BERYLLIUM

THESIS.

"BERYLLIUM".

by

C.Greaves.

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"FOREWORD."

This work was carried out under the direction of Dr.F.M.G.Johnson, who was untiring in devising new methods for the preparation of pure beryllium. The writer takes this opportunity of thanking him for his very many suggestions and his keen interest in the work.

"BERYLLIUM".

GENERAL INTRODUCTION.

Preliminary Remarks. Beryllium offers a vast field for research. Though not generally recognized to be such, it is a common metal, as later remarks will show. Its position in the periodic table, which for a time was a matter of doubt, ensures that it will possess properties of great interest, since it lies on the border line of the non-metals. As the first element of a group its properties are peculiar to itself. Of these properties very little is known. It has been the object of this work to add at least a little to the already small store of information which we have concerning this important metal. To quote Dr.J.W.Richards:-(I) "Beryllium is a metal which will well repay extended metallurgical research and minute physical and chemical study of its many unique properties".

History. Beryllium was discovered in 1787 by L.N. Vauquelin.(2) There is no doubt that the discovery was delayed 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 separated with difficulty. 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, on account of the sweet taste of solutions of salts of beryllium, the name "glucine" for the oxide, from which was derived the name "glucinum". Vauquelin in a subsequent paper adopted the term "glucine", but apparently with no very great enthusiasm. Link,(3) a contemporary of Vauquelin, from the very beginning objected to the name "glucine" because of its similarity to "glycine" already in general use; several other writers of this period also objected to the term "glucine".

Both of the names beryllium and glucinum are still in general use. American, English, and German journals for the most part have adopted the name beryllium, but the International Congress of Chemists has selected the name glucinum. Parsons, who has given much attention to this diversity of opinion concerning the name, says:- "General usage is overwhelmingly in favour of the name beryllium".

Occurrence. It has been estimated (4) 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 (I908) of the percentage composition by weight of the earth's crust - which is given below - we see that beryllium is relatively a common element, the percentage being between that of sulphur and bromine, and yet to the average person it is practically unknown.

F.W.Clarke's Estimate,

Oxygen	49.78	Carbon	.I9
Silicon	26.08	Phosphorus	.II
Aluminium	7.34	Sulphur	.II
Iron	4.II	Barium	.09
Calcium	3.I9	Manganese	.07
Sodium	2.33	Strontium	.03
Potassium	2.28	Nitrogen	.02
Magnesium	2.24	Fluorine	.02
Hydrogen	.95	Bromine	.08
Titanium	.37	All other elements	.48
Chlorine	.2I		

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

One would expect from its place in the periodic table that beryllium would be a very reactive element; 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.(5) It is likely that the percentage 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 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.

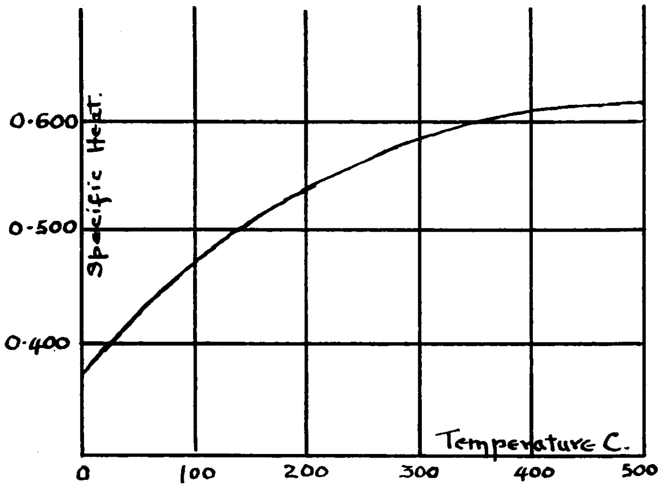
Preparation of Metallic Beryllium. Two steps are involved, firstly the separation of beryllium oxide from the mineral,(6) and secondly the preparation of the metal from beryllium oxide. As a starting material for the preparation of beryllium oxide most investigators have used beryl, since it can be readily obtained in most localities. Beryl is unattacked by any acid so it must first be treated with a flux, or heated in an electric furnace(7) to a high 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"(8), he reduced beryllium chloride with potassium, his product was not very pure. Several other investigators have since prepared it by the same general method, namely the reduction of a halide using either potassium or sodium. Nilson and Pettersson(9) first obtained 87 per cent. and later 94 per cent. Humpidge(IO) in I885 obtained a metal of 99.2 per cent. purity. However it remained for Lebeau(II) in I898 to develop another and simpler method for the preparation of the metal, he electrolysed the fused double fluoride $BeF_2.NaF$ and obtained a metal 99.8 per cent. pure. Later Fichter and Jabloczynski(I2) used a modified method of Lebeau's but it would seem that they did not obtain a product as pure as Lebeau's since they mention the necessity of separating beryllium oxide from the metallic beryllium. 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(I3) is reported by Parsons as being very doubtful. A fourth method has quite recently been patented by two Germans(I4) who claim to have discovered a method for the production of compact metallic beryllium by electrolysing a fused mass containing a mixture of barium fluoride, sodium fluoride and beryllium fluoride at a temperature of I300 degrees C. Very meagre, and probably inacurate, details are given in the patent.

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 said to be a steel grey metal, malleable, easily cold rolled, and capable of taking a high polish; its specific gravity, according to the best results,(I5) which are not in very good accord, is about I.7; it will scratch glass, the hardness being between 6 and 7; there is no definite information concering 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 rigidity, or how it might be strengthened by the addition of other metals. The melting point is considered to be about II00 degrees C. but it has never been determined, as under atmospheric pressure the metal is said to vapourize before the melting point is reached. This may be concluded from the work of Pollok(I6) 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(I7) 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 temperature has a low value but increases to a maximum steady value above 450 degrees C.



Assuming the specific heat to be o.62, the atomic heat = 9.1 by o.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 (I8) of all metals. The latent heat of fusion is abnormal, the value being thought to be somewhere about 300 calories 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 (I9) 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 Parsons (20) of very nearly 9.I, is highly accurate. Berzelius in I8I5 was the first to determine the atomic weight and up to the present day many other determinations (2I) 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.

According to the latest views on atomic structure, all atoms - with the exception of hydrogen - should possess whole number atomic weights. That many atomic weights are not whole numbers is explained by the fact that elements are often mixtures of isotopes, each isotope having a whole number atomic weight. Now the atomic weight of beryllium had been very definitely fixed at 9.I. Hence it was to be expected that beryllium consisted of two or more isotopes. But contrary to expectations G.P.Thomson (22) has found evidence of only one atom of beryllium of atomic weight 9.0. Very recently O.Honigschmid and L.Birckenback (23) have obtained the value 9.0I, a difference of one per cent. from the accepted value. This is certainly remarkable considering the extreme care taken by previous workers. It seems therefore that this value is still a doubtful quantity, the preponderance of the evidence being still in favour of the value 9.I.

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 definite.

Chemical Properties. Beryllium is chemically a metal slightly less basic than magnesium and more basic than aluminium. According to Brauner (24) its chemical nature can be summed up as follows:-

Li: Be = Be:B,

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

Li: Mg = Be:Al = 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 (25) 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, but - if in a finely divided state - it combines with oxygen at high temperatures.(26) It is slightly - or not at all - acted upon by water or steam. It combines directly and easily with fluorine, chlorine and bromine,(27) and with iodine when heated in iodine vapour.(28) At the temperature of the electric furnace it combines with carbon, boron and silicon.(29) It is attacked by dilute hydrochloric acid and dilute sulphuric acid yielding hydrogen, and by concentrated sulphuric acid yielding sulphur dioxide, but it is not attacked by dilute or concentrated nitric acid when cold. It is only slightly acted upon by hot concentrated nitric acid. It is 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(30) replacing the iodine and forming beryllium methyl and beryllium ethyl, beryllium also replaces mercury from mercury methyl and similar compounds.(3I)

The Valence. Previous to I879 some authorities held the view that beryllium was divalent whilst others thought that it was trivalent, but after Mendeleef(32) 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 (33) who conducted a magnificent piece of research on the density of beryllium chloride vapour 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, (34) 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 (35) who argues in favour of trivalency, and Tanatar (36) 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 the 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. If an aqueous solution is evaporated 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. Parsons (37) says:- "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 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 it has been shown by Ley (38) and also Brunner (39) - using the inversion method - that the sulphate, chloride and nitrate of beryllium are less hydrolysed 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 (40) 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 evaporation 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, nitrites 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.(4I) 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. Among those described are the formate, acetate, propionate and several others. Of this unique series of beryllium compounds the one that has been most studied by Lacombe and Urbain and others is the basic beryllium acetate, $Be_4O(C_2H_3O_2)_6$. The chemical and physical properties have been throughly examined and it has proved to be a most important compound. Parsons (42) used it as a means of determining the atomic weight, and Parsons and others have found in it an easy means for the separation and purification of beryllium compounds due to its solubility in either chloroform or glacial acetic acid. It melts at 283° and boils at 330°, sublimes without decomposition, is almost insoluble in water, and is easily soluble in nearly all organic solvents.

Object of the Research. The chemistry of beryllium is at present in its infancy. On reviewing the work of previous investigators it is evident that very little is known about the pure metal, although numerous attempts have been made to prepare it. The very unreliable data, concerning the physical properties that previous workers attribute to the metal, seem to indicate that the metal beryllium would have considerable commercial value if it could be prepared cheaply. It has been the intention of this research to add to the chemical knowledge of this important element

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EXPERIMENTAL.

Raw Material. There were two raw materials used, the mineral beryl and beryllium nitrate. The former was obtained from the Foote Mineral Co. and was powdered to I00 mesh. The beryllium nitrate was obtained from the Welsbach Light Co. and the National Drug and Chemical Co. of Montreal which donated 4 lbs of this material for this work, for which the author wishes to express his appreciation.

Experiments on Beryl.

Analysis. Analyses were made by the method of Parsons and Barnes (I) which is very similar to an ordinary rock analysis. The following is a brief outline of the method. The sample is fused with sodium carbonate and the silica determined. Aluminium, iron and beryllium hydroxides are precipitated by means of ammonia. The beryllium hydroxide is separated by treatment with hot, ten per cent., sodium bicarbonate solution in which it is soluble. The results were in good agreement, the mean of several analyses gave:-

SiO_2,	67.60%
Al_2O_3 (containing a trace of iron)	I7.84%

BeO,	I0.74%
Other Material,	3.82%
	I00.00%

Preparation of Beryllium Oxide from Beryl. The use of beryl as a raw material necessitated as a first step the preparation of beryllium oxide. The most convenient method seemed to be that of Parsons and Barnes.(2) The difficulty however of removing the contents of the nickel crucible was so great that it had to be abandoned. A modification of this method was therefore used of which the following is an outline. 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 evaporating 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 is obtained in the form of a basic carbonate by diluting with water and then passing live steam into the solution. This basic carbonate can then be easily filtered off and washed. If it is desired to remove any adhering salts the basic beryllium carbonate is dissolved in hydrochloric acid and precipitated as beryllium hydroxide by ammonium hydroxide. This process is repeated until the desired degree of purity is reached. On heating either the basic carbonate or the hydroxide the oxide is produced.

By this method a 60 per cent. yield of beryllium oxide was obtained, the process however is long and tedious.

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

1. Beryl was fused with sodium chloride. There was no evidence of any action even after long treatment.

2. Powdered 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 due to the ease with which it is attacked under these conditions.) It was hoped that there might be a selective action on the beryllium, several analyses proved that this did not occur though 20 to 30 per cent. of the beryl was dissolved. The method was therefore abandoned. It may be remarked that the attack of beryl by a solution of sodium hydroxide is not mentioned previously in the literature.

3. It is known that beryllium chloride is produced when a mixture of beryllium oxide and carbon is heated in a stream of chlorine. It was thought that possibly beryllium chloride might be prepared in a similar way when beryl is substituted for the oxide. This was tried. 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. The beryl lost only 7 per cent. in weight after 4 hours treatment, and no indication of the formation of beryllium chloride was observed.

Preparation of Metallic Beryllium.

The methods used in the attempts to prepare the metal may be divided into the two usual classes chemical and electrolytic, as follows:-

A. Chemical Methods:-

I. The reduction of beryllium oxide with carbon in a vacuum.

2. The reduction of beryllium chloride vapour by heated tungsten filament.

3. The reduction of the double flouride $2BeF_2 . NaF$ with metallic sodium.

4. The reduction of beryllium nitrate with metallic sodium in liquid ammonia.

B. Electrolytic Methods:-

I. Electrolysis of solutions of beryllium nitrate in liquid ammonia.

2. Electrolysis of molten double fluorides of sodium and beryllium.

A.I. Reduction of Beryllium Oxide with Carbon.

It was hoped that at a high temperature the following reaction would occur,

$$BeO + C = Be + CO.$$

It seemed probable that equilibrium would be reached in the presence of a very small amount of carbon monoxidee. By working in a high vacuum, and thus removing the CO as formed, beryllium metal would be obtained.

The vacuum furnace employed is shown in figure I. It consists of two alundum crucibles fitting one within the other, the inner one being wound with michrome 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 1000 degrees C. is obtainable.

The carbon used was prepared from sugar. The sugar was heated at a not very high temperature until it was 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 by heating 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, then placed in the vacuum furnace. The temperature was kept just short of the fusing point of the nichrome 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. In no case was there any indication of a reduction of the beryllium oxide. The reaction might proceed at higher temperature, but this is not likely as Lebeau(3) has shown that under such conditions only the carbide of beryllium is formed from a mixture of beryllium oxide and sugar charcoal.

A.2. Reduction of Beryllium Chloride.

R.Edson and D.McIntosh(4) have shown that pure vanadium can be deposited from the vapour of vanadyl chloride on a hot platinum wire in an atmosphere of hydrogen. It seemed probable that beryllium could be obtained by a similar method.

A volatile salt is necessary and the chloride seemed most suitable for this purpose. Nilson and Pettersson found the boiling point to be about 520 degrees C. The chloride was prepared by passing chlorine through a mixture of BeO and sugar charcoal heated in a pyrex tube, care being taken to exclude moisture This method was essentially that of Pollock.(5) The apparatus used is shown in figure 2. The mixture of beryllium oxide and charcoal is 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 the 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 3, and the stopper of the quartz tube with its attachments is immediately placed in position.

The apparatus in which the tungsten wire is heated in an atmosphere of beryllium chloride vapour is shown in figure 3. 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 completes the circuit with the loop 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 cholride 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.

A.3. Reduction of the Double Fluoride with Sodium.

Kruss and Moraht (6) claim that metallic beryllium can be obta ned by the reduction of the double fluoride of potassium and beryllium which they obtained from the evaporation of a solution containing a mixture of potassium and beryllium fluorides. This was probably $BeF_2 . 2KF$.

In this work the action of metallic sodium on $2BeF_2 . NaF$ was investigated. The apparatus is shown in figure 4. A nickel crucible covered with asbestos paper is wound with nichrome wire. This is then placed in a porcelain crucible and the intermediate space lagged with asbestos. The crucibles are then supported on a pipe-clay triangle with legs attached as shown in the diagram. A bell jar and mercury seal ensure the exclusion of air. A stream of CO_2 is led under the mercury and passed out by the glass tube that contains the wire leads. An atmosphere of CO_2 is necessary to prevent oxidation of the sodium

The mixture consisting of the double fluoride and metallic sodium was placed in the nickel crucible and heated by sending a current through the nichrome wire. The $2BeF_2 \cdot NaF$ melted quietly and on further heating a violent reaction took place. The mixture was then allowed to cool. The product contained an excess of sodium. This was removed by dropping by small amounts into a large beaker of water. A certain amount of beryllium hydroxide formation could not be avoided. Some of this was removed by stirring the contents of the beaker and decanting. The other insoluble material settled rapidly. The residue was crushed finely and repeatedly washed with hot water and finally dried.

Under the microscope metallic beryllium was easily observed. The residual powder had a shiny grey appearance. On analysis the percentage of beryllium was found to be 22 per cent. Hence this method yields - as we would expect - a very impure product.

A. 4. Reduction of Beryllium Nitrate by Sodium in Liquid Ammonia Solutions.

It was found that hydrated beryllium nitrate dissolves readily in liquid ammonia to form a milky solution. On allowing it to stand a clear solution can be obtained by decantation. The addition of sodium to this solution, or the mixing of liquid ammonia solutions of sodium and hydrated beryllium nitrate, gave no metal although a reaction occurred.

B. I. Electrolysis of Solutions of Beryllium Nitrate in Liquid Ammonia.

In order to prepare anhydrous solutions in liquid ammonia an attempt was made to remove the water of crystallization of beryllium nitrate. It is likely that if such anhydrous solutions could be obtained they would on electrolysis be more likely to yield the metal then if water was present.

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 5 - 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 NO_2 were seen showing that some decomposition had occurred, this was further verified by the following analyses:-

Original Sample before Treatment.

$Be(NO_3)_2$, by mitrometer 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 only the oxide remains. 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.

In the first experiment liquid ammonia was prepared by a method used by Foote and Brinkley,(7) which is briefly as follows. Commercial ammonia water is warmed up to a maximum temperature of 45 degrees C. and the gas is dried by passing it in succession through three towers of caustic soda (sticks). It 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 gas into a test tube cooled in CO_2 and ether.

After using the above method for sometime it was found more convenient to use commerical ammonia (liquid). This is quite pure enough for most work. It is a poor conductor.

As previously mentioned hydrated beryllium nitrate dissolves in liquid ammonia. The solubility was found to decrease with decrease in temperature as might be expected. In no case was it found possible to dissolve entirely a given sample in liquid ammonia, no matter how much ammonia was used. This is likely due to the separation of beryllium hydroxide.

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 a very low temperature was shown by filtering and then allowing the ammonia to evapourate off. A crystalline white substance separated out, which 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, 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 NO_2, and the residue was beryllium oxide.

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 6 - 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 analysis was difficult.

The apparatus shown in figure 7 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 collect the gases evolved. The mercury levels are 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 be the same at the beginning and the end of the experiment, to ensure this the current is run for about I5 minutes before a reading is taken. Then the voltameter is connected in series and an experiment is 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 - 2I. C.

No of experiment	I	2	3	4	5
Current in amps	0.20	0.I6	0.I6	0.I6	0.7
Voltage in volts	4.6	4.5	4.3	4.5	II0.0
Grs. Cu deposited	0.I50I	0.II86	0.II99	0.I25I	0.I224
A (in c.c.)	43.9	4I.7	42.0	44.3	4I.7
B (in c.c.)	I5.6	I2.I	I2.3	I3.0	I2.8
C	I:2.8I	I:3.47	I:3.43	I:3.46	I:3.27
D	.835	I.006	I.005	I.0I2	.974
E	4.I3	4.05	4.07	4.I2	4.I6

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 grams of hydrogen obtained for one equivalent gram weight of copper.

E = The number of grams of nitrogen obtained for one equivalent gram 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. In order 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 I c.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 - 2I. C.

No. of experiment	I	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
Grs. Cu deposited	.I3I9	.I287	.I208	.I327
A (in c.c.)	44.5	45.6	43.I	45.8
B (in c.c.)	I3.5	I3.65	I2.7	I3.77
C	I:3.3I	I:3.35	I:3.32	I:3.32
D	.967	I.0I5	I.020	.988
E	4.07	4.23	4.I8	4.I3

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.

Cady (8) claims to have prepared the metals silver, copper, and barium by electrolysis of the nitrates of these metals in liquid ammonia. These experiments were repeated. It was found impossible to obtain metallic barium in this way, but good results were obtained for silver.

B.2. Electrolysis of Molten Double Fluorides of Sodium and Beryllium.

Introductory Remarks. The electrolysis of the double fluoride, BeF_2. NaF, to obtain beryllium metal has been successfully carried out by Lebeau.(9) Later, in 1913, Fichter and Jabloczynski(10) claimed to have obtained better results by using the double fluoride, 2 BeF_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. As this method seemed promising a number of experiments were carried out along these lines.

Preparation of Double Fluorides. To prepare a double fluoride such as $2BeF_2$. NaF, a weighed quantity of beryllium oxide - obtained by heating beryllium nitrate in a platinum crucible - was dissolved in hydrofluoric acid and the calculated amount of sodium bicarbonate (or better sodium fluoride) added. Extreme care was taken to ensure complete solution, as beryllium fluoride can not be dehydrated by simple evaporation owing to hydrolysis; however the double fluorides of beryllium can be easily dehydrated. The hydrofluoric acid was now evaporated off and the residue fused in a platinum crucible.

