhering layer of metal deposited, the electrolized metal being disseminated throughout the melt.

The contents of the crucible were then transferred to a beaker and washed repeatedly with large quantities of water. At first there was much gas evolved having a distinct odour of acetylene and the water became alkaline, showing that some carbide had been produced, and very possibly some metallic sodium. Much local polarization was observed at the anode, this resulted in there being a continuous sparking at the anode. This might be the cause of the production of beryllium carbide since previous investigators[9] have shown that at high temperatures beryllium and carbon combine.

Finally after the washing was complete there remained

a grey powder which on examination under the microcope showed a metallic appearance but was also seen to be contaminated with a white solid. On analysis only 30 per cent. of beryllium was obtained.

A second electrolysis was tried. Forty-two grammes of the double fluoride were prepared and its melting point observed by immersing into it a mercury-quartz thermometer which had a tight-fitting platinum cylinder over that part of the thermometer which was immersed in the melt. (Quartz or glass would be attacked by the double fluoride) The melting point was not well defined but was somewhere about 300 degrees C. In order to obtain a suitable metal to contain the double fluoride, it was decided to try the action of a typical fluoride on various metals. The typical fluoride chosen was a mixture in molecular proportions of sodium fluoride and potassium fluoride. This mixture melts at a red heat. The following results were obtained.

Metal	Loss per sq.inch of surface per hour.
Silver	.00094 grs
Nickel	.00313
Copper	.00122
Iron	.05180

It was decided from these results that silver looked the most promising. Hence the 42 grammes of the double fluoride

were melted in a silver crucible and the silver crucible was made the cathode and a graphite rod the anode, The molten mass was kept stirred with a silver stirrer. The current was allowed to pass for about 48 hours.The current could not be kept constant, due to local polarization, and varied from .08 amps to 1.40 amps, the voltage varying from 5 to 50 volts. No metal was deposited on the cathode, On the washing treatment being applied much gas was evolved of the same character as before. Instead of the residue being a grey powder , it consisted of a little of the grey powder contaminated with much white material, presumably BeO. Hence the experiment was a failure.

Knowing that oxygen easily passes through silver, it is possible that a silver crucible might increase the production of BeO. Accordingly in the next experiment it was decided to electrolize in the absence of oxygen.

In the third electrolysis 12 grammes of the double fluoride were placed in a nickel crucible and this was kept molten in an electric furnace - see figure 5 - A stream of dry CO_2 was kept flowing so that the melt was never in contact with oxygen. A current of 4 amps was passed for 40 minutes. No metal deposited on the cathode. On treating as before with water the same phenomina were obtained as in the previous experiments but only very slight traces of adhering white solid could be observed under the microscope.

On analysis the powder gave 83 per cent. beryllium but the yield was only 8 per cent. of the theoretical value. This was a great improvement but four subsequent experiments, carried out under as nearly as possible the same conditions, failed to give any better result than the earlier value of 30 per cent. of beryllium.

Analysis of Beryllium Metal. The following method was used for the analysis of the metallic beryllium obtained in the previous experiments. See figure 6, Weigh about .02 grammes of the sample into a dry test tube and make connections as in the figure. Raise tube A until the water is at the level B and close taps C and D. Lower tube A until the water in tube E is less than atmospheric. Now pipette 2 c.c. of boiled (1:1) hydrochloric acid into the dropping funnel, allow these 2 c.c to go into the test tube and after all the gas has been evolved and everything is at room temperature, read the burette. Subtract 2 c.c. from the reading.

This method was checked on a sample of magnesium, giving results that were in very close agreement.

Solubility of Beryllium Oxide.

An ideal solution of the problem of obtaining metallic beryllium would be to discover some solvent in which beryllium oxide is soluble and from which it could be deposited electrolytically - c.f. cryolite($3NaF.AlF_3$) in which alumina is soluble, and from this solution aluminium is electrolized

on a commercial scale.