Determination of the Melting Point of $2BeF_2$. NaF.

To determine the approximate melting point of the double fluoride, $2BeF_2$. NaF, 42 grams were prepared and its melting point observed by immersing into it a mercury-quartz thermometer, which had a tightly-fitting platinum cylinder over that part of the thermometer, which was immersed in the melt. A platinum cover was necessary because both quartz and glass are attacked by the double fluoride. The melting point was not well defined, but was about 325 degrees C.

Containing Vessel. In order to obtain a suitable vessel to contain the double fluoride, the action of a typical fluoride was tried on various metals. The fluoride 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. cm. of surface per hour.
Silver	.000146 grs.
Nickel	.000486 "
Copper	.000189 "
Iron	.008030 "

Preliminary Experiments. As a preliminary experiment, to indicate whether results similar to those of previous workers might be obtained, the following experiment was carried out. Twelve grams of $2BeF_2 . NaF$ were kept molten by heating in a platinum crucible with a Bunsen burner. A platinum wire was used as cathode and a graphite rod as anode. Carbon is the only material that can possibly be used for the anode, as all metals (including platinum) are readily attacked, and would therefore contaminate the metallic beryllium. A current of 0.5 amperes at 20 volts was passed through the melt for 5 hours. The metal did not adhere to the cathode, but was distributed throughout the melt. The contents of the crucible were transferred to a beaker and washed repeatedly with large quantities of hot water. At first there was much gas evolved having a distinct odour of acetylene, and the water became slightly alkaline. The residue was washed in alcohol and dried.

Finally there remained a grey powder, which on examination under the microscope showed a metallic appearance, but was also seen to be contaminated with a white solid. On being analysed, by the method described below, it was found to be 30 per cent. beryllium.

Analysis of Beryllium Metal. The following method was used for the analysis of the metallic beryllium obtained in the previous experiment. See figure 8. Weigh about 0.02 grams 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 pressure in tube E is less then atmospheric. Now pipette 2 c.c. of boiled (I:I) hydrochloric acid into the dropping funnel, allow these 2c.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.

Method No. I. As silver had been shown to be very slightly attacked by fluorides, 42 grams. of $2BeF_2$. NaF were melted in a silver crucible, which was made the cathode. The anode consisted of a graphite rod dipping into the molten mass, The double fluoride was kept molten by means of a Bunsen burner, and was stirred with a silver stirrer. The current, which could not be kept constant due to the local polarization, varied from 0.08 to I.40 amperes during 40 hours. The voltage varied from 5 to 50 volts. No metal was deposited on the cathode. The contents of the crucible were transferred to a beaker, then washed and dried as in the preliminary experiment. There remained a greyish white powder, which under the microscope appeared to be metal contaminated with much white material. The material presumably was beryllium oxide.

Knowing that oxygen easily passes through silver, it is probable that a silver crucible tends to increase the production of beryllium oxide. Accordingly in subsequent experiments it seemed better to use nickel, and to avoid the presence of oxygen.

Method No. 2. Twelve grams of the double fluoride were placed in a nickel crucible and this was kept molten in an electric furnace - see figure 9 - A stream of dry CO_2 was kept flowing so that the melt was never in contact with oxygen, A current of 4 amperes was passed for 40 minutes. No metal deposited on the cathode. On treating as before with water the same phenomena were observed as in the previous experiments, but only very slight traces of adhering white solid could be seen under the microscope. On analysis the powder gave 83 per cent. beryllium, but the yield was only 8 per cent. of the theoretical value. 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.

Method No. 3. This was very similar to No.2. The only difference being that a stout platinum wire was used, in place of the graphite rod, as anode. There was considerable loss in weight of the platinum wire and the result was no better than that of No.2.

Method No. 4. A nickel crucible containing I2 grams of $2BeF_2 \cdot NaF$ was fitted tightly into a piece of asbestos board, and the rest of the apparatus constructed as shown in figure IO. To prevent the presence of air a stream of nitrogen was used. The bottom of the Winchester was lagged with asbestos in order to exclude air as much as possible. A current of 4 amperes was used for half an hour and then I.5 amperes for 3 hours. After cooling in a stream of nitrogen the melt was treated as in previous electrolyses. Only a small amount of metal was obtained.

The above experiment was repeated, care being taken to keep the melt just molten. A current of I.5 to 2 amperes was used for 3.5 hours. After cooling, the melt was broken up coarsely and those pieces, apparently rich in metal, selected,.These were crushed to a not very fine powder and washed as before. Under the microscope beautiful crystals of metal were observed and a small quantity of white material. On being analysed the product was found to be 90 per cent. beryllium.

To make certain that this method would give reliable results a third experiment was carried out. An average of 4 to 6 amperes was used for 3 hours. The melt was perhaps kept at a higher temperature than the previous one. The proceedure was otherwise the same. Under the microscope there appeared to be considerable white material. Two analyses gave 62.3 and 59.6 per cent. beryllium.

The Effect of Water on the Impure Metal. In order to get some idea as to whatn the white material might be, some of the impure metal, prepared in the last experiment, was placed in boiling water for 2 hours, then dried. It had the same appearance under the microscope as before treatment, and an analysis gave 64 per cent. beryllium. Hence the treatment with water is not the cause of the impurity. The white material could not have been $2BeF_2$. NaF as this is soluble in water.

Method No. 5. For a diagram of the apparatus see figure II. The apparatus was designed to exclude any possible presence of air. A nickel crucible containing the double fluoride was wrapped with asbestos paper and heated by means of a nichrome wire wound around the asbestos paper. Over the crucible was placed a Woulff bottle which had had the bottom cut off. The Woulff bottle rested in a glass vessel, which contained mercury in the bottom, and above the mercury a continuous stream of cold water flowed. A stream of dry nitrogen continuously passed through the apparatus. An arrangement of two glass tubes, one within the other, and a piece of rubber tubing - see figure II - allowed the anode to be lowered without any air entering the apparatus.

In this experiment another double fluoride, BeF_2. NaF, was tried. About I4 grs were used and a current of one ampere passed through the melt for 6 hours. The melt never became very hot. The conductivity was better than for the double fluoride previously used. The electrolysed mass was broken up and those pieces rejected that contained black pieces of graphite (this had all collected at the top). After washing and drying as before, there remained beautiful iron-grey crystals of metal. No white material could be seen under the microscope. The analysis gave 99 per cent. beryllium.

Another experiment was carried out in an exactly similar way to the above one. A current of one ampere was used for 6 hours. A yield of I5 per cent. beryllium was obtained which analysed 94 per cent. beryllium.

In order to obtain a larger yield the above experiment was repeated with a current of one ampere passing for I2 hours. After treatment the residue consisted almost entirely of white material. Another experiment was continued for I2 hours with the same result. The duration of the electrolysis is therefore an important factor.

Discussion on the Impurities of the Metal. Previous investigators state that the white impurity in the metal is beryllium oxide, and it does not seem possible for it to be anything else. The only substances present during the electrolysis are carbon, nickel, beryllium, sodium, fluorine and nitrogen, hence beryllium oxide can not be produced during the electrolysis. It must therefore be produced by the subsequent treatment with water. Previous investigators also state that beryllium is unattacked by boiling water, and previous work by the writer confirms this statement. It seems therefore that the only explanation possible is that during electrolysis some metallic sodium is produced, and this reacts with water to give sodium hydroxide and hydrogen. The sodium hydroxide would cause the production of insoluble beryllium hydroxide. Sodium reacts violently with cold water, but no such reaction was observed, however it is quite possible that a sodium beryllium (or a sodium nickel) alloy is produced, which does not react with cold water, but does react with hot water.

Analysis of the Gas Evolved from the Product of Electrolysis. On every occasion, when the electrolysed double fluoride is treated with hot water, a large quantity of gas is evolved. Cold water produces little if any gas. An examination of this gas might throw some light on the formation of the white material which always contaminates the metal. Accordingly some freshly electrolysed melt was placed at the bottom of a test-tube - see figure 8. Cold distilled water was poured into tube A of the gas burette until the test tube was full up to tap D. Tap D was then closed and the test-tube heated. Gas was soon given off and IOO c.c. was collected in the gas burette for analysis. The analysis is given below:-

CO_2	0.4 per cent.
Unsaturated hydrocarbons	0.3 " "
O_2	0.5 " "
CO	0.5 " "
H_2	93.5 " "
Unaccounted for	5.0 " "

Apparently there is little or no carbide produced and hence this cannot be the cause of the production of beryllium hydroxide.

Analysis of the Impure Metal. Another electrolysis was carried out in the same manner and with the same apparatus as in the other experiments of Method No. 5. A current of I ampere at 60 volts for 4.5 hours was used, and o.23 grams of impure metal was obtained, which under the microscope evidently contained some beryllium oxide. A complete analysis of this impure metal was carried out as follows.

On one sample a nickel determination is made by the dimethylglyoxime method. Another sample of 0.05 grams is placed in a dry test-tube and a measurement of the hydrogen evolved by hydro-hlori chloric acid is made in the usual way. From this the percentage of metallic beryllium can be calculated. The contents of the test-tube are then filtered through a Gooch, washed, dried and weighed. This gives the quantity insoluble in hydrochloric acid. Beryllium hydroxide is then precipitated from the filtrate by ammonia, filtered, washed, ignited and weighed as BeO. If from the total BeO thus obtained an allowance be made for the metallic beryllium as determined above the quantity of BeO actually present can be calculated. The results are given below:-

I. Be (by hydrogen evolved)---------------- - 67.5%
2. Be (by precipitation with NH_3)------------(76.0%)
3. Undissolved by HCl-------------------------- 2.8%
4. Ni-- 0.4%
5. BeO (calculated from I and 2)------------23.4%
6. Unaccounted for----------------------------- 5.9%
I00.0%

The material which is insoluble in hydrochloric acid is carbon (derived from the anode). It is very probable that the beryllium oxide is comtaminated with very appreciable quantities of beryllium hydroxide, which would account for the 5.9 per cent. left over.

<u>Method No. 6.</u> Since it is probable that the production of sodium is the cause of the impurity, it did not seem that the exclusion of air was necessary, so an experiment was carried out in the presence of air. A product of 95 per cent. beryllium was obtained. However there is a possibility that the metal itself may be oxidised during the electrolysis, and therefore it is safer to work in an inert atmosphere.

<u>Method No. 7.</u> With an idea of minimizing the anode effect, by using a larger anode surface, the following experiment was

carried out. An apparatus similar to the one described in Method No.5 was used. The nickel crucible was replaced by a graphite crucible which was made the anode. A platinum rod was used as cathode. These alterations involved changes in the electrical connections. The electrolysis was carried on in an atmosphere of nitrogen for 4 hours, a current of 1 ampere being used. The anode effect was by no means illiminated and the product was no purer than in previous experiments.

Miscellaneous Experiments.

1. In order to detect if possible the presence of a sodium alloy which is unattacked by cold water, one sample of $BeF_2 \cdot NaF$- after it had been electrolysed--was kept in contact with cold running water for several days. The residue of impure metal was placed in a quartz tube which was evacuated to a pressure of 0.01 m.m. of mercury. The end of the tube containing the material was heated with a Bunsen burner. No sodium could be distilled off.

2. An attempt to fuse beryllium was made. Some of the 95 per cent. metal was placed in a boat made of beryllium oxide, and the boat placed in a quartz tube which was evacuated to a pressure of 0.01 m.m. of mercury. The tube was then heated with a Meker burner, but no evidence of fusion was observed.

Discussion of Results. The above experiments on the electrolysis of double fluorides indicate that it is possible, under the right conditions, to prepare metallic beryllium of 99 per cent.

purity. If the conditions are not exactly correct the metal will be contaminated with beryllium oxide, this has always been the experience of previous investigators. The exclusion of oxygen during the electrolysis does not prevent the metal from being contaminated with beryllium oxide, and the presence of oxygen during the electrolysis does not hinder the production of metal of 95 per cent. purity. It is evident therefore that the contamination of the metal must be due to the treatments after the electrolysis. The impurity most likely is due to an alloy of sodium which reacts with water. No positive evidence of the presence of sodium has been discovered, although its presence has not not been disproved. The fact that only hydrogen is evolved, when the electrolysed product is treated with water, strongly confirms this possibility.

The previous experiments also show that the double fluoride BeF_2. NaF gives better results than $2BeF_2$. NaF.

The Determination of Melting Points of Mixtures of Beryllium Fluoride and Sodium Fluoride.

Introduction. It is known that at a high temperature beryllium combines with carbon, and that at a dull red heat, it alloys with nickel. It is also suspected that beryllium combines with oxygen at temperatures above 100 degrees C. It is evident therefore that, in carrying out an electrolysis to obtain the metal by any of the previously described methods, the fused fluoride should be kept at as low a temperature as possible. This can best be ascertained by determining the melting point curve of mixtures of sodium fluoride and beryllium fluoride. The lowest temperature can then be obtained from the curve.

Very little is known about the double fluorides of beryllium. Most of the previous work has been done by Marignac(11) and Lebeau(12). These investigators have shown that the double fluoride $BeF_2 . NaF$ is formed, by evapo~~u~~rating a solution of the constituents and by then analysing the crystals thrown down. A determination of the melting point curve of mixtures of beryllium fluoride and sodium fluoride would also indicate how many double fluorides are formed from these two substances. This determination would therefore serve two purposes, it is however a difficult problem, and previous investigators have so far avoided it.

Experimental Work.

Preparation of the Melting Point Mixture. Since the supply of beryllium salts is limited only small amounts could be used in this work. Accordingly only mixtures of about I5 grams were prepared at one time. To do this, beryllium oxide was first prepared by heating hydrated beryllium nitrate until it was of constant weight, and since beryllium oxide is very hygroscopic it was kept in a closed weighing bottle. An accurately weighed quantity of this substance (about 5 grams) was placed in a platinum basin. This was covered with a sheet of platinum foil and hydrofluoric acid added. On warming, all of the beryllium oxide goes into solution. After diluting with water an accurately weighed quantity of sodium fluoride was added and stirred until all was dissolved. The solution was then evapourated to dryness in a water bath and the solid removed to the platinum vessel in which the melting point was to be determined. The double fluoride was now fused in this vessel, in order to drive off the last trace of hydrofluoric acid, cooled and weighed. The weight of the fluoride was inappreciably less than the calculated weight, proving that very little loss had occurred during the operations.

The first mixture contained a large percentage of beryllium fluoride. After the melting point of this mixture had been determined a weighed quantity of sodium fluoride was added, and the mixture fused and stirred. The melting point of this new mixture was then taken. This process was repeated as long as was desired.

The only suitable material, that is not attacked by fluorides at the temperatures used, is platinum. Hence the mixture was placed in a platinum container and the bulb of the thermometer was covered with an air-tight jacket of platinum. The thermometer was so arranged that it could be used as a stirrer.

The Method of Taking the Melting Points. As such a small quantity of the mixture was used, the most exact method of taking the melting point was by constructing a cooling point curve for each mixture. From this curve the melting point was easily read off. Accordingly the mixture was heated until quite liquid and, whilst it was cooling, the temperature was read at intervals of I0 seconds. A nitrogen-filled, mercury-glass thermometer, whose range was from 0 to 550 degrees C. was used. The thermometer was carefully calibrated by taking the boiling points of sulphur, diphenylamine and water. For every reading a stem correction was also made.

The Apparatus Used. See figure I2. The mixture, of which the cooling curve is to be determined, is placed in the platinum vessel A. A is then placed in position in the pyrex test-tube B. The test-tube is then placed in a continuously stirred bath of a mixture of potassium nitrate (54.5%) and sodium nitrate (45.5%) . This mixture melts at about 220 degrees C. and can be easily heated to 550 degrees C. The nitrate mixture is contained in a copper vessel C, which is surrounded with asbestos, and heated by a Bunsen burner.

To take a cooling point curve the bath is heated until the mixture in A is quite liquid. A small flame is kept under the bath to prevent too rapid cooling. The thermometer is rotated between the operator's fingers and the temperature is observed every IO seconds. The last readings are taken without rotating the thermometer as the mixture is then solid.

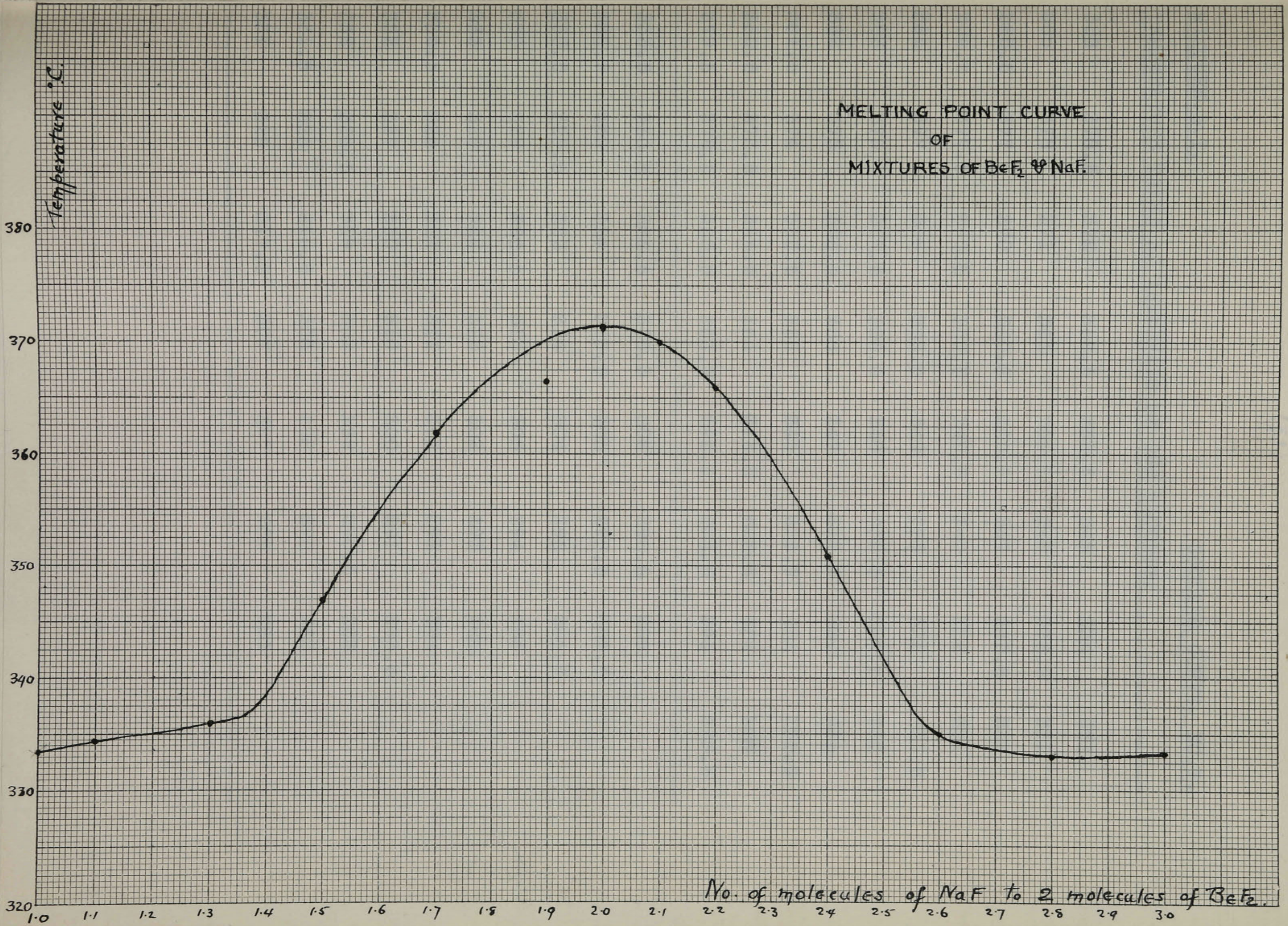
Results. In the following pages there is given a table of the melting points of mixtures of BeF_2 and NaF, and the melting point curve corresponding to this table. Tables of the temperatures of the cooling curves are also given and the corresponding cooling curves.

Table of Melting Points of Mixtures of BeF_2 and NaF.