With this in view the double chloride, $BeF_2.3NaF$, was prepared - it is a crystalline solid with a melting point above red heat. On the addition of some beryllium oxide to the molten salt there was no evidence of solution. Three other substances were tried, namely NaCl, NaF and $2BeF_2.NaF$, but again there was no sign of solubility.

Experiments with Liquid Ammonia.

An extremely good reference book on liquid ammonia is "Verflussigtes Ammoniak als Losungsmittel" by J.Bronn. On reviewing this book it is seen that the majority of the metallic nitrates are soluble in liquid ammonia, Also H.P.Cady[10] claims to have deposited on the cathode the metals silver, copper and barium when a current is passed through the solutions of their salts in ammonia.

There seemed to be a very good chance of obtaining metallic beryllium in a similar manner. And it appeared that very likely hydrated beryllium nitrate might be soluble in liquid ammonia.

At first the liquid ammonia was prepared by a method used by Foote and Brinkley[11] Commercial ammonia water is warmed up to a maximum temperature of 45 degrees C. The ammonia gas is dried by passing it in succession through three towers of caustic soda (sticks). The ammonia gas is then passed through a bottle of solid ammonium thiocyanate

which is kept in a cooling mixture of snow and ice. The ammonia is readily absorbed . Finally there is obtained a liquid which is a solution of ammonia in ammonium thiocyanate, there being about 45 per cent. of ammonia present. Pure dry ammonia can then be obtained by warming up the ammonium thiocyanate solution and leading the ammonia into a test tube cooled in CO_2 and ether.

After using the above method for sometime it was found more convenient to obtain a cylinder of commercial ammonia (liquid). This commercial ammonia is quite pure enough for most work; it is a very poor conductor, only a very small current (less than one hundredth of an amp) being observed with a voltage of 110 volts.

A little hydrated beryllium nitrate was added to a test tube containing some liquid ammonia and stirred. It did not appear to be very soluble at this low temperature (the temperature of the cooling mixture being about -79 degrees C.) but it appeared to be much more soluble in the neighbourhood of the boiling point of ammonia (-38), In no case was it found possible to dissolve entirely a given sample of beryllium nitrate in liquid ammonia, no matter how much ammonia was used. It seems probable that some impurity - such as beryllium hydroxide - is contained in the beryllium nitrate. This has already been shown to be likely. Also it is quite possible that some beryllium hydroxide is formed on adding

the hydrated beryllium nitrate to the liquid ammonia.

Later it was discovered that quite concentrated solutions of hydrated beryllium nitrate could be obtained at temperatures above the boiling point of ammonia. These solutions were prepared by adding liquid ammonia to a test tube containing a large excess of hydrated beryllium nitrate and by stirring continuously until the temperature reached the required value of - say -20 degrees C. The test tube and contents could then be kept in a cooling mixture at a temperature of -20 degrees C.

That there was an appreciable amount of solution even at very low temperatures was shown by filtering and then allowing the ammonia to evapourate off. A crystalline white substance separated out, this on standing for some time lost all smell of ammonia. This substance was certainly not the same as the original hydrated beryllium nitrate, the most marked difference being that it was not hygroscopic whereas hydrated beryllium nitrate, on exposure for only a few minutes, becomes quite moist. On heating some of the new substance in a test tube there was evolved water, ammonium nitrate and brown fumes of N_2O_4, and the residue was beryllium oxide. Hence this substance is a new compound.

The clear solution of hydrated beryllium nitrate in liquid ammonia proved to be an excellent conductor of the electric current. The first experiments were carried out in

a simple apparatus - see figure 7 -Two platinum electrodes are immersed in a solution of hydrated beryllium nitrate in ammonia. The solution is warmed until all of the air is driven out of the apparatus. A current of 0.5 amperes is passed and the gases discharged at the electrodes collected. Nearly always there is obtained a small quantity of a black deposit on the cathode. The platinum anode is very perceptibly attacked Gases are evolved from both electrodes. An analysis of the mixed gases gave:- Hydrogen 57.3 per cent., no oxygen, and no oxides of nitrogen; hence the residue could be no other gas than nitrogen.

The black deposit is very peculiar. It is not metallic beryllium as it is only slowly attacked by concentrated hydrochloric acid. It might be platinum -but so little was obtained that no analysis could be made.

After many unsuccessful attempts the apparatus shown in figure 8 was designed to separate the gases obtained at the two electrodes.The platinum electrodes are situated in the two arms of the U-tube. The entire U-tube is immersed in ether. The ether is easily kept at a constant temperature of -20 degrees C.by continually adding small amounts of solid CO_2. Capillaries connect the two branches of the U-tube with bulbs containing mercury. Over these bulbs are placed inverted graduated glass tubes to contain the gases evolved. The mercury is so adjusted that the pressures of the gases

in the two branches of the U-tube are the same when gases are being given off from the ends A and B. The amount of current used is measured by a copper voltameter in series. It is essential that the temperature of the gases in the U-tube is the same at the beginning and the end of the experiment; to ensure this the current is run for about 15 minutes before a reading is taken. Then the voltameter is connected in series and an experiment started. At the end of an experiment tubes AC and BD are placed in a tank of water of known temperature before the readings are taken.

It was found that hydrogen was given off at the cathode and nitrogen at the anode. The results are given in the following table.

Electrolysis of Hydrated $Be(NO_3)_2$ in Liquid NH_3 at -21.C.

No.of experiment	1	2	3	4	5
Current in amps	0.20	0.16	0.16	0.16	0.7
Voltage in volts	4.6	4.5	4.3	4.5	10.0
Copper deposited	0.1501gr	0.1186gr	0.1199gr	0.1251gr	0.1224gr
"A"	43.9c.c	41.7c.c	42.0C.C	44.3c.c	41.7c.c.
"B"	15.6c.c	12.1c.c	12.3c.c	13.0c.c	12.8c.c.
"C"	1:2.81	1:3.47	1:3.43	1:3.46	1:3.27
"D"	.835	1.006	1.005	1.012	.974
"E"	4.13	4.05	4.07	4.12	4.16

A= The amount of hydrogen evolved at the cathode, S.T.P.

B= The amount of nitrogen evolved at the anode, S.T.P.

C = The ratio of nitrogen to hydrogen.

D = The number of grammes of hydrogen obtained for one equivalent gramme weight of copper.

E = The number of grammes of nitrogen obtained for one equivalent gramme weight of copper.

It is evident that an equivalent of hydrogen is being given off for every equivalent of copper deposited, but the value for nitrogen is too low. There must be therefore some other reaction at the anode. Inorder to discover if this behaviour was due to the beryllium present, a solution of ammonium nitrate in liquid ammonia was examined in exactly the same way. And as ammonium nitrate is anhydrous about 1c.c. of water was added to the solution to complete the similarity of conditions. The following are the results obtained.

Electrolysis of NH_4NO_3 in Liquid NH_3 at -21.C.

No.of experiment	1	2	3	4
Current in amps	0.35	0.35	0.35	0.80
Voltage in volts	5.5	5.5	5.5	9.0
Copper deposited	.1319grs	.1287grs	.1208grs	.1327grs
"A" (in c.c.)	44.5	45.6	43.1	45.8
"B" (in c.c.)	13.5	13.65	12.7	13.77
"C"	1:3.31	1:3.35	1:3.32	1:3.32
"D"	.967	1.015	1.020	.988
"E"	4.07	4.23	4.18	4.13

Note. A,B,C,D,E have the same values as in the previous table.

We must conclude therefore that the low value obtained for nitrogen is not due to the presence of beryllium.

As a result of the above described experiments with ammonia we are led to conclude that metallic beryllium can not be obtained from the electrolysis of hydrated beryllium nitrate in solution in ammonia.

Summary of Experimental Results.

The analysis of beryl and the preparation of beryllium oxide from beryl are described.