Mixture NO.	BeF_2 used. in grams.	NaF added. in grams.	A.	B.	m.p.°C.
B.I.	II.87	5.289	2:I	.272	333.5
B.2.		.523	2:I.I		334.5
B.3.		I.046	2:I.3		336
B.4.		I.046	2:I.5		347
B.5.		I.046	2:I.7		362
B.6.		I.046	2:I.9		366.5
C.I.	II.897	I0.559	2:I.99I	.247	37I.5
C.2.		.57I	2:2.I		370
C.3.		.524	2:2.2	.35I	366
C.4.		I.033	2:2.4		35I
C.5.		I.033	2:2.6		335
C.6.		I.033	2:2.8		333
C.7.		I.033	2:3.0		333.5

A = The ratio of the no. of molecules of BeF_2 to the no. of molecules of NaF.

B = Loss in grams of the mixture used.


MELTING POINT CURVE
OF
MIXTURES OF BeF2 & NaF.
Temperature °C.
380
370
360
350
340
330
320
1·0
1·1
1·2
1·3
1·4
1·5
1·6
1·7
1·8
1·9
2·0
2·1
2·2
2·3
2·4
2·5
2·6
2·7
2·8
2·9
3·0
No. of molecules of NaF to 2 molecules of BeF2.

MIXTURE.B.I. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

388	378.5	372	362.5	352.5	343	334	331
386	378	371	361	351.5	342	333.5	331
385.5	377	370	360.5	350.5	341	332.5	331
384.5	377.5	369.5	359.5	349.5	340	332	331
384	377	369	358.5	349	339	332	331.5
383	376	367.5	356.5	348	338.5	331.5	332
382	375	366.5	356	347	337.5	331	332
381.5	374	365.5	355	345	336.5	331	332.5
380.5	373.5	364.5	354	344.5	335.5	331	333
379.5	372.5	363.5	353.5	343.5	334.5	331	333.5

333.5	330.5	324.5	316.5	306	296.5	288
333.5	330	324	315.5	305	295.5	387.5
333.5	329.5	323	314	304	295	286.5
333	329	322.5	313	303	294	286
333	328	322	312	302	293	285
332.5	328	321	311	301	292	284
332	327	320	310	300	291	283.5
332	326.5	319	309	299	290.5	283
331.5	326	318.5	308	298	290	282
331	325	317.5	307	297	289	281

MIXTURE.B.I. COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

372	363	352	34I	333	329	329	325
37I.5	362	35I	340.5	332	329	329	324
37I	36I	350	340	33I	329.5	329	324
370	359.5	349	339	330.5	329.5	328.5	323
369	358	348	338	330	329.5	328	322
368	356.5	347	337	329	329.5	328	32I.5
367	356	345	336.5	328.5	329.5	327	320.5
366	355	344	335.5	328	329.5	327	320
365	354	343	334.5	328	329.5	326	3I9
364	353	342	334	329	329.5	326	3I8.5

3I8	3I0	303	297	292
3I7	309	302.5	296.5	29I
3I6	308	302	296	
3I5	307.5	30I	295.5	
3I4.5	307	300.5	295	
3I3.5	306.5	300	294	
3I3	306	299.5	293.5	
3I2	305	299	293	
3II	304.5	298	292.5	
3I0	304	297.5	292	

MIXTURE.B.2. **COOLING CURVE. NO.I.**

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

381	374.5	366	355	345	336	332	332.5
380	374	365	354	344	335	332	332.5
380	373	364	353	343	334	332	333
379	372	363	352	342	333.5	332	333
378	37I	362	35I	34I	333.	332	333
377	370	36I	350.5	340	332.5	332	333
377.5	369.5	360	349.5	339.5	332.5	332	333.5
377	369	359	348	338.5	332.5	332	333.5
376	367.5	358	347.5	338	332.5	332	333.5
375	366.5	356	345.5	337	332	332	334

334	334	33I	327	320	307	293	282
334	333.5	33I	326.5	3I9	305	292	28I
334	333.5	330.5	326	3I8	304	290.5	
334	333	330	325	3I7	302	289	
334	333	329.5	325	3I5	30I	288	
334.5	333	329	324	3I4	299.5	287	
334.5	332.5	328.5	323	3I2.5	298	286	
334.5	332	328	322.5	3II	297	285	
334	332	328	322	309.5	295.5	284	
334	33I.5	327.5	32I	308	294	283	

MIXTURE. B. 2.

COOLING CURVE. NO. 2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

382	373.5	364	352.5	342.5	332.5	331.5	333
381	372.5	362	351.5	341.5	331.5	331.5	333
380	371.5	361	350.5	340.5	331	331.5	333
379	370.5	360	349.5	339	331	331.5	334
378.5	369.5	359	348.5	338	331	332	334
377.5	368.5	358	348	337	331.5	332	334
377.5	368	356.5	347	336	332	332	334
376.5	367	355.5	345	335	332	332.5	334
375.5	366	354.5	344	334	332	332.5	334
374.5	365	353.5	343	333	332	333.5	334

333.5	331	326	317	306	295.5	285.5
333.5	330.5	325.5	316	305	294.5	284.5
333.5	330	325	315	304	293.5	283.5
333.5	329.5	324	314	303	292.5	282.5
333	329	323	313	302	291.5	281.5
333	329	322	312	301	290.5	
332.5	328.5	321	310.5	299.5	289.5	
332	328	320.5	309.5	298.5	288.5	
332	327	319.5	308.5	297.5	287.5	
331.5	326.5	318.5	307.5	296.5	286.5	

MIXTURE.B.3. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

376	364	35I.5	340	328	3I8	323	33I.5
375	362.5	350	339	327	3I7	324	332
374	36I.5	349	338	326	3I6	326	332
372	360.5	348	336	325.5	3I5	327	332
37I	359.5	347	335	325	3I4	328	332
370	358	345	334	323	3I3	329	332
369	356	344	333	322	3I3	330	332
368	355	343	332	32I	3I4	330	33I.5
366	354	342	33I	320	3I8	33I	33I
365	353	34I	330	3I9	32I	33I	33I

330.5	323	3I3.5	304	292
330	322	3I2.5	303	29I
329	32I	3II.5	302	290
328.5	320	3II	30I	288.5
328	3I9	3I0	299.5	287.5
327	3I8	309	298.5	286
326	3I7	308	297	285
325.5	3I6	307	296	283.5
324.5	3I5	306	295	282.5
324	3I4.5	305	293.5	28I

MIXTURE. B. 3. COOLING CURVE NO. 2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

382	372.5	362	350	338	327	334	336	335.5
380.5	371	361	349	336.5	326	334	336	335.5
379.5	370	359.5	347.5	335.5	326	334.5	336	335
378.5	369	358	345.5	334.5	326	335	336	335
378	368	356	344.5	333.5	328	335	336	334.5
377.5	367	355	343.5	332.5	329	335.5	336	334.5
376.5	366	354	342	331.5	331	336	336	334
375.5	365	353	341	330.5	332	336	336	334
375	364	352	340	329	332.5	336	336	333.5
374	363	351	339	328	333	336	336	333

333	328	320.5	305	288
332.5	327	319.5	303	287
332	326.5	318.5	301	285
331.5	326	317	299.5	284
331	325.5	316	298	282.5
330.5	325	314	296	281
330	324	312.5	294.5	
329.5	323.5	311	293	
329	322.5	309	291	
328.5	321.5	307	289.5	

MIXTURE. B. 4. COOLING CURVE NO. 1.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

395.5	384.5	374.5	364	352	343	347	342
394.5	384	374	363	351	344	347	342
393	382.5	373	362	350	345	345	341
392	382	372	361	349	345	345	341
391	380.5	371	360	348	345	345	340
390	379	369.5	358.5	347	345	344	340
389	378	368.5	356.5	345	345.5	344	339
388	377	367.5	355.5	344	347	344	339
386	377	366	354.5	343	347	343	338
385.5	375.5	365	353	342	347	343	338

337	33232	326	320	315	308.5	299.5
336	331	325	319.5	314.5	308	298.5
336	330	325	319	314	307	297.5
335	330	324	319	313.5	306	296
334	329	324	318	313	305	295
334	329	323	317.5	312	304	294
334	328	322.5	317	311.5	303.5	293
333	327.5	322	317	311	302.5	292
332.5	327	321.5	316	310	301.5	291
332	326.5	320.5	315.5	309.5	300.5	

MIXTURE.B.4. COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

381	370	358	344.5	335	342	344	339
380	369	356	343.5	334	343.5	343.5	338
379	368	355	342.5	333	344	343	337.5
378	367	353.5	341.5	331.5	345	343	337
377	365.5	352	340	330.5	345	342	336.5
376.5	364	351	339	330	345	342	336
375	363	350	338	331	345	341	335.5
374	362	349	337	334	345	340	335
373	361	348	336.5	337	344.5	340	334
371.5	360	345.5	336	340	344	339	334

333	327	322	317.5	309.5	296.5	283
332.5	326.5	321.5	317	308	295	282
332	326	321	316	307	294	281
331.5	325	320.5	315.5	306	292	
331	325	320	315	305	291	
330	324	319.5	314	303.5	289.5	
329.5	324	318.5	313	302	288	
329	323	318.5	312	301	287	
328	323	318	311.5	299	285.5	
328	322.5	318	310.5	298	384.5	

MIXTURE.B.5. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

378	367.5	356	36I	359	355	349.5	340.5
377.5	366	355	36I	359	354.5	349	339.5
376	365	354.5	36I	359	354	348	339.5
375	364	355	360.5	358	353.5	347.5	339
374	363	356	360.5	358	353	347	338
373	362	358	360.5	358	352	345	337
372	36I	359	360	356.5	352	344.5	336
37I	360	360	360	356	35I	344	335
369.5	359	360	360	355.5	350.5	343	334
369	358	359.5	359.5	355	350	342	333

332.5	322	3I2.5
33I.5	32I	3II
330.5	320	3I0
329.5	3I9	309
328.5	3I8	308
327.5	3I6.5	307
326	3I6.5	306
325	3I5.5	305
324.5	3I4.5	304
323.5	3I3	303

MIXTURE. B.5. COOLING CURVE. NO. 2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

393	379	367.5	355	362	361	356.5	349
392	378	366	355	362	360.5	356	348
390.5	377	365	355	362	360.5	355	347.5
389	377	369	355.5	362	360	354.5	345.5
388	375.5	362	356	362	360	353.5	345
385.5	374	361	358	362	360	353	344
384	373	360	359	362	359.5	352	343
383	372	358	359.5	362	359	351.5	342
382	370	356.5	x 360	361.5	358.5	350.5	341
380.5	369	355.5	361.5	361	358	349.5	340

339	328	316	305	293.5	283
338	327	315	303.5	292.5	281.5
337	326	314	302.5	291.5	
336	325	313	301	290.5	
335	323.5	311.5	300	289	
334	322	310	299	288	
333	321	309	298	287	
332	320	308	297	286	
330.5	318.5	307	296	285	
329	317.5	306	294.5	284	

MIXTURE.B.6. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

393	386.5	378	368.5	358	345	366	365.5
392	386	377	367.5	355.5	344	366	365
392	385	377	366.5	354	343.5	366	365
39I.5	384	376	365.5	353	343	366	365
39I	383	375	364.5	352	342.5	366	364.5
390.5	382	374	363.5	35I	35I	366	364.5
390	38I	373	362	350	358	366	364
389.5	380.5	372	36I.5	349	362	366	364
389	379.5	37I	360	348	364	366	363.5
388.5	378.5	370	359	347	365	365.5	363

363	359	35I	338.5	324
362.5	358	350	337	322
362	356.5	349	336	320.5
362	356	348	334.5	3I9.5
36I.5	355.5	347	333	3I8.5
36I	355	345	33I	3I7
360.5	354	344	329.5	3I5.5
360	353	343	328.5	3I4
359.5	352.5	342	327	3I3
359.5	35I.5	340	325.5	3II

MIXTURE.B.6. COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

392	380	369	359	366.5	365.5	363	359
39I	379	367.5	356.5	366.5	365.5	362.5	358
390	378	366.5	355	366.5	365	362	356.5
389	377	365.5	354	366.5	365	362	356
386.5	377	364.5	353	366.5	364.5	36I.5	355.5
386	375	364	356	366.5	364	36I	355
384.5	374	363	360	366	364	360.5	354
383.5	372.5	362	363	366	363.5	360	353.5
382	37I.5	36I	365	366	363.5	360	353
38I	370	360	366	365.5	363	359.5	352.5

34I	328	3I4.5
340	327	-
338.5	325.5	-
337.5	324	-
336	323	309
335	32I	-
334	320	-
332	-	-
330.5	-	304.5
329	-	

MIXTURE.C.I. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

375	374.5	375	373	370.5	372	372	37I
375	374.5	375	373	370.5	372	372	37I
375	374.5	375	372.5	37I	372	372	37I
375	374.5	375	372	37I	372	372	37I
375	375	374.5	372	37I.5	372	372	37I
375	375	374.5	37I.5	37I	372	37I.5	37I
375	375	374	37I	37I.5	372	37I.5	37I
375	375	374	370.5	37I.5	372	37I.5	37I
374.5	375	374	370.5	372	372	37I.5	37I
374.5	375	373	370.5	372	372	37I.5	370.5

370.5	369	368	366	362.5	355.5	342	329
370.5	369	367.5	365.5	362	355	34I	328
370.5	369	367.5	365	36I.5	354	339	326.5
370	369	367	365	36I	352.5	338	325.5
370	368.5	367	364.5	360	35I.5	336.5	324
370	368.5	366.5	364.5	360	350.5	335	323
370	368	366.5	364	359	349.5	333.5	322
370	368	366	364	358.5	347.5	332.5	32I
369.5	368	366	363.5	358	345	33I	320
369.5	368	366	363	356	343.5	330	3I9

MIXTURE.C.I. **COOLING CURVE. NO.2.**

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

383.5	378.5	373	37I.5	37I	37I	370	368
383	378	372	37I.5	37I	370.5	369.5	368
382.5	377.5	37I	37I.5	37I	370.5	369.5	368
382	377	37I.5	37I.5	37I	370	369	367.5
382	377	370.5	37I.5	37I	370	369	367.5
38I	376	37I	37I.5	37I	370	369	367
380.5	375.5	37I	37I.5	37I	370	369	367
379	375	37I	37I.5	37I	370	369	367
379	374	37I.5	37I.5	37I	370	368.5	366.5
379	373.5	37I.5	37I	37I	370	368.5	366

366	363	360	354.5	347.5	335	324	3I5
365.5	363	359.5	354	345	334	323	3I4
365	362.5	359	353.5	344	333	322	3I3.5
365	362.5	359	353	343	332	32I	3I2.5
365	362	358	352	342.5	33I	320	3I2
364.5	362	358	35I.5	34I	330	3I9	3II
364	36I.5	356.5	350.5	340.5	328.5	3I8	3I0
364	36I	356	350	339	327.5	3I7	309.5
363.5	36I	355.5	349	338	326.5	3I6.5	309
363.5	360.5	355	348.5	337	325	3I6	308

307.5	305.5	303	302	300	298.5	297
307	304.5	303	30I	299.5	298	
306	304	302	300.5	299	297.5	

MIXTURE.C.2. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

393	384	377.5	370.5	369	370	369	368
392.5	383.5	377	369.5	369	370	369	368
392	383	376.5	369	369.5	370	369	368
39I	382	375.5	368	369.5	370	369	368
390	38I	375	368	369.5	370	369	368
389	380.5	374	367.5	369.5	369.5	369	368
388.5	380	374	368	370	369.5	369	367.5
386.5	379	373	368	370	369.5	369	367.5
386	378	372	368.5	370	369.5	368.5	367
385	377.5	37I	369	370	369.5	368.5	367

367	365	362	358	352	345	339
367	365	362	356.5	35I	344.5	338
367	365	36I.5	356	35I	344	337.5
366.5	364.5	36I	355.5	350	343	337
366.5	364	36I	355	349	343	336.5
366	364	360	354.5	349	342	336
366	363.5	360	354	348.5	34I	335
365.5	363.5	359.5	353.5	348	340.5	334.5
365.5	363	359	353	347.5	340	334
365.5	362.5	358	352	347	339	333

MIXTURE.C.2. COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

378.5	375.5	370	369.5	369	368	366.5	364.5
378.5	375	370.5	369.5	369	368	366.5	364
378	374.5	370.5	369.5	369	368	366.5	363.5
378	373	370	369.5	369	368	366	363
377.5	373	370	369.5	369	367.5	366	362.5
377.5	372.5	370	369.5	369	367.5	366	362.5
377	372	369.5	369.5	368.5	367.5	365.5	362
377	37I.5	369.5	369.5	368.5	367	365	362
376.5	37I	369.5	369.5	368.5	367	365	362
376	370	369.5	369	368	367	364.5	36I

36I	353	344	334
360	352	343	333
360	35I.5	342.5	332
359	35I	34I.5	33I.5
358.5	35I	340.5	
358	350	339.5	
356	349	338.5	
355.5	348	337.5	
354.5	347	336.5	
354	345	335.5	

MIXTURE.C.3. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

378
377.5
377
376
375
374.5
373
372
37I
270
369
368
367
366
365
365
365
365.5
365.5
365.5
365.5
365.5
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363.5
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362.5
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36I.5
36I.5
36I
360.5
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358
356.5
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355.5
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354.5
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353.5
353
352.5
352
35I
350.5
349.5
349
348
347
345.5
344.5
343.5
343
342
34I
340
339
338.5

338
337
336
335
334
333.5
332.5
332
33I
330
329.5
329
328
328
327
326.5
326
325.5
325
324.5
324
323.5
323
322
32I
320
3I9
3I8
3I7
3I6
3I4.5
3I3.5
3I2
3I0.5
309
308
306.5
305
304
302.5
30I

MIXTURE.C.3. COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

382	375.5	367	366	365
387	374.5	366	366	
380	374	365	366	
379.5	373	365.5	366	
379	372	366	366	
378	37I	366	366	
377	370	366	366	
377	369	366	366	
377	368.5	366	366	
376	367.5	366	366	

MIXTURE.C.4. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

373	369	363	355.5	35I	350.5	348.5	344
372.5	368.5	362.5	355	35I	350.5	348	344
372.5	367.5	362	354	350	350	348	344
372	367	36I	353.5	350	350	347	343.5
37I.5	366.5	360	353	349.5	350	347	343
37I	366	359.5	353	350.5	350	347	343
370.5	365.5	359	352.5	35I	349.5	345.5	342.5
370.5	365	358	352	35I	349	345	342
370	364.5	356.5	35I.5	350.5	349	344	34I.5
369.5	364	356	35I	35I	348.5	344	34I

34I	337.5	334	332	330
340.5	337	334	332	330
340	337	333.5	332	330
340	336.5	333.5	33I.5	330
339.5	336	333	33I.5	329.5
339	335.5	333	33I	329.5
339	335.5	332.5	33I	329
338	335	332	33I	329
338	335	332	330.5	328.5
338	334.5	332	330.5	328.5

MIXTURE.C.4. COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

374	375	37I	366	360	35I	350.5	348
374	375	37I	365.5	359	35I	350.5	348
374.5	375	370	365	356.5	35I	350.5	347.5
374.5	374	370	364.5	356	350.5	350	347
375	374	369	364	355	350.5	350	345.5
375	373	368.5	363	354.5	350.5	350	345.5
375	373	368	362	353.5	350	349.5	345
375	372	367.5	36I.5	353	350	349.5	344.5
375	372	367	36I	352	350	349	344
375	372	366.5	360.5	352	350.5	348.5	343.5

343	338.5	334	33I.5	329	324	3I7
342.5	338	334	33I	328.5	323.5	3I6
342	337.5	333.5	33I	328	323	3I5
34I.5	337	333	330.5	328	322.5	3I4
34I	337	333	330.5	327.5	322	3I3
340.5	336	332.5	330	327	32I	3I2
340	336	332	330	326.5	320	3II
339.5	335.5	332	330	326	3I9.5	
339	335	332	330	325.5	3I9	
339	334.5	33I.5	329.5	325	3I8	

MIXTURE.C.5. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

372.5
372
37I
37I
370
369
368
367
366
365.5
365
364
363
362.5
36I.5
360.5
359.5
359
358
356
355
354
353.5
352.5
35I
350
349.5
349
348
347
345
344
343.5
343
342
34I
340
339
338.5
337.5
336.5
335
334
333.5
332.5
332
33I
330
329
328
327
326.5
326
325
324.5
324
323.5
323
322
323
325
328
330
33I
332
332.5
333
333.5
333
333
333
333
333
333
333
333
332.5
332
332
332

33I.5
33I.5
33I
33I
330.5

MIXTURE.C.5.

COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

353.5	343.5	337	335	333.5	332.5	33I	328
352.5	342.5	336	335	333.5	332.5	330.5	328
35I.5	342	336	335	333	332.5	330.5	327.5
35I	34I	335.5	334.5	333	332.5	330.5	327
350	340	335	334.5	333	332	330	327
354	339.5	335	334.5	333	332	330	326
348	339	335	334.5	333	332	329.5	326
347	338	335	334	333	33I.5	329	325.5
345	337.5	335	334	333	33I.5	329	325
344	337	335	334	332.5	33I	328.5	325

324.5	3I8	307	294	286
324	3I7	305	293	285
323.5	3I6.5	304	292	284
323	3I5.5	303	29I	283.5
322.5	3I4.5	30I	290.5	282.5
322	3I3	300	290	282
32I	3I2	299	289	28I
320.5	3II	298	288	
320	309.5	396.5	287.5	
3I9	308	295	287	

MIXTURE.C.6. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

353	348.5	343	338.5	334.5	333	33I	328.5
353	348	342.5	338	334	333	330.5	328.5
352.5	347.5	342	337.5	334	333	330.5	328.5
352	347	34I.5	337	334	332.5	330	328.5
35I.5	345.5	34I	336	333.5	332	330	328
35I	345	340.5	336	333.5	332	329.5	327.5
35I	344.5	340	335.5	333	332	329.5	327.5
350	344	339.5	335.5	333	33I.5	329	327
349.5	344	339	335	333	33I.5	329	326.5
349	343	339	334.5	333	33I	328.5	326

325.5	320	3I2.5	304	296	289	282
325	3I9.5	3II.5	303	295	288	28I
325	3I9	3II	302	294.5	287	
324	3I8	3I0	30I.5	293.5	286.5	
324	3I7.5	309	300.5	293	286	
323	3I7	308	300	292	285	
322.5	3I6	307	299	29I.5	284.5	
322	3I5	306.5	298	29I	284	
32I.5	3I4	305.5	297.5	290	283	
32I	3I3	304.5	297	289.5	282.5	

MIXTURE. C.6. COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

368	359	350	34I	335.5	333	33I.5	329.5
367.5	358.5	349	340	335	332.5	33I	329
367	358	348	339	335	332.5	33I	328.5
366	356	347	338.5	334.5	332	33I	328.5
365	355	345.5	338	334.5	332	33I	328
364	354.5	345	338	334	332	330.5	328
363	353.5	344	337.5	333.5	332	330.5	327.5
362	352	343	337	333.5	332	330	327
36I	35I.5	342	336.5	333.5	332	330	327
360	35I	34I.5	336	333	33I.5	329.5	326.5

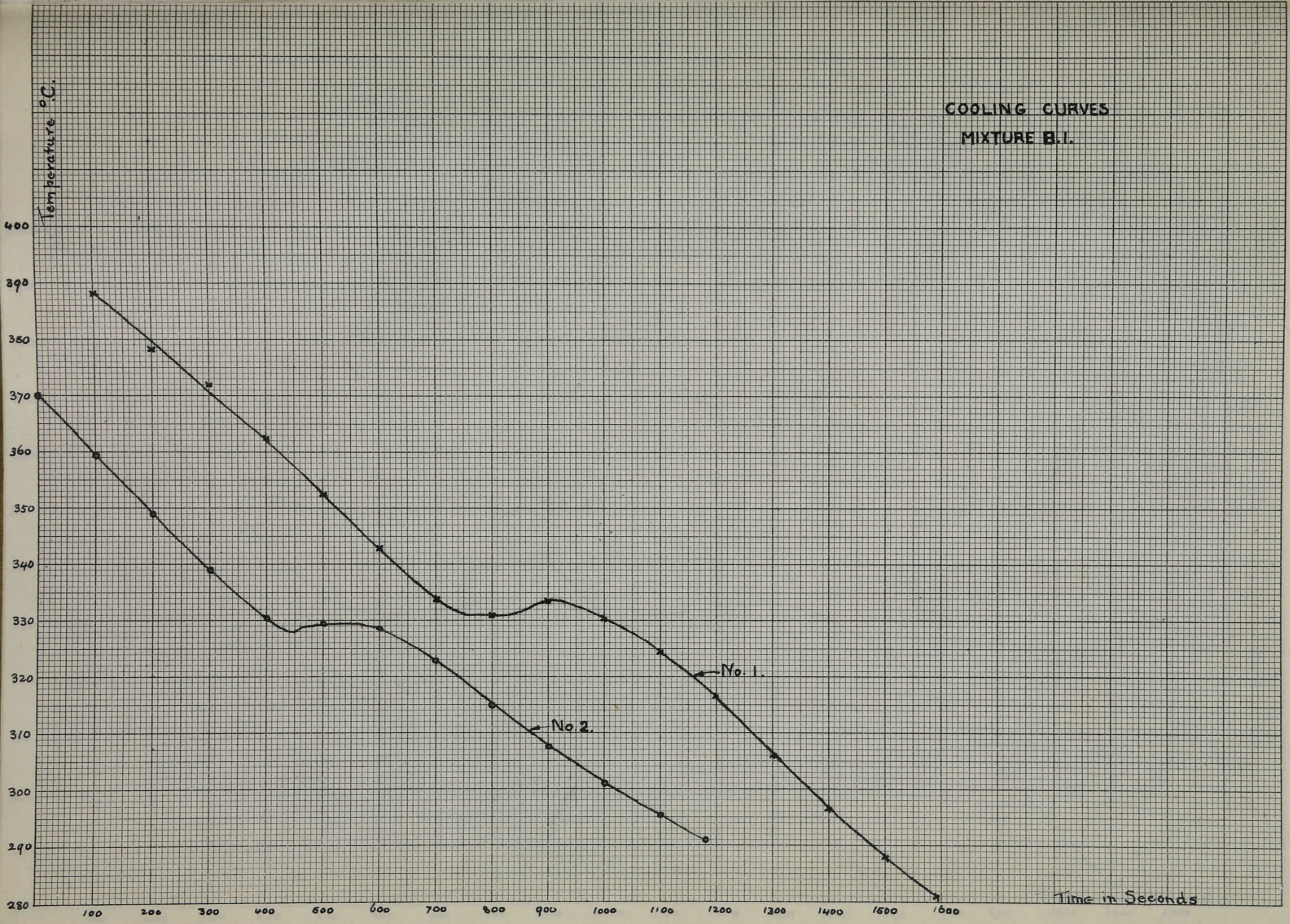
326	32I.5
326	32I
325.5	
325	
324.5	
324	
324	
323	
322.5	
322	

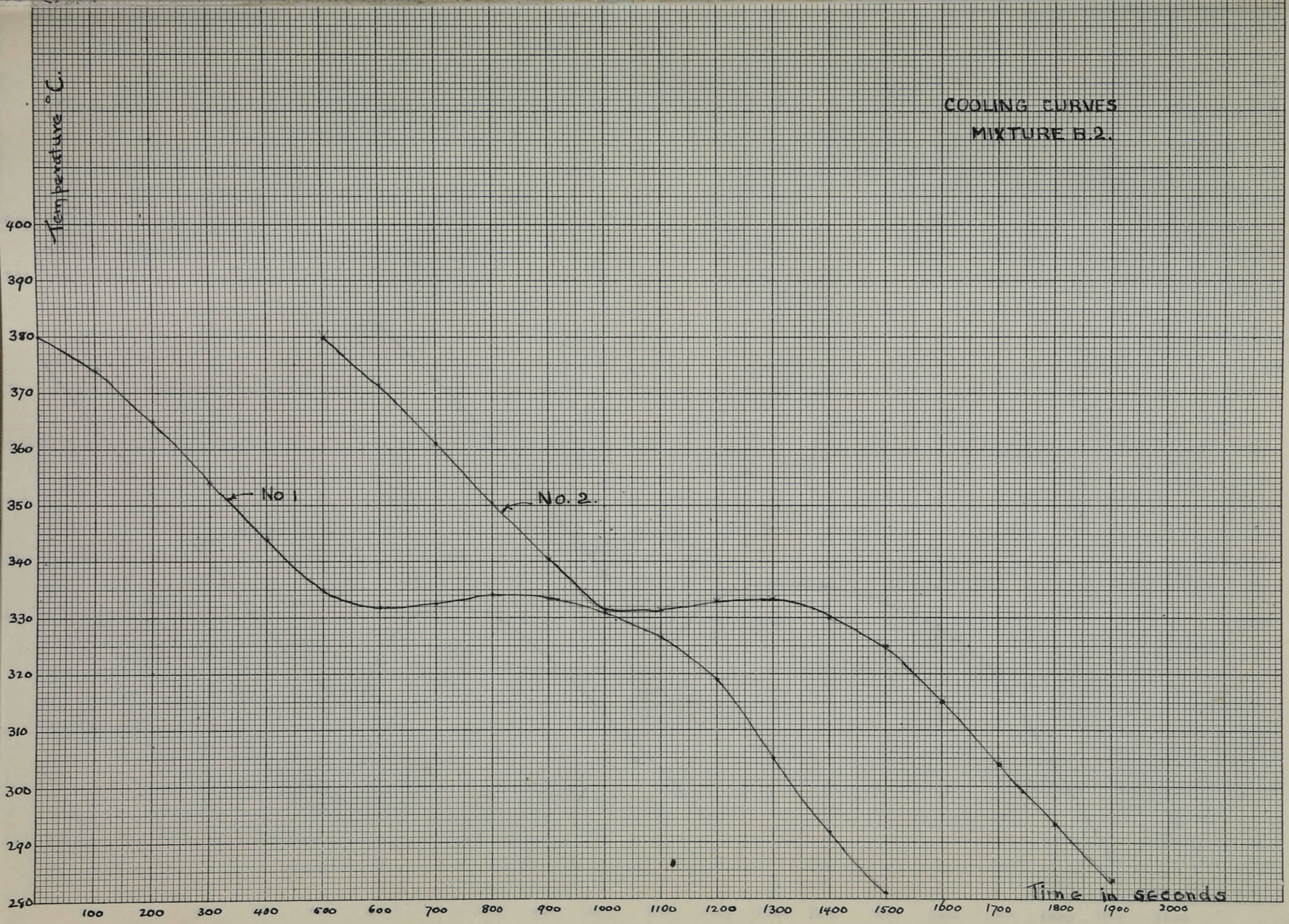
MIXTURE. C.7. **COOLING CURVE. NO.I.**

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

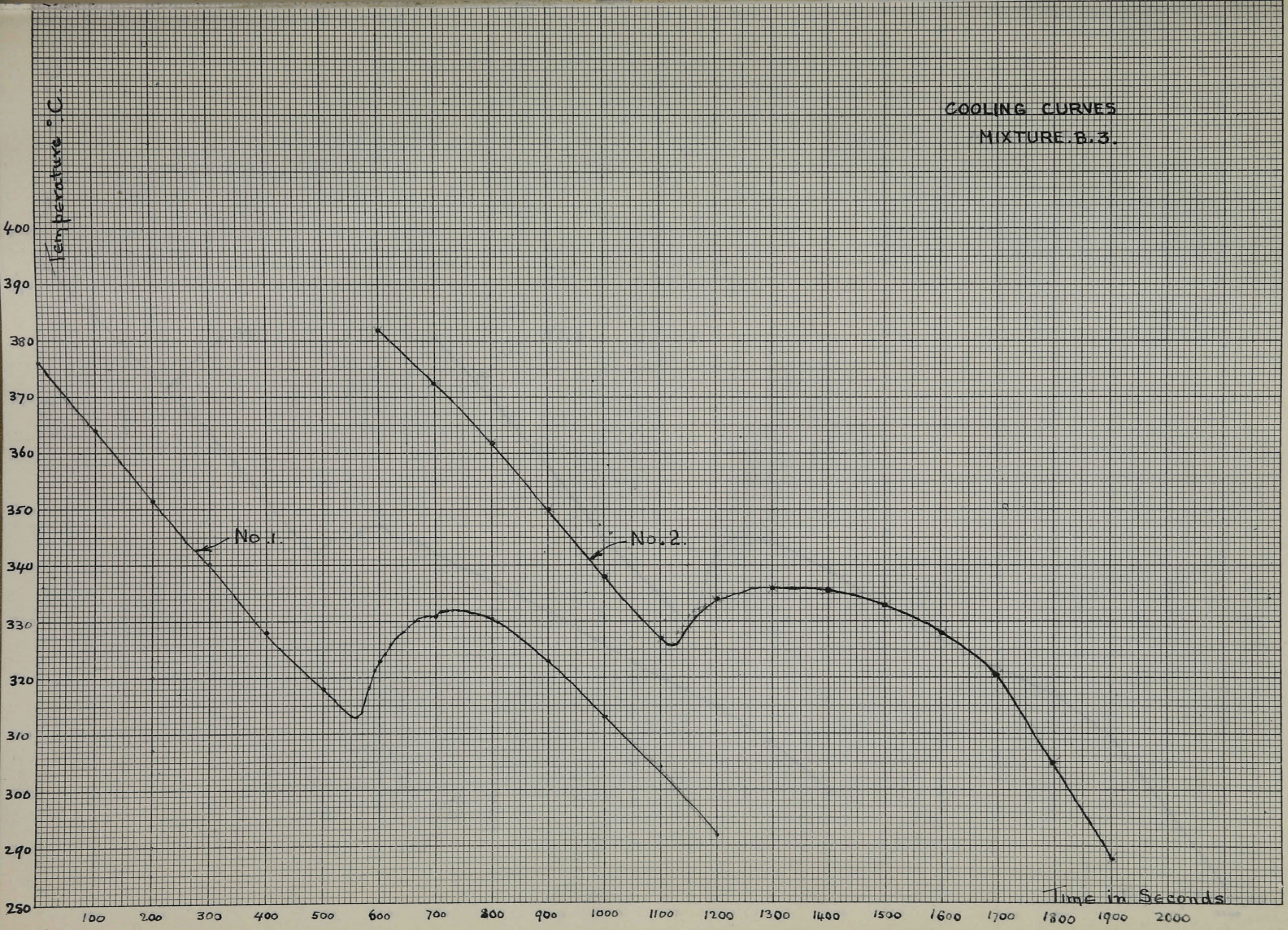
359	347	336.5	332.5	333	330.5	327	32I.5
358	345.5	335.5	333	333	330	326.5	32I
356	344.5	334.5	333	333	330	326	320
355.5	343.5	333.5	333	333	329.5	325.5	3I9.5
354.5	342.5	333	333	332.5	329.5	325	3I8.5
354	34I	332	333.5	332	329	324.5	3I8
35I,5	340	33I	333.5	332	328.5	324	3I7
350	339	330.5	333.5	33I.5	328	323.5	3I6
349.5	338.5	33I	333.5	33I	328	323	3I5
348	337.5	332	333.5	33I	327.5	322	3I4

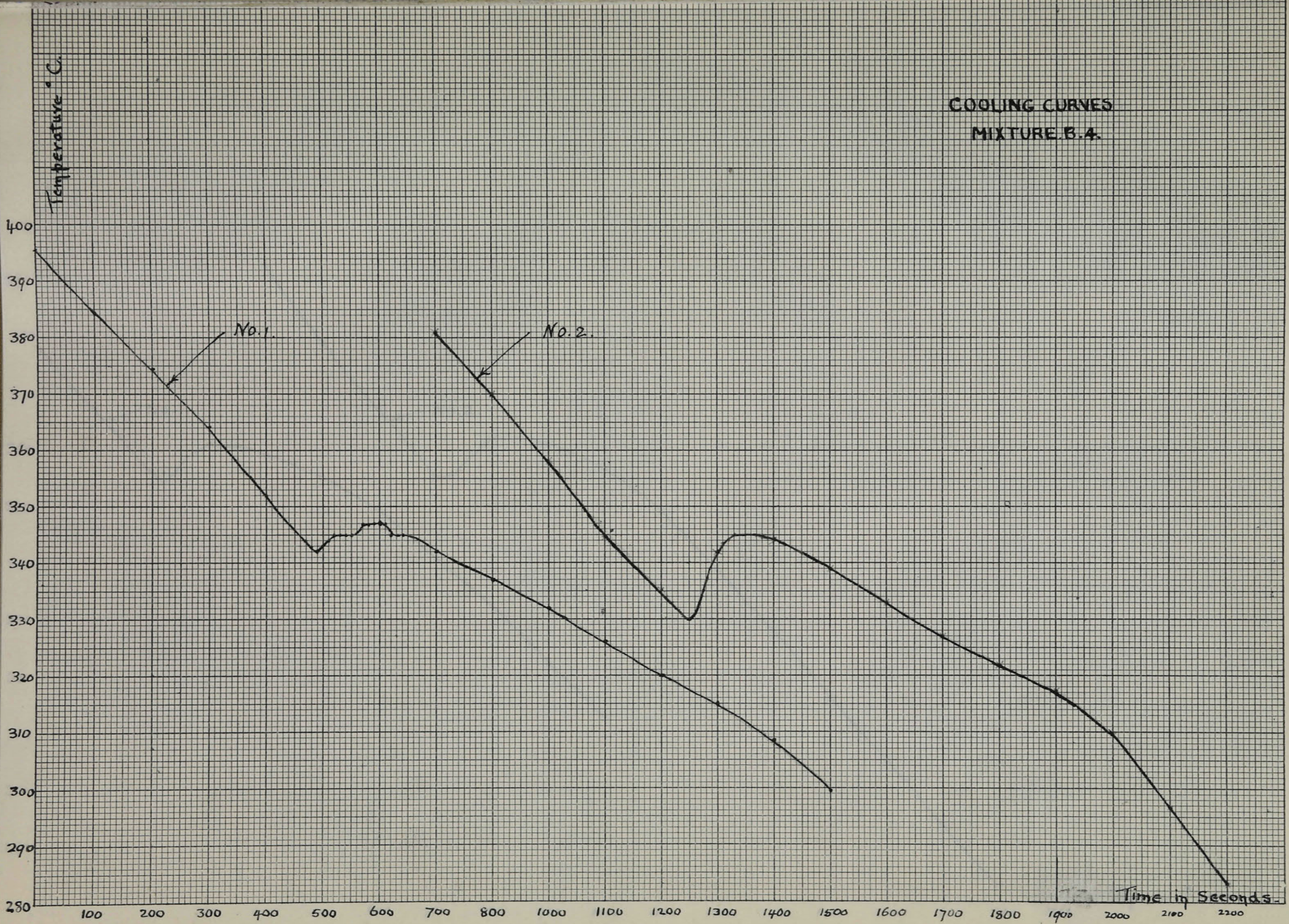
3I3	304
3I2	303
3II	302
3I0	30I
309	300.5
308.5	299.5
307.5	299
306.5	298
305.5	297.5
305	296.5


COOLING CURVES
MIXTURE B.I.