It is shown that hydrated beryllium nitrate can not be dehydrated by evacuating over P_2O_5 at ordinary temperatures.

It is shown that metallic beryllium can not be prepared by:- 1. The reduction of BeO by carbon.

2. The reduction of $BeCl_2$ by hydrogen.

3. The electrolysis of a liquid ammonia solution of hydrated beryllium nitrate.

Itis shown that impure metallic beryllium can be prepared by the electrolytic method of Fichter and Jableczynski and that better results can be obtained by electrolizing in an atmosphere of CO_2.

An investigation has been made on the products of the electrolysis of a liquid ammonia solution of hydrated beryllium nitrate and a similarity to the behaviour of an ammonium nitrate solution in liquid ammonia is observed.

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9. Loc.cit."5".

10. J.Phys.Chem.,Vol.1, p.707 (1896).

11. J.A.C.S., Vol.43, p.1178 (1921),.

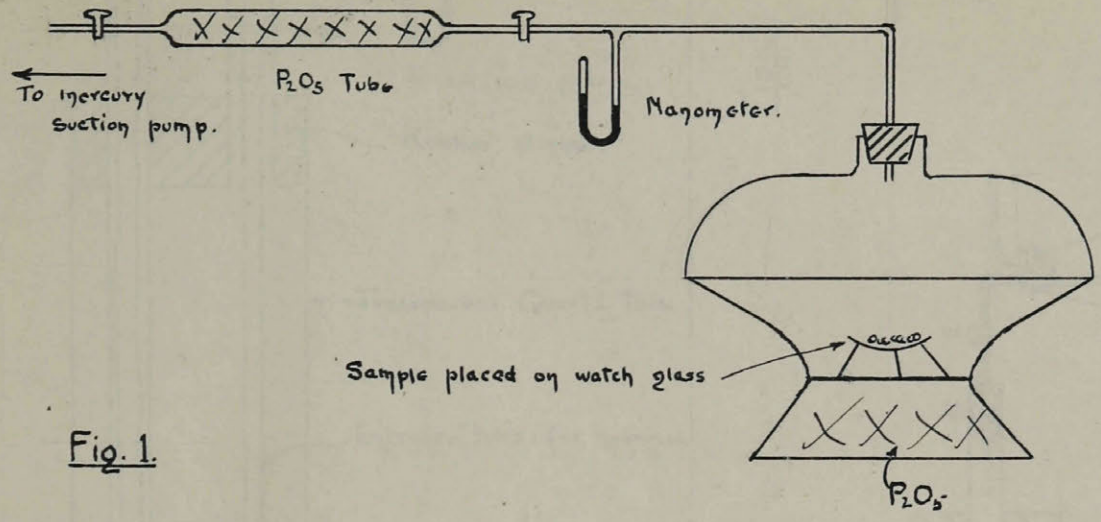
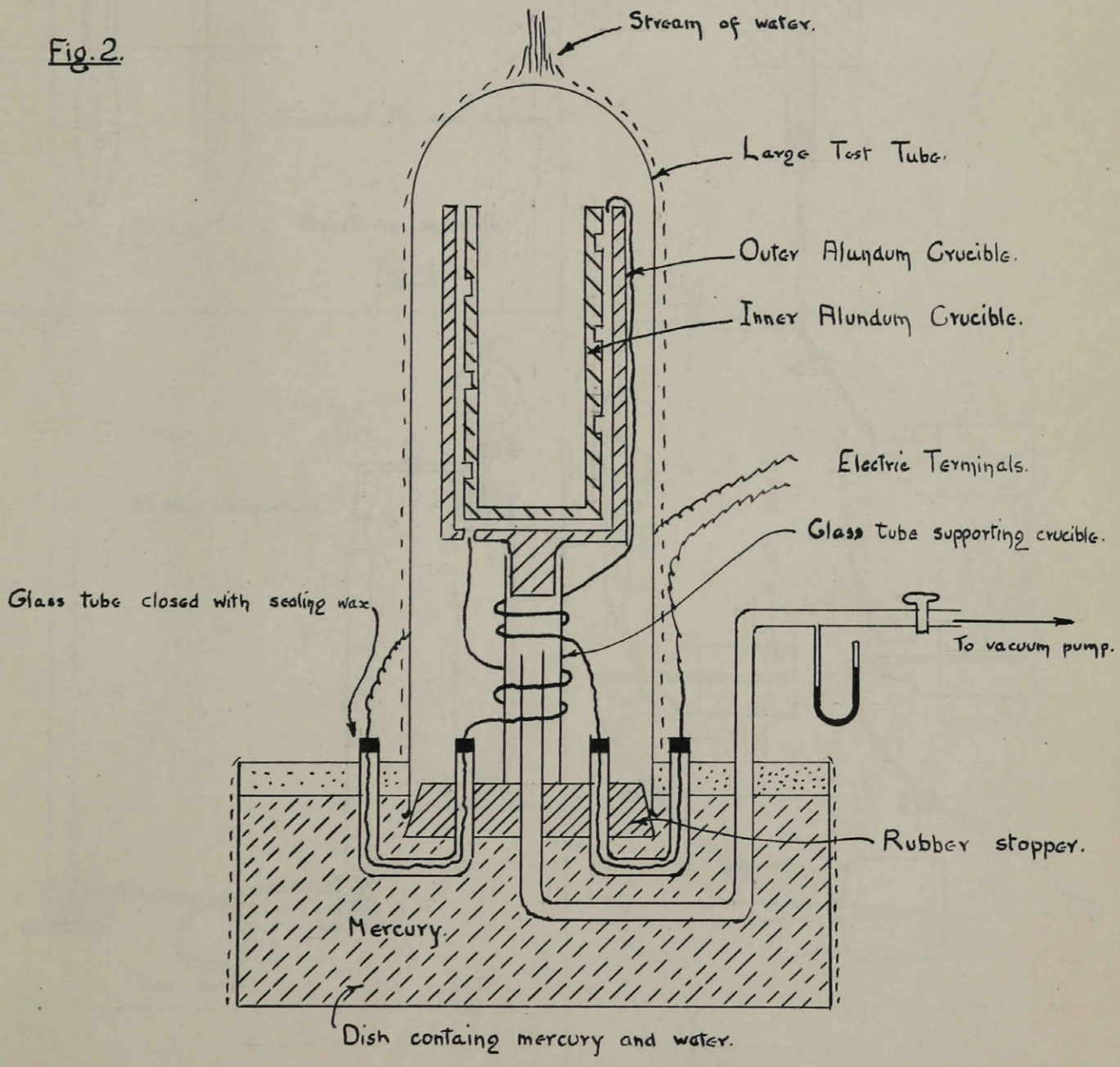