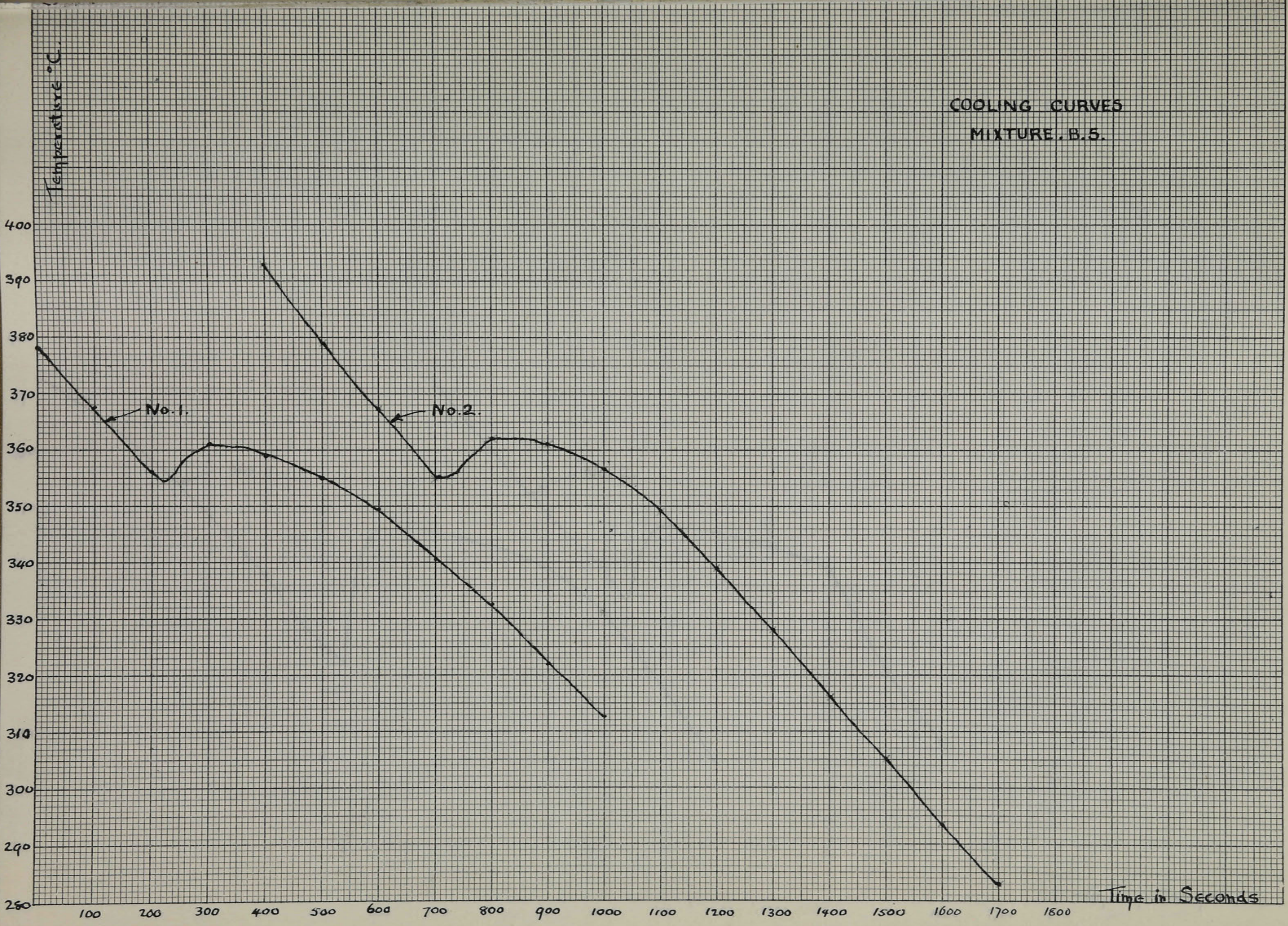


COOLING CURVES
MIXTURE B.2.

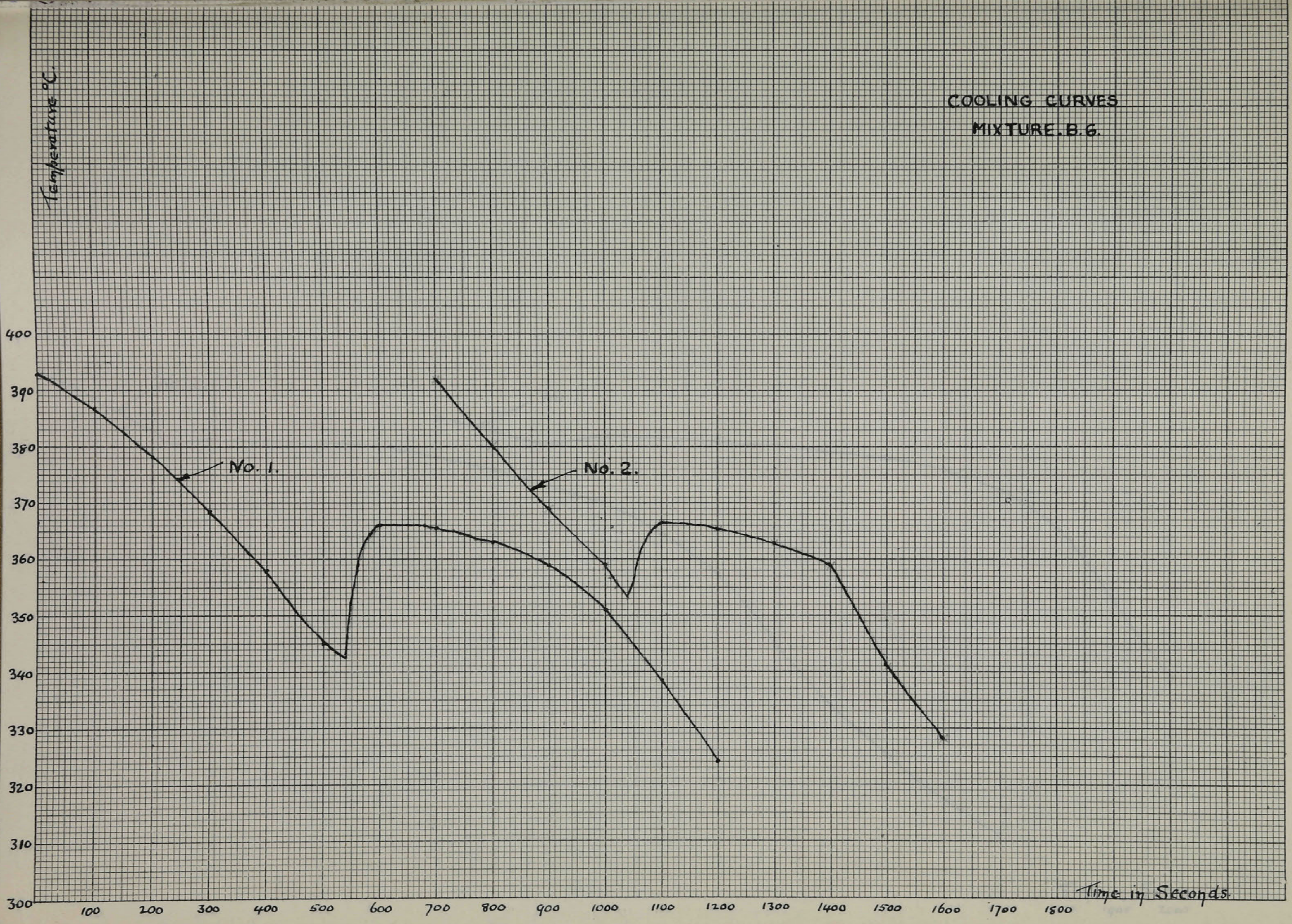

COOLING CURVES
MIXTURE. B. 3.



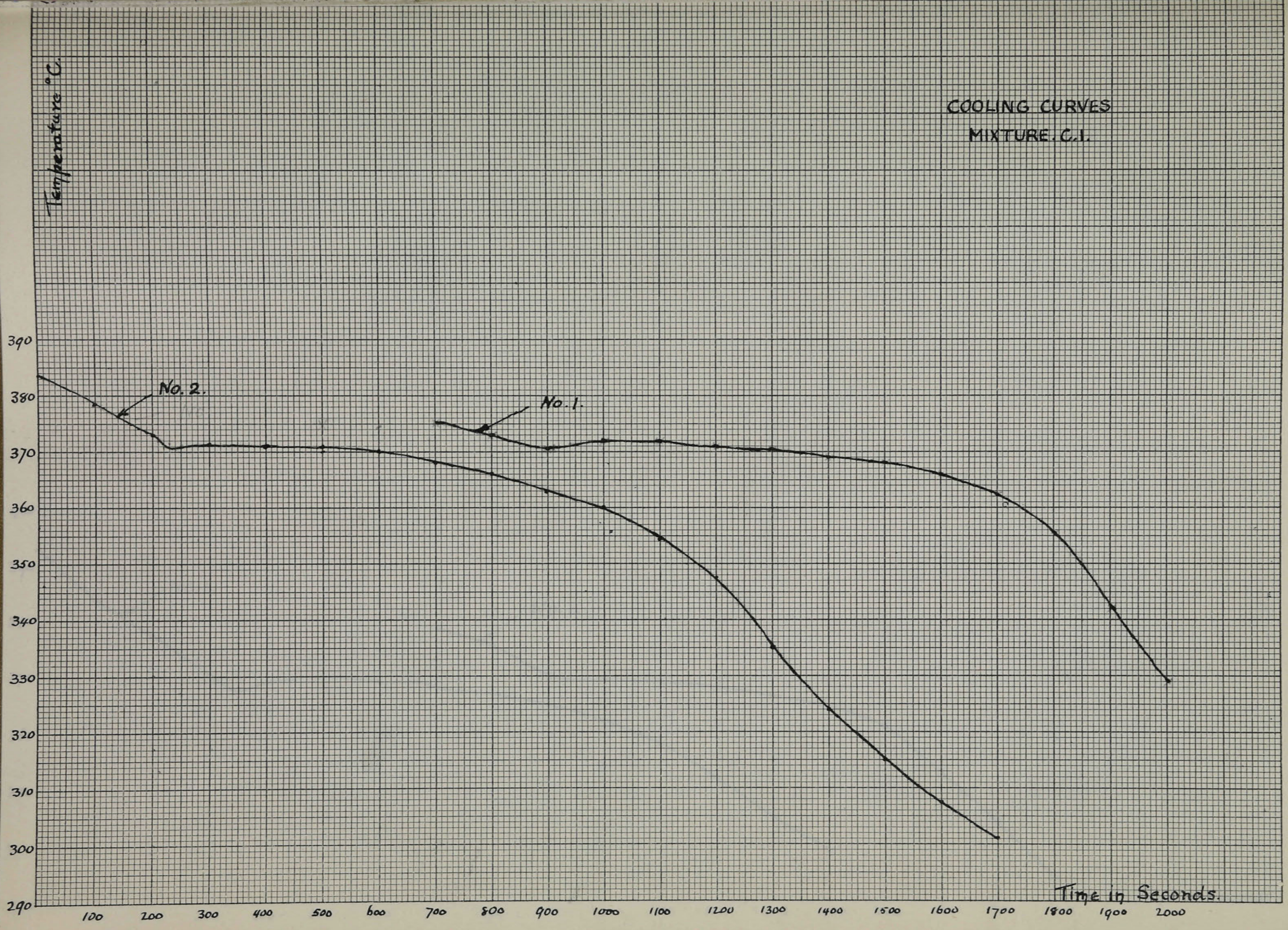
COOLING CURVES
MIXTURE B.4.



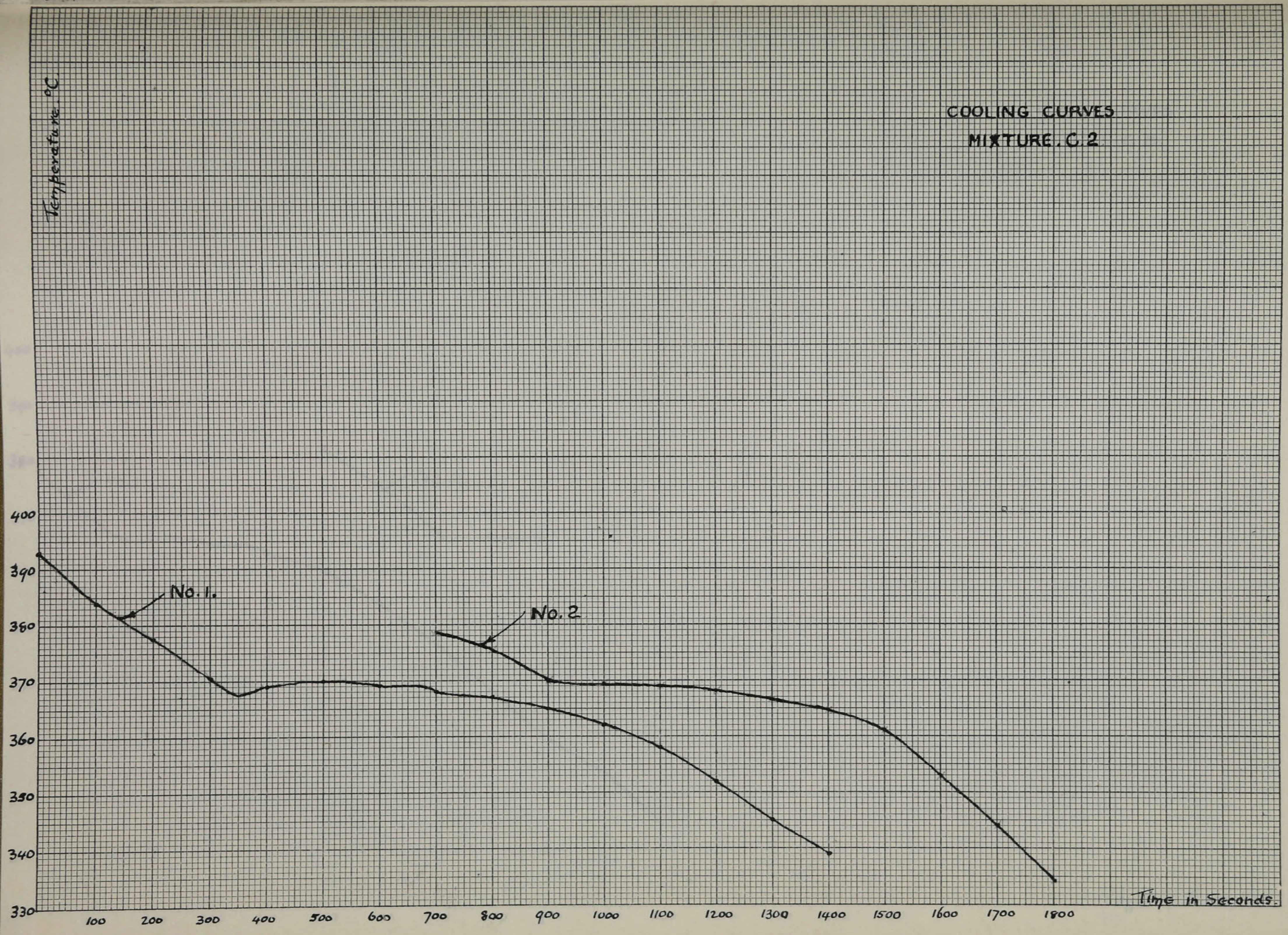
COOLING CURVES
MIXTURE. B.5.

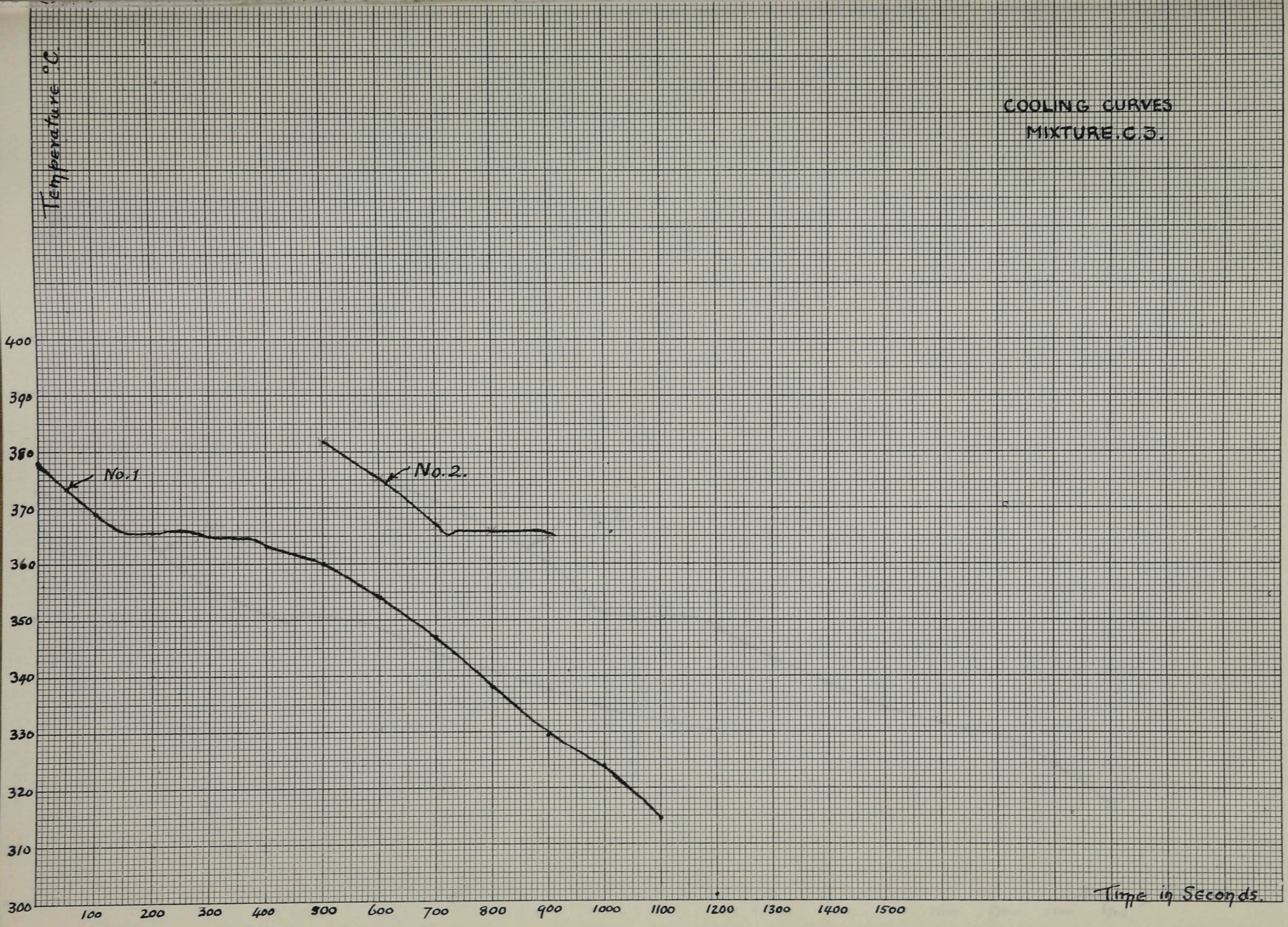


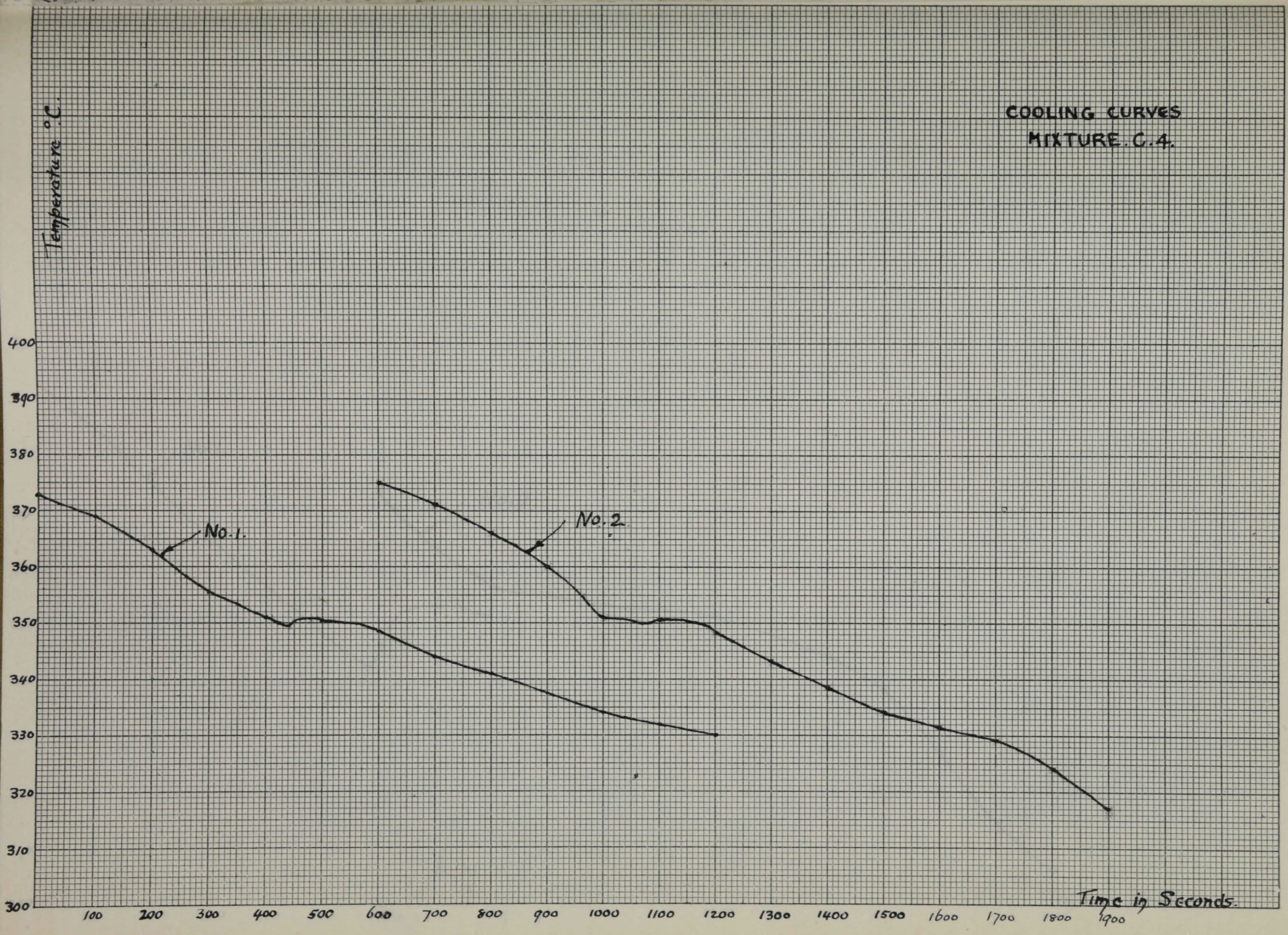
COOLING CURVES
MIXTURE. B. 6.



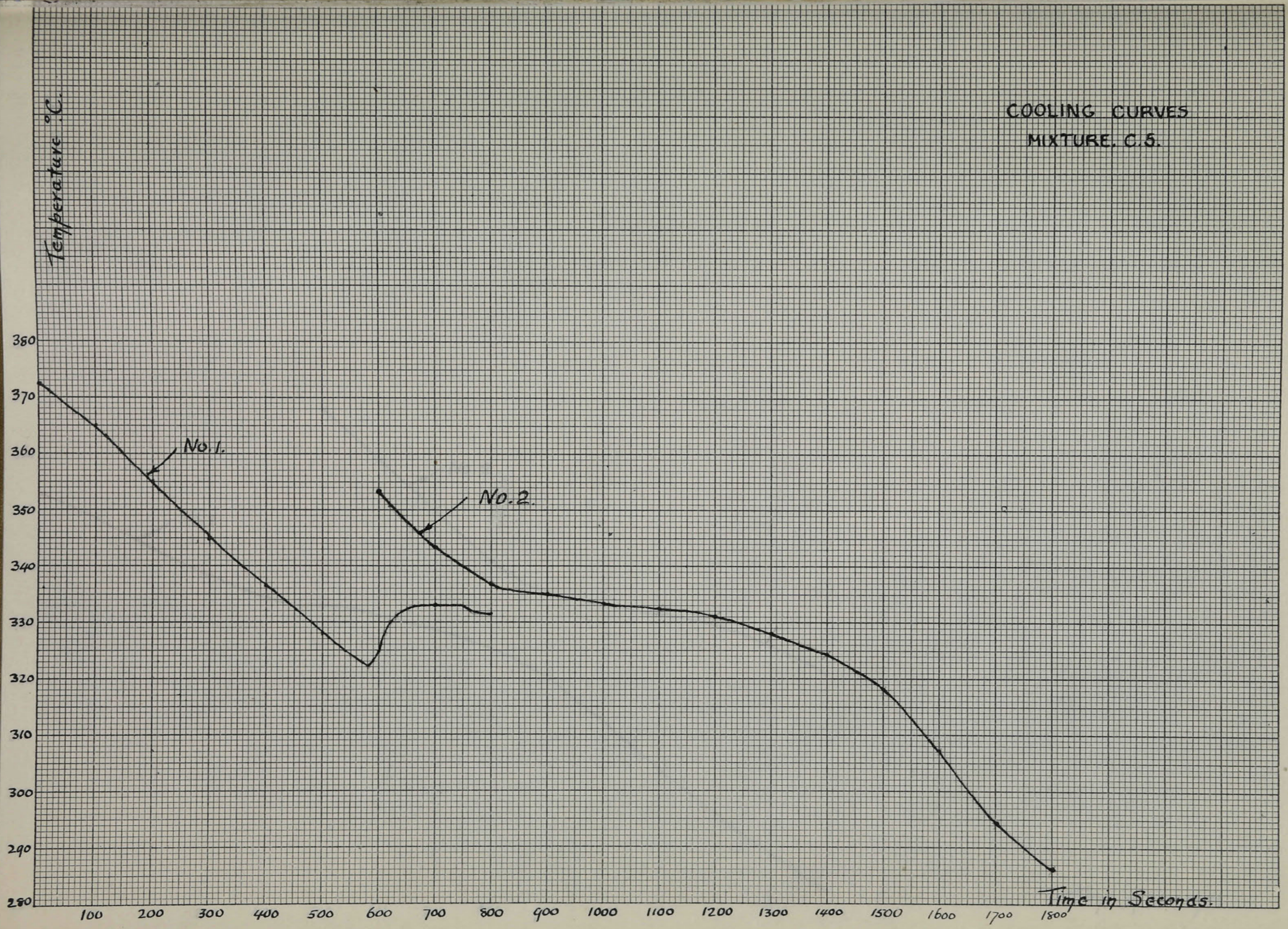
COOLING CURVES
MIXTURE. C.I.

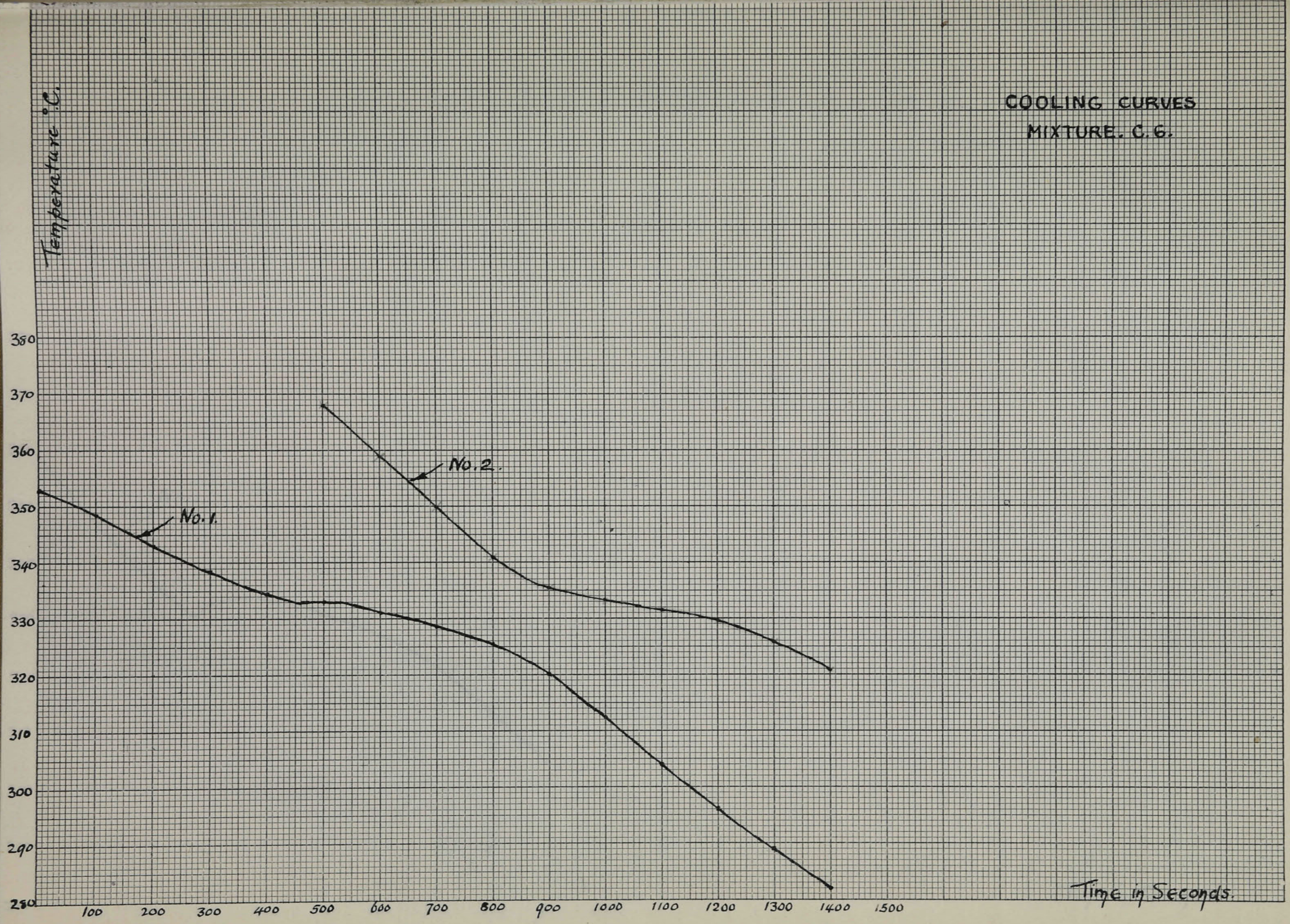

COOLING CURVES
MIXTURE. C 2
Temperature °C
No. 1.
No. 2
400
390
380
370
360
350
340
330
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
Time in Seconds.


COOLING CURVES
MIXTURE. C.3.
Temperature °C.
400
390
380
370
360
350
340
330
320
310
300
No. 1
No. 2.
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
Time in Seconds.

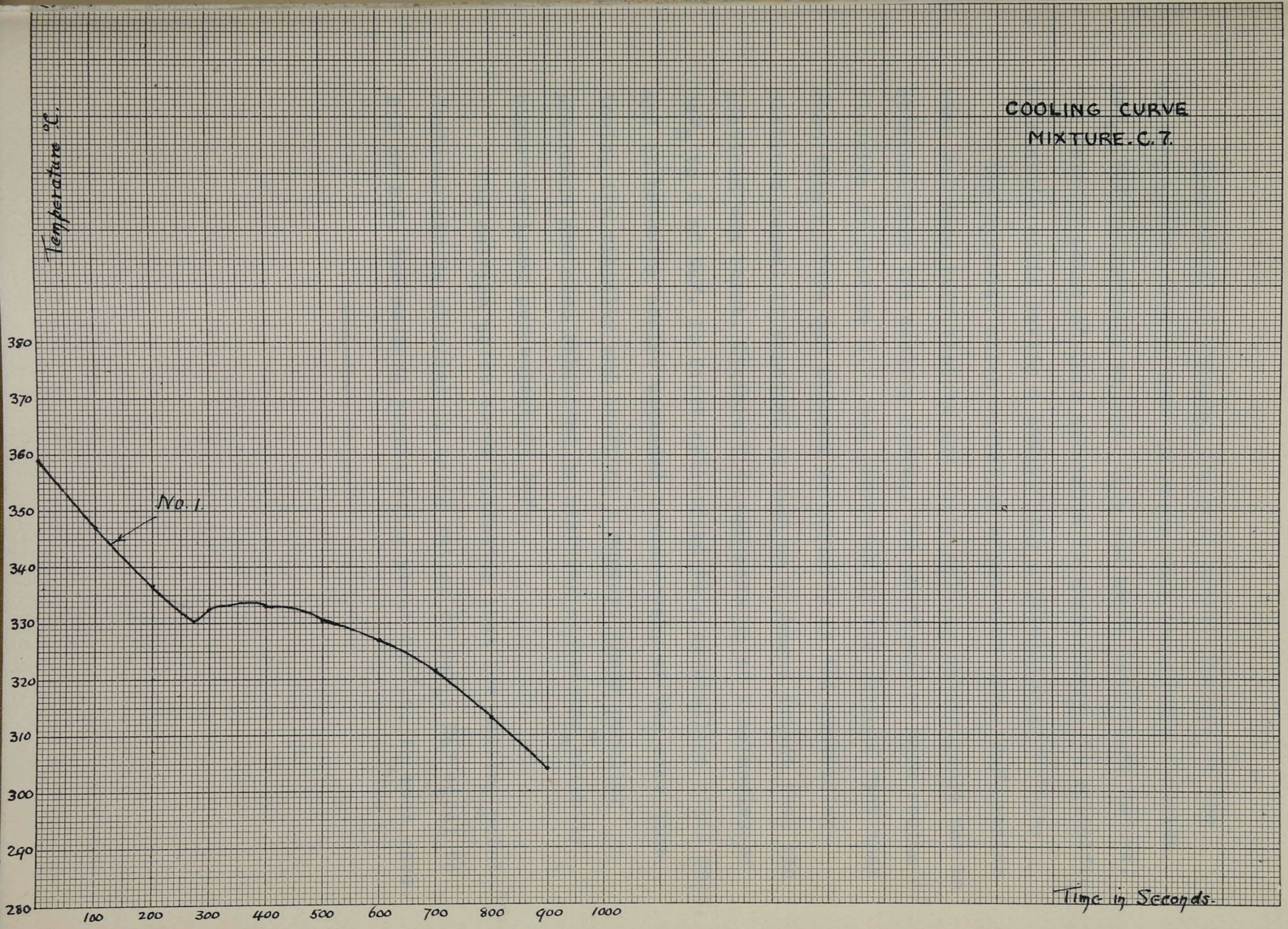


COOLING CURVES
MIXTURE. C.4.


COOLING CURVES
MIXTURE. C.S.



COOLING CURVES
MIXTURE. C.6.


COOLING CURVE
MIXTURE. C. 7.
Temperature °C.
380
370
360
350
340
330
320
310
300
290
280
No. 1.
100
200
300
400
500
600
700
800
900
1000
Time in Seconds.

Discussion of Results. The most marked feature of the melting point curve is that it shows that the double fluoride BeF_2. NaF undoubtedly exists. This has never been shown before. The melting point of this substance is quite sharp. It solidifies to a white solid having a beautifully crystalline structure.

The mixtures which contained a ratio of BeF_2: NaF greater than 2:I were very viscous and their melting points could not be obtained from the cooling curves. The additions of more sodium fluoride to mixture C.7. was prevented by the curious fact that when this mixture was allowed to solidify in the containing platinum vessel it expanded to such an enormous extent that the platinum was burst. Mixture C.7. was made up of 2 molecules of BeF_2 to 3 of NaF. It first solidified to a crystalline rigid mass, and on becoming cooler expanded tremendously at the same time losing its rigidity and becoming a powder. These peculiar phenomena are also exhibited by mixtures containing a slightly higher or lower percentage of NaF.

The melting point curve indicates that low melting point mixtures can be obtained by using ratios of BeF_2: NaF equal to 2:I or 2:3, the melting points being about 330°.C. in each case.

The Determination of Melting Points of Mixtures of Beryllium Fluoride and Potassium Fluoride.

Mixtures of potassium fluoride and beryllium fluoride can also be electrolysed to **obtain** the metal. A determination of their melting points is therefore also important. Previous work (13) had only proved the existence of the double fluoride $BeF_2 . 2KF$, and it was considered probable that BeF_2. existed.

The experimental work was carried out in an exactly similar manner to the previous work and in the same apparatus. The potassium fluoride used contained water of crystallization and accordingly for additions of this substance the hydrate was first heated in a platinum crucible until all of the water had been driven off and then added in weighed amounts as required.

Tables and curves are given in the following pages.

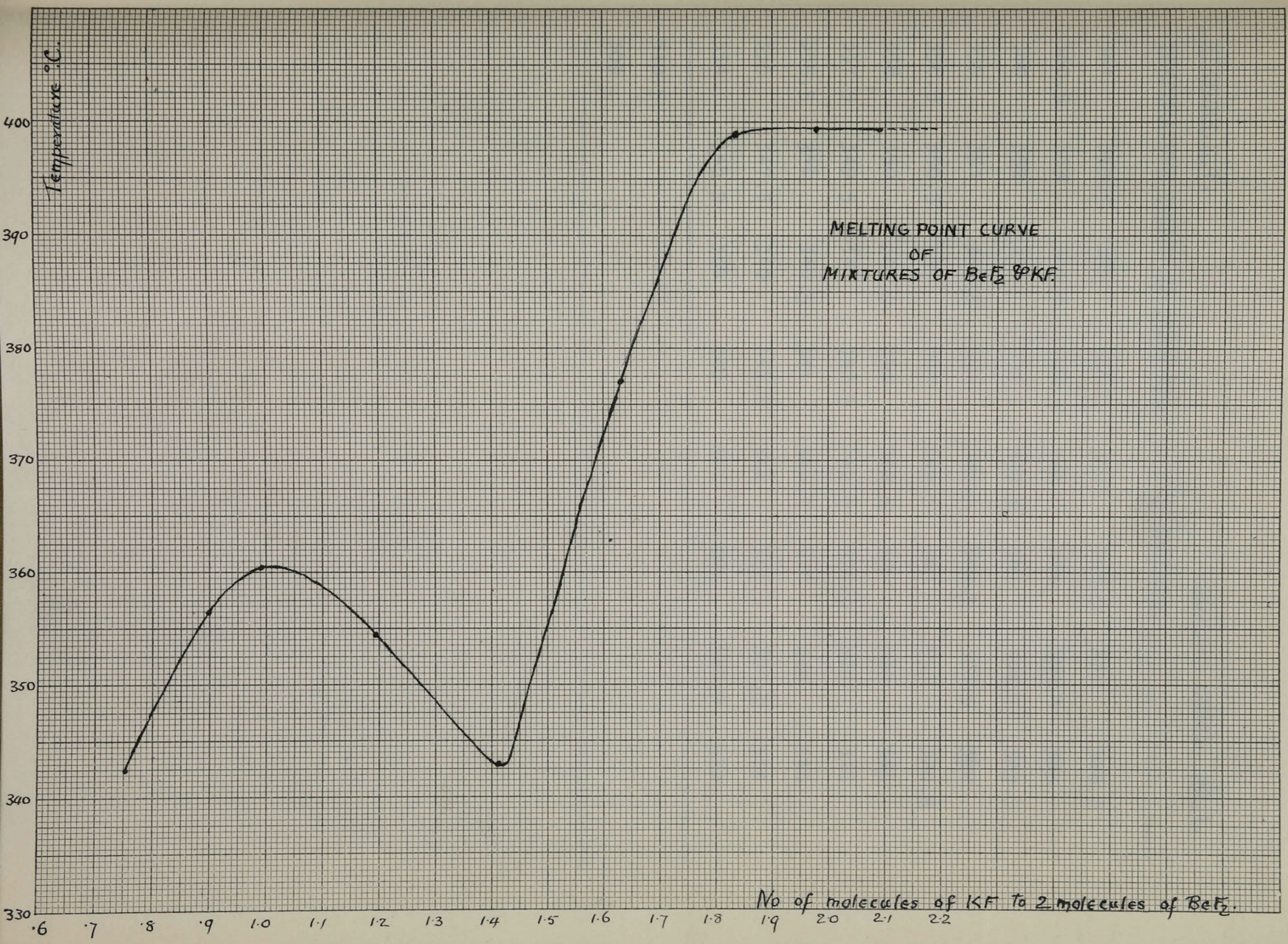
Table of Melting Points of Mixtures of BeF_2 and KF.

Mixture No.	BeF_2 used in grams	KF added in grams	A.	B.	m.p.° C.
E.1.	11.072	5.149	2:0.7543		342.5
E.2.		.978	2:0.898		356.5
E.3.		.630	2:0.990		360.5
E.4.		1.385	2:1.192	.232	354.5
E.5.		1.494	2:1.414		343
E.6.		1.467	2:1.631		377
E.7.		1.369	2:1.834		399
E.8.		.949	2:1.974		399
E.9.		.780	2:2.090		399

A = The ratio of the no. of molecules of BeF_2 to the no. of molecules of KF.

B = Loss in grams of the mixture used.

NOTE. Mixtures containing further additions of KF assumed the consistency of a porridge at temperatures above 400° C., and satisfactory curves could not be obtained. The same was true for Mixture 9. It seems likely that the temperature of 399° is that of an eutectic mixture. Certainly the mixture of the composition $BeF_2.KF$ has no sharp melting point.


MELTING POINT CURVE
OF
MIXTURES OF BeF₂ & KF.
Temperature °C.
400
390
380
370
360
350
340
330
·6
·7
·8
·9
1·0
1·1
1·2
1·3
1·4
1·5
1·6
1·7
1·8
1·9
2·0
2·1
2·2
No of molecules of KF to 2 molecules of BeF₂.