To mercury suction pump.
P_2O_5 Tube
Manometer.
Sample placed on watch glass
P_2O_5

Fig. 1.

Fig. 2.


Stream of water.
Large Test Tube.
Outer Alundum Crucible.
Inner Alundum Crucible.
Electric Terminals.
Glass tube supporting crucible.
Glass tube closed with sealing wax.
To vacuum pump.
Rubber stopper.
Mercury.
Dish containg mercury and water.

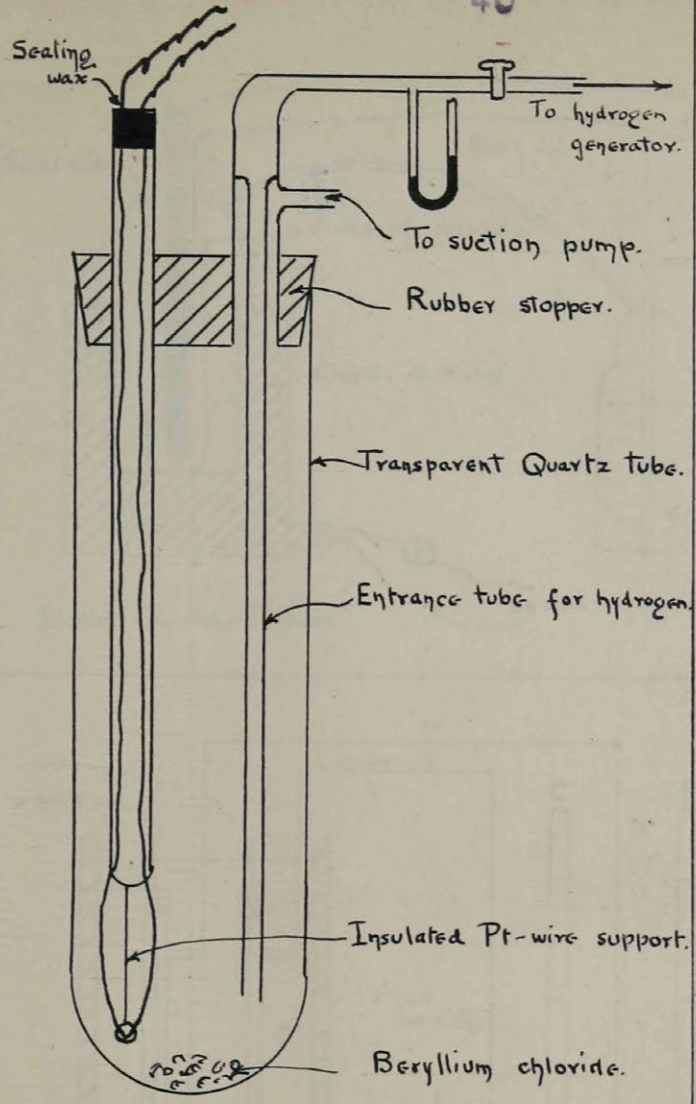


Fig. 4.