MIXTURE.E.1. COOLING CURVE. NO.1.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

361	353.5	345	338.5	342	341.5	336	326.5
360.5	353	344.5	338.5	342	341	335.5	325
360	352	344	338	342.5	341	334.5	323.5
359	351	342.5	339	342.5	340.5	333.5	322
358.5	350.5	342	339	342.5	340	333	320.5
358	350	341.5	340	342.5	339	332	319
357.5	349.5	341	340.5	342.5	338.5	331	318
355.5	348	340.5	341	342.5	338	330	316
355	347.5	340	341.5	342	337.5	328.5	314
354	345.5	339	342	342	337	327.5	312

310.5

309

MIXTURE.E.I. COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

354	344	340	3I9.5
353	343	340	
352	342.5	339.5	
35I	34I	339	
350	340.5	338	
349.5	340	337.5 (x)	
348.5	340	333.5	
348	340	329.5	
347	340.5	326	
345	340.5	323	

After (x) the intervals are increased to 60 seconds

MIXTURE.E.2.

COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

376	367	356.5	348	354	349.5	34I
375.5	366.5	355	348.5	354	349	340.5
375	366	354	349.5	354	348	340
374	365.5	353	35I	353.5	347.5	339
373	363.5	352	352	353	347	
372	362	350.5	353	352.5	345	
37I	36I	349.5	353.5	352	344.5	
370	360.5	349	354	35I.5	344	
369	359	348.5	354	35I	343	
368	359	348	354	350	342	

MIXTURE.E.2. COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

380	370	359	353.5	356.5	354	349	340.5
379	369	358	354.5	356.5	353.5	348	340
378	368	356	355	356	353	347.5	338.5
377	367	354.5	355.5	356	352.5	347	337 xxx
376	365	354	356	355.5	352	345	330
375	364	352.5	356	355.5	35I.5	344	322
374	363	352	356.5	355	35I	343	3I4
372.5	36I	352	356.5	354.5	350	342.5	306.5
37I	360	353	356.5	354.5	349.5	34I.5	299

After (x) the intervals are increased to 60 seconds.

MIXTURE.E.3. **COOLING CURVE. NO.I.**

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

378	365	359	358.5	345
377.5	364	359.5	358	340
376	362.5	360	358	333
374	361.5	360	356.5	325
372.5	360.5	360	356	315.5
371.5	359	360	355.5	307.5
370.5	358	360	355	
369	358	359.5	354.5	
368	358	359	354 xxx	
366	359	359	350.5	

After (x) the intervals are increased to 60 seconds.

MIXTURE.E.3. COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

386	373	359	360.5	356	340
384.5	371.5	358	360.5	355.5	333
383	370	356.5	360.5	355	324
382	369	358	360	354	314
380.5	367.5	358.5	360	353.5	305
379	366	359	359.5	353	
378	364.5	359.5	359	352	
377.5	363	360	359	351.5	
375.5	361.5	360.5	358.5	350.5	
374	360	360.5	358	xxx 345	

After (x) the intervals are increased to 60 seconds.

MIXTURE.E.4. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

377	364	353.5	354	35I.5	347
376	363	353	354	35I	xxx 342
374.5	362.5	353	354	35I	336.5
374	36I	353	354	350.5	330
373	360	354	353.5	350	320.5
37I.5	359	353.5	353	349.5	3II
370	358	353.5	353	349	303
368	355.5	354	352.5	348.5	
366	354.5	354	352.5	348	
365	353.5	354	352	347.5	

After(x) the intervals are increased to 60 seconds.

MIXTURE.E.4. COOLING CURVE. NO.2.

TEMPERATURES TAKEN AT INTERVALS OF TEN SECONDS.

364	349	353	354	350
362	348	353.5	354	349
360.5	348	353.5	354	348.5
359	348	354	353.5	xxx 342
358	348	354	353	335
356	348.5	354	352.5	325
354	349	354.5	352	314.5
353	349.5	354.5	351.5	305
352	351	354.5	351	
350	352	354	350.5	

After (x) the intervals are increased to 60 seconds.

MIXTURE.E.5.

COOLING CURVES. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

375.5	388	356	344	343	340.5	335.5
375	366	355	343	343	340	335
374	365	354	343	342.5	339.5	334 (x)
373	364.5	353	343	342.5	339	-
372.5	364	352	343	342	338.5	-
37I.5	363	35I	343	342	338	33I.5
37I	362	350	343	34I.5	337.5	-
370	36I	349	343	34I.5	337	-
369.5	360	348	343	34I	336.5	329
369	359	345	343	34I	336	-

-	3I6
326.5	-
-	-
-	3I2
323	-
-	-
-	308
320	-
-	-
-	

After (x) the intervals are increased to 30 seconds.

MIXTURE.E.5. COOLING CURVE. NO.2.

TEMPERATURE ATKEN AT INTERVALS OF TEN SECONDS.

367.5	353.5	342.5	342.5	34I	327
366	352	342.5	342.5	34I	323.5
365	35I	342.5	342.5	340.5	320
363.5	349	343	342.5	340.5	3I6
362	348	343	342	340	3I2
36I	347	343	342	xxx 339	308
360	344.5	343	342	337	303
358.5	343.5	343	34I.5	335	299
356	343	343	34I.5	333	
355	342	342.5	34I.5	330	

After (x) the intervals are increased to 30 seconds.

MIXTURE.E.6. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

405	39I	378	373	366	355.5	332	305
404	390	377	372	365	354	329	300.5
403	389	377	37I.5	364	353	327	296
40I	386	377	370.5	363	352	325.5	29I.5
400	384	377	370	362.5	35I	324.5	287
399	383	376.5	369.5	362	350 (x)	323	
397	38I.5	376	369	360.5	345	32I	
396	380	375	368	359.5	342	3I8	
394	379.5	374.5	367.5	358	338.5	3I4.5	
393	378.5	374	366.5	356.5	335.5	3I0	

After (x) the intervals are increased to 30 seconds.

MIXTURE.E.6.

COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

409
407
404.5
403
401
399.5
398
397
395.5
394

392
390
388
385.5
384
383
381
380
379
378

377
377
377
376
376
376
375
374.5
374
373

372
371
370
369.5
369
368
367.5
367
366
365

364
363
362
361
360
359
358
356
355
353.5

352.5
351
350
348.5
347
345
344
342.5
341
340

339
337.5
336.5
335
334
333
332
330.5
329.5
329

328
327.5
327
326.5
326
326
326
325.5
325
325

324
323.5
322.5
321.5
320.5
319.5
318
317
315
314

312
310.5
309
307
305
303.5
302
300.5
298.5
297

296
294
292
291
289.5
288

MIXTURE. E.7. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS

4I3	40I	399	397	378	329.5
4II	400.5	399	396.5	374	325
409	400	398.5	396	370	320.5
308	399.5	398.5	396	365	3I6
407	399.5	398	395.5	360.5	3I2
406	399.5	398	xxx 394	354.5	308.5
405	399	398	392	349.5	305
404	399	398	390	344	302
403	399	397.5	386	339	299
402	399	397	382	334	

After (x) the intervals are increased to 30 seconds.

MIXTURE.E.7. COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

403	399	397	374
402	399	397	369.5
40I	398.5	396.5	365
400	398.5	xxx 395.5	
400	398	394	
399.5	398	392	
399	398	389.5	
399	398	385.5	
399	397.5	382.5	
399	397.5	377.5	

After (x) the intervals are increased to 60 seconds.

MIXTURE. E.8. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

433	420	406	399	397
432	4I9	404	399	396.5
43I	4I6	403	399	xxx 396.5
430.5	4I4	403	399	395
428.5	4I3	402	399	393
427.5	4I2	40I	398.5	390
426	4II	400.5	398	385.5
424.5	409	400	397.5	382
423	408	399.5	397	377
42I.5	407	399.5	397	372.5

After xxx the intervals are increased to 30 seconds.

MIXTURE.E.8. COOLING CURVE. NO.2.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

43I	4I5	403.5	398.5	396	374	3I9.5
430	4I4	403	398.5	395.5	369	3I5
428	4I2.5	402	398.5	395	363	
427	4II	40I	398	394	358	
425	409	400.5	398	394	35I	
424	408	400	397.5	393	345	
422	407	399.5	397.5	xxx 39I	339.5	
420	406	399	397	388	334	
4I9	405	399	396.5	383.5	329	
4I7	405	398.5	396	378.5	324	

After xxx the intervals are increased to 30 seconds.

MIXTURE. E.9. COOLING CURVE. NO.I.

TEMPERATURE TAKEN AT INTERVALS OF TEN SECONDS.

427	4I4	403	399	397	389	372.5
426.5	4I2	402	399	397	388	xxx 366.5
425.5	4II	40I	398.5	396	385.5	36I
424	409.5	40I	398.5	395.5	384	354
423	408	400.5	398.5	395	382.5	348.5
422	407	400	398.5	394	380.5	342
420	406	399.5	398	393.5	379	
4I9	405	399	398	392.5	377	
4I6.5	404	399	398	39I.5	376	
4I5	403.5	399	397.5	390.5	374	

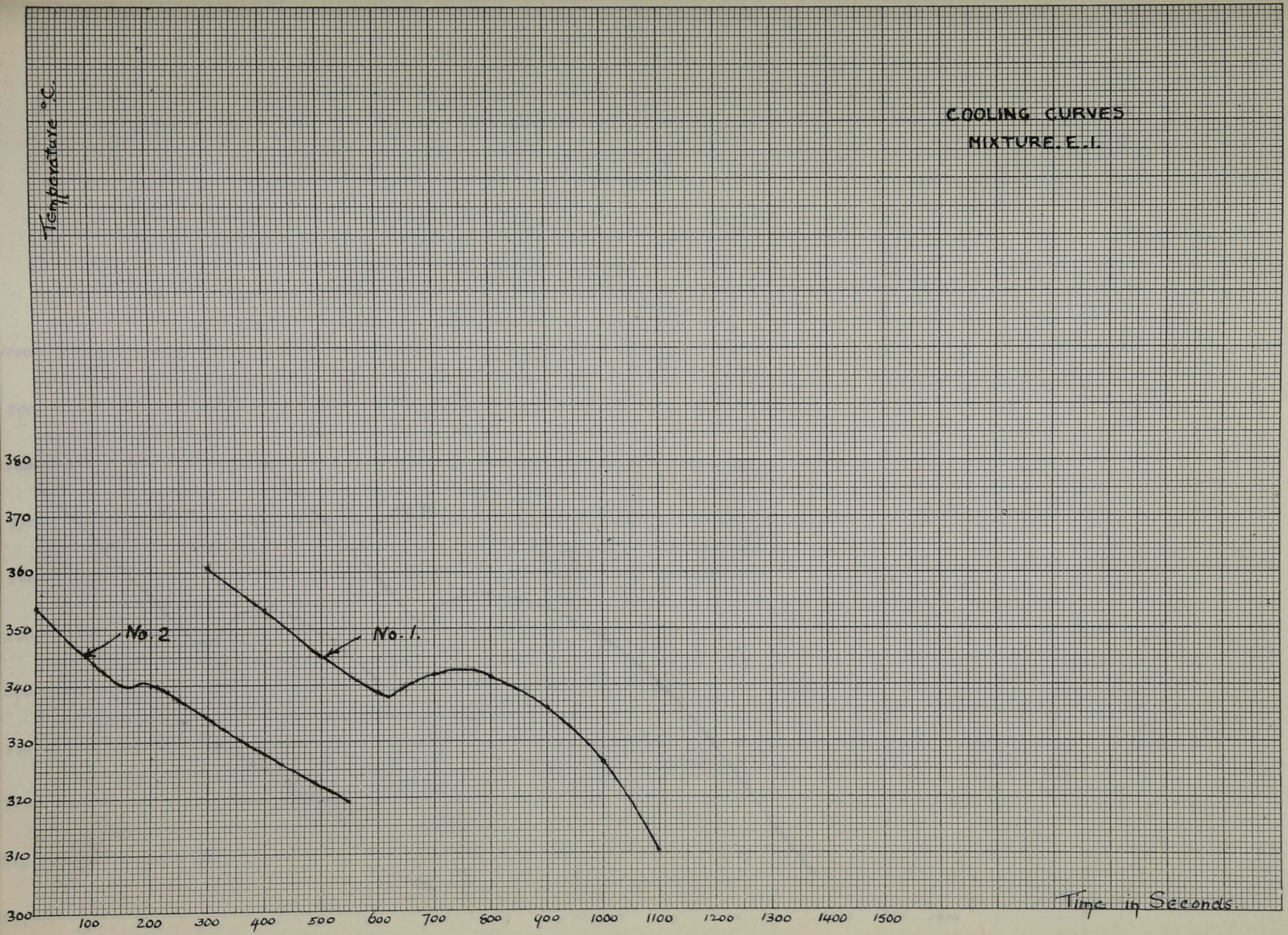
After xxx the intervals are increased to 30 seconds.

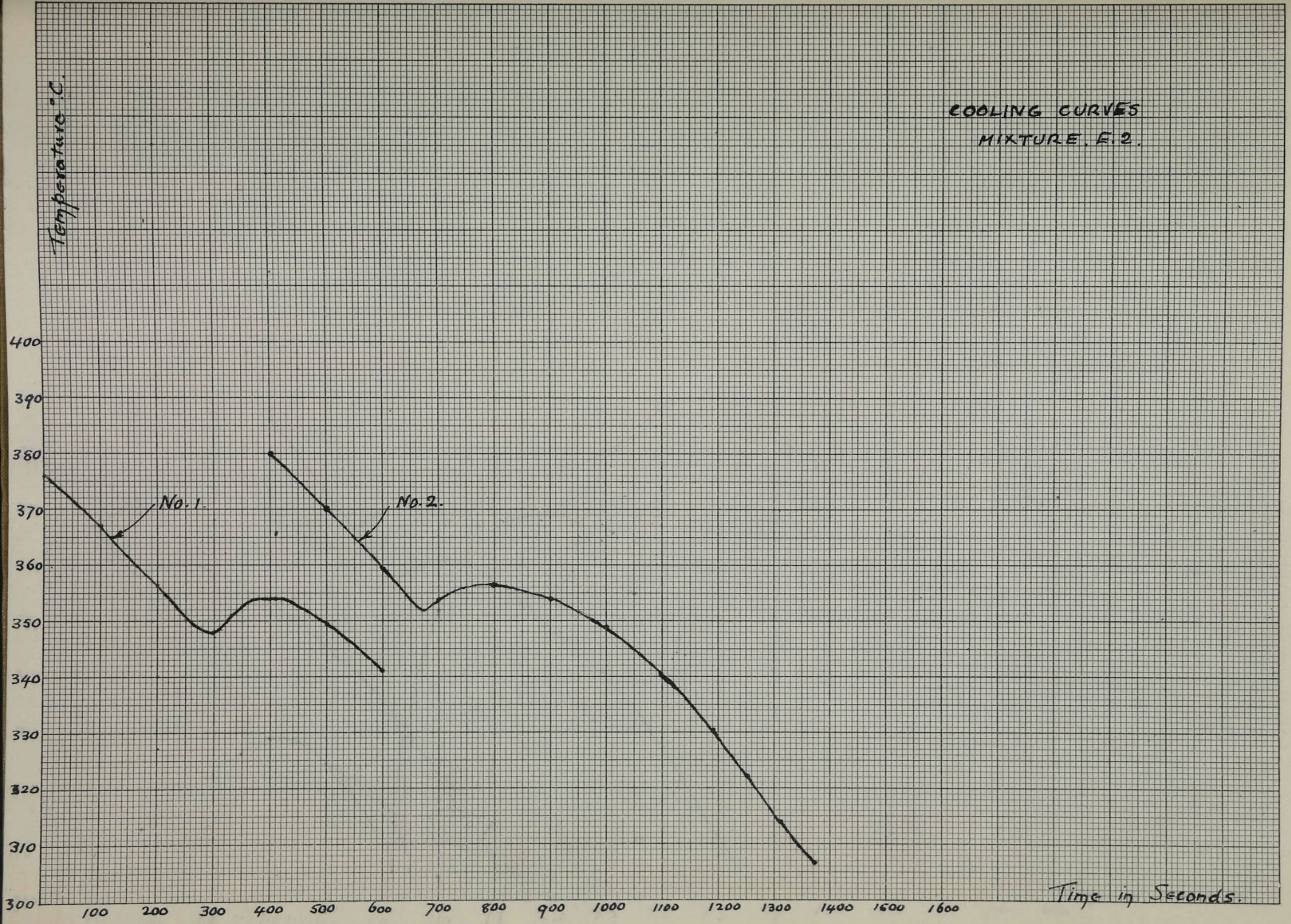
MIXTURE.E.9. COOLING CURVE. NO.2.

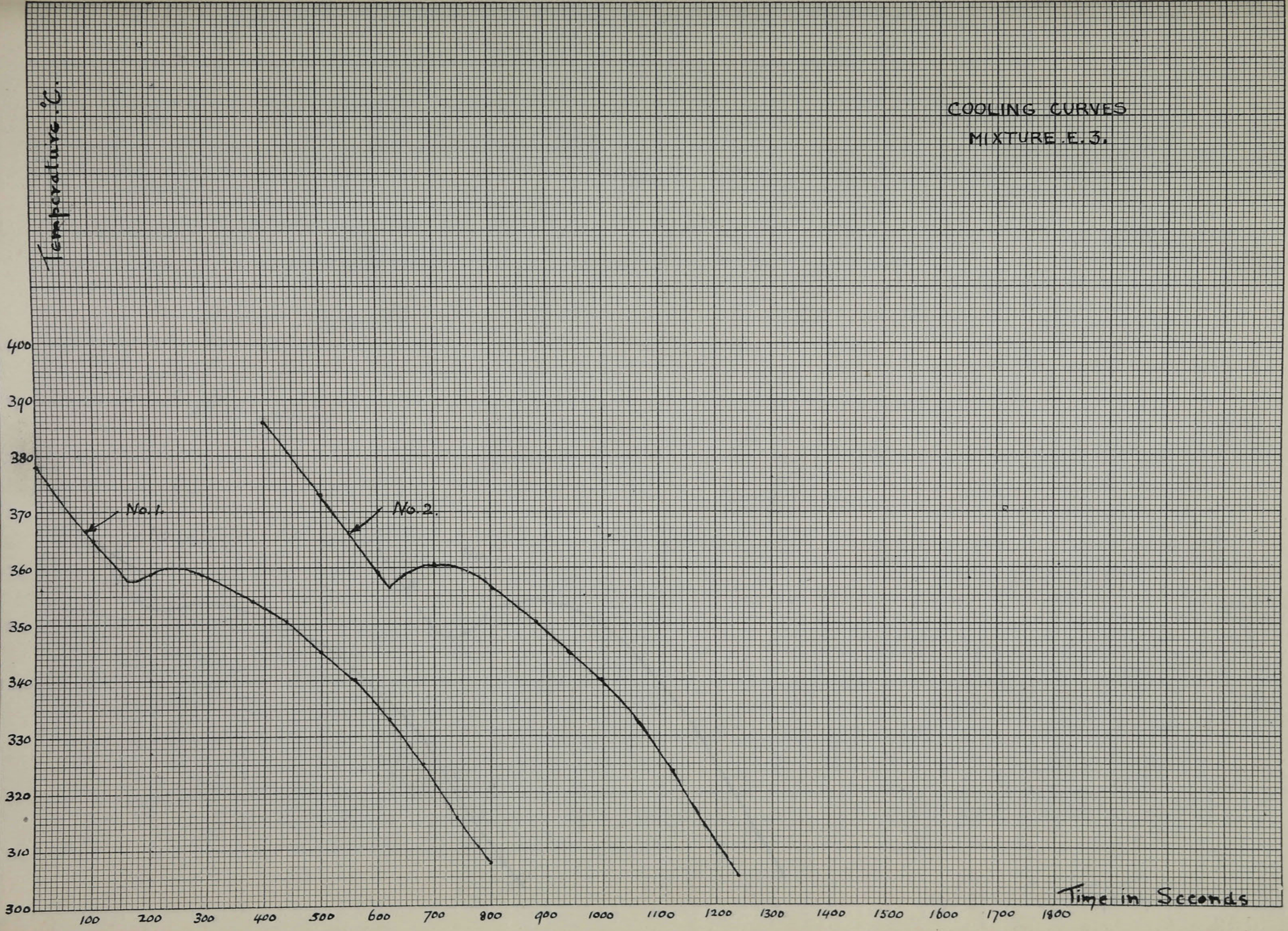
TEMOERATURE TAKEN AT INTERVALS OF TEN SECONDS.