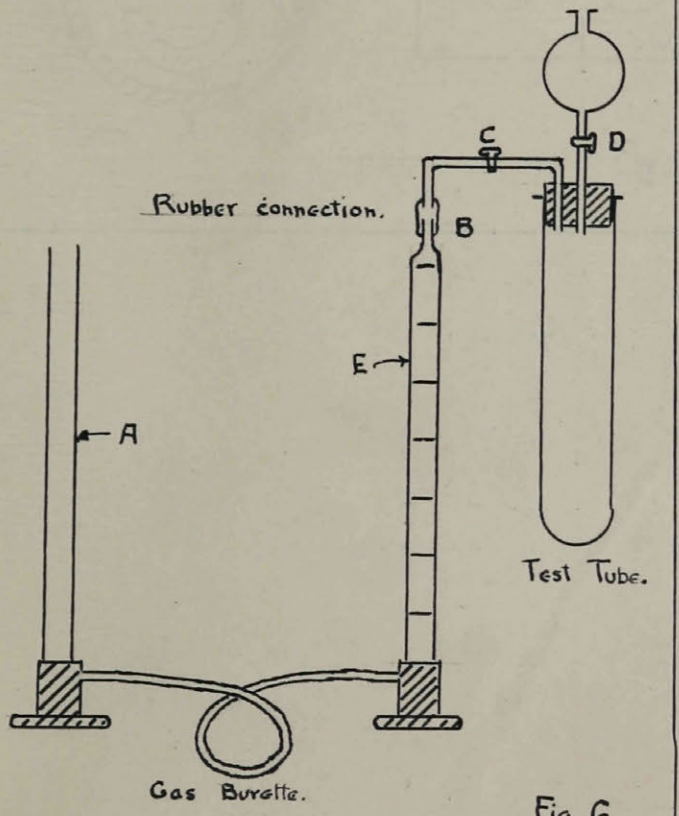
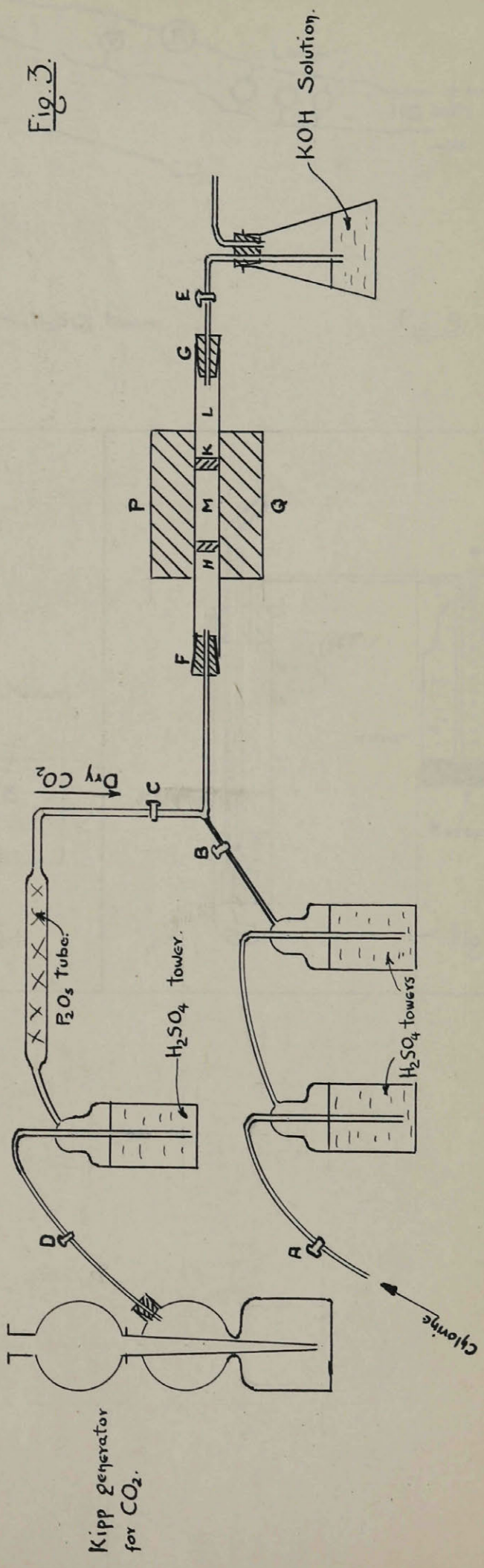


Fig. 6.

Fig. 3.



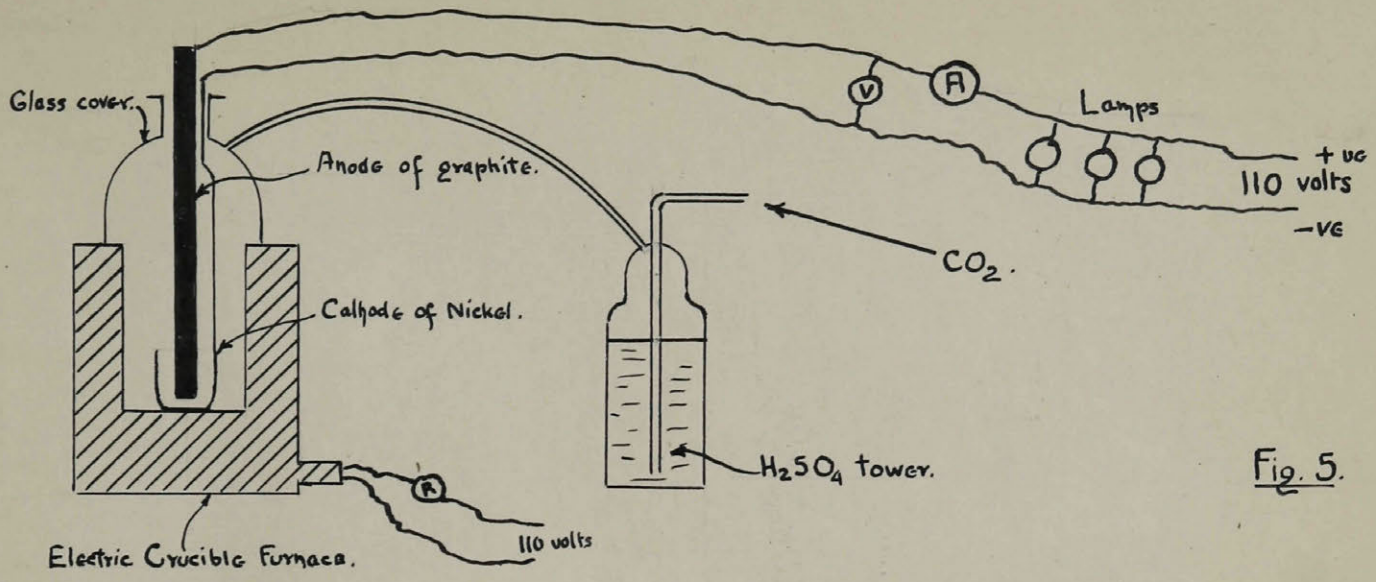


Fig. 5.

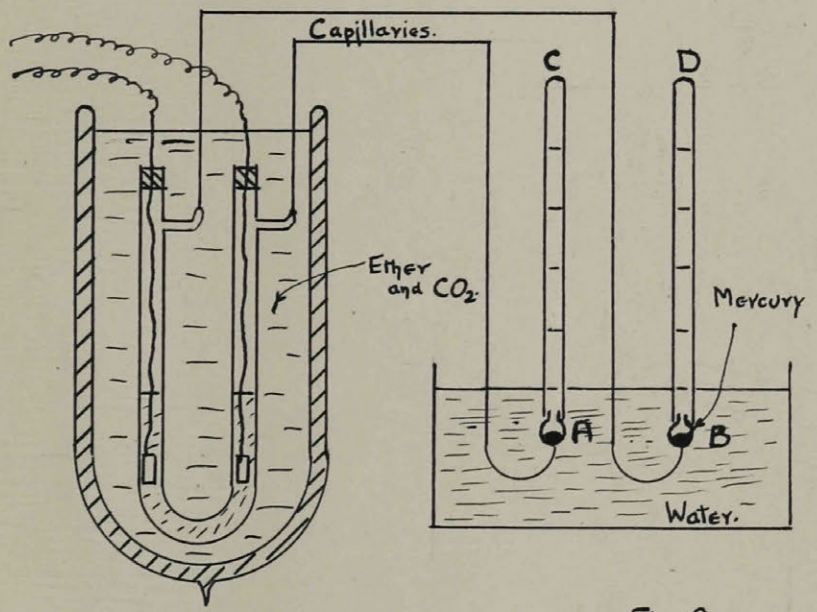


Fig. 8.

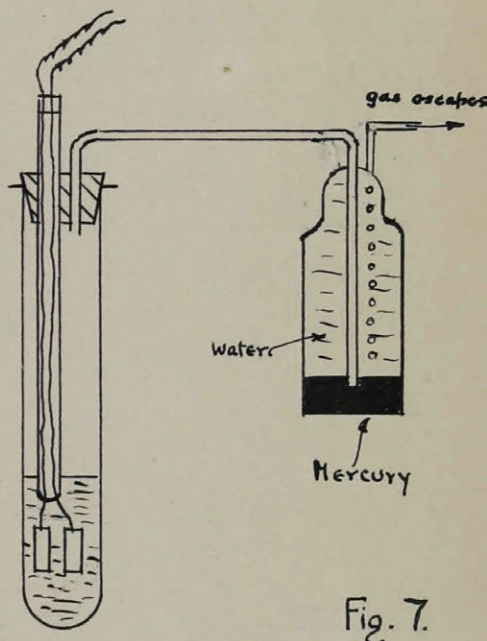


Fig. 7.