437	415	402.5	397.5	395	368
434	413.5	401.5	398	394	362
431	411.5	400.5	398	393	355
428	410	399.5	398	392	349
426	409	398.5	397.5	391	343
425	408	398	397.5	390	337
423	406.5	398	397	389 xxx	331
420.5	405.5	397.5	396.5	383	326
417.5	404.5	397.5	396	378	
416	403	397.5	395.5	373	

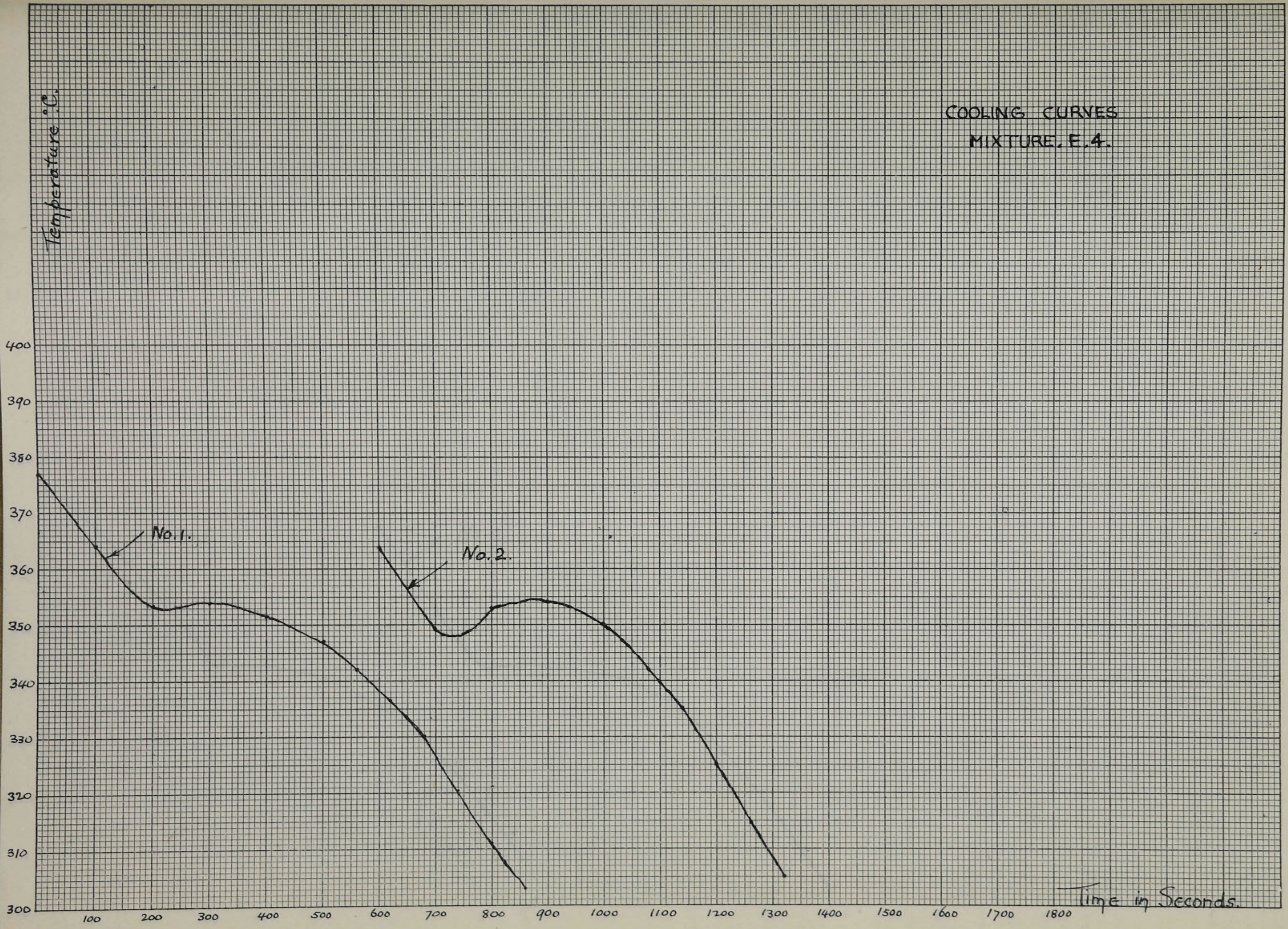
After xxx the intervals are increased to 30 seconds.


COOLING CURVES
MIXTURE. E.I.
Temperature °C.
380
370
360
350
340
330
320
310
300
No. 2
No. 1.
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
Time in Seconds.

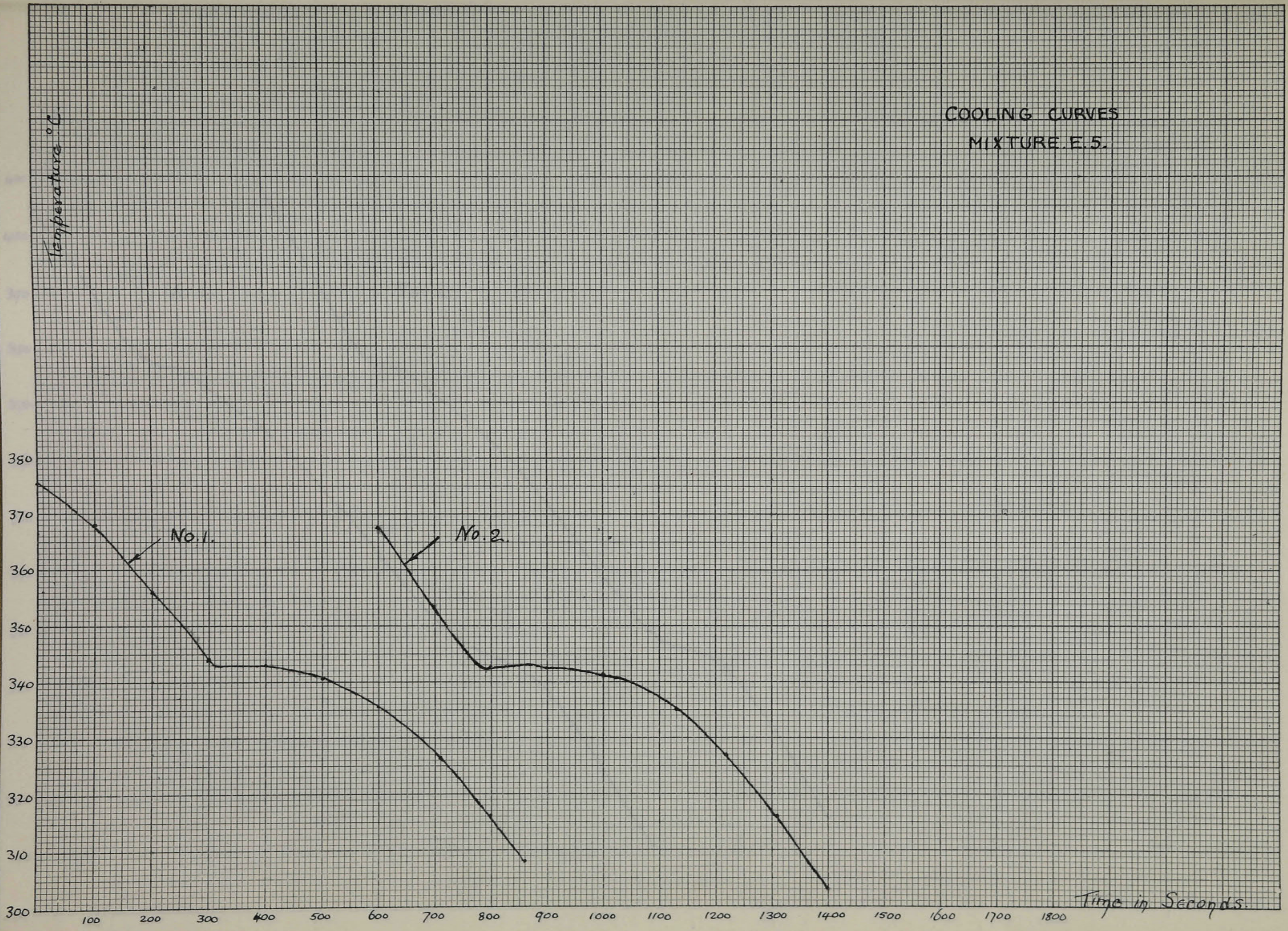

COOLING CURVES
MIXTURE. E. 2.
Temperature °C.
400
390
380
370
360
350
340
330
320
310
300
No. 1.
No. 2.
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
Time in Seconds.

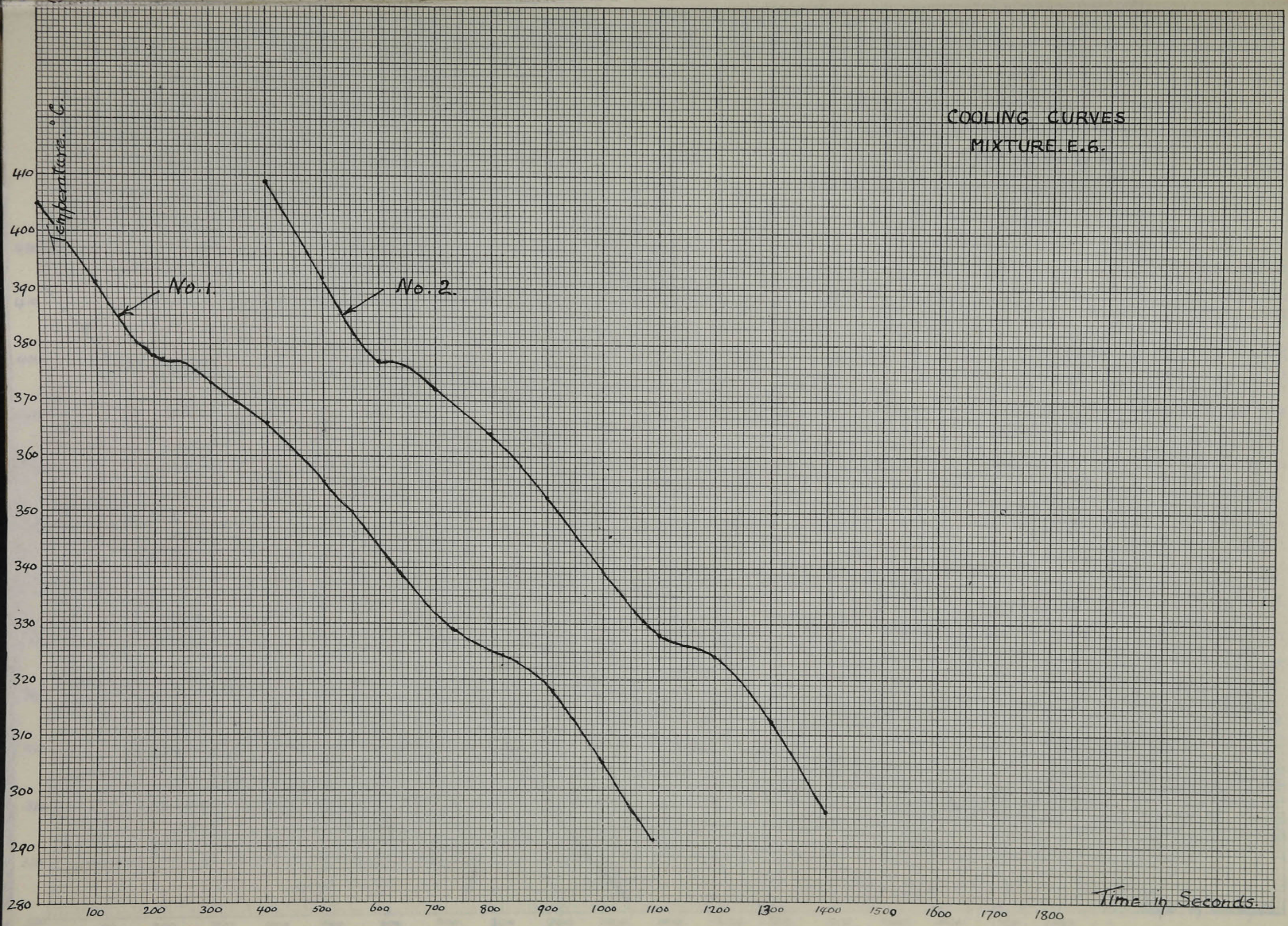


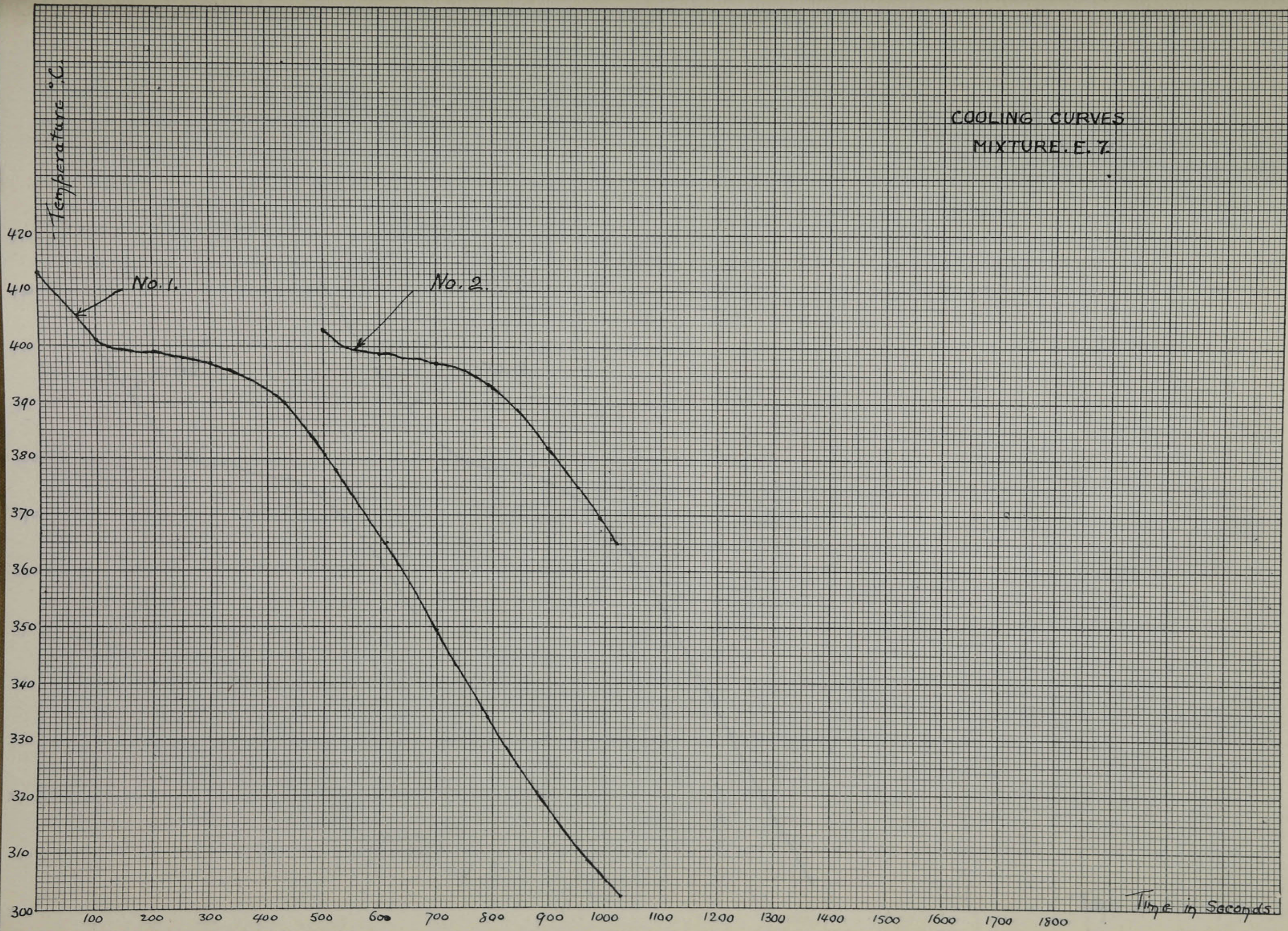
COOLING CURVES
MIXTURE E.3.



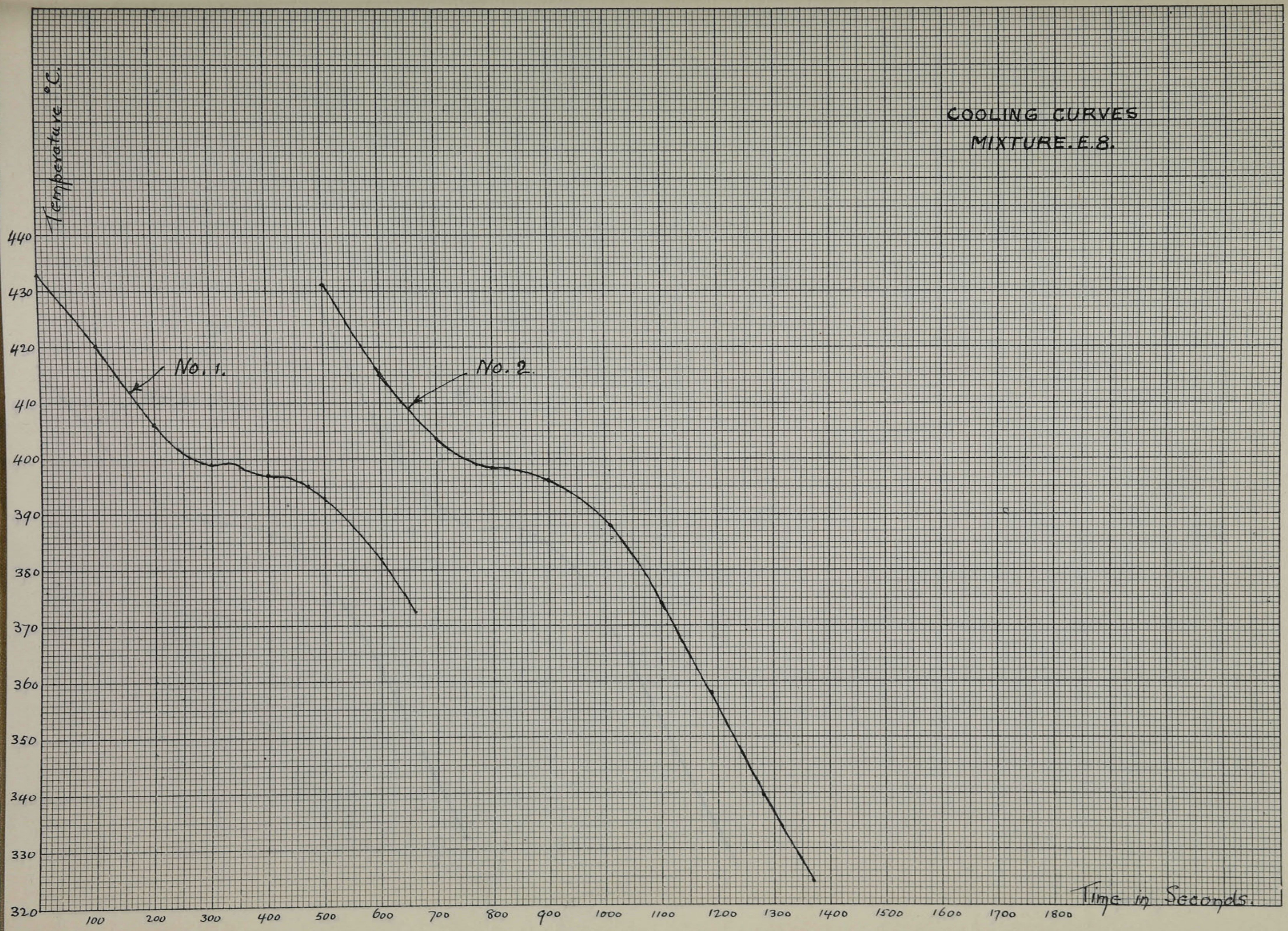
COOLING CURVES
MIXTURE. E.4.


COOLING CURVES
MIXTURE. E.5.
Temperature °C
380
370
360
350
340
330
320
310
300
No. 1.
No. 2.
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
Time in Seconds.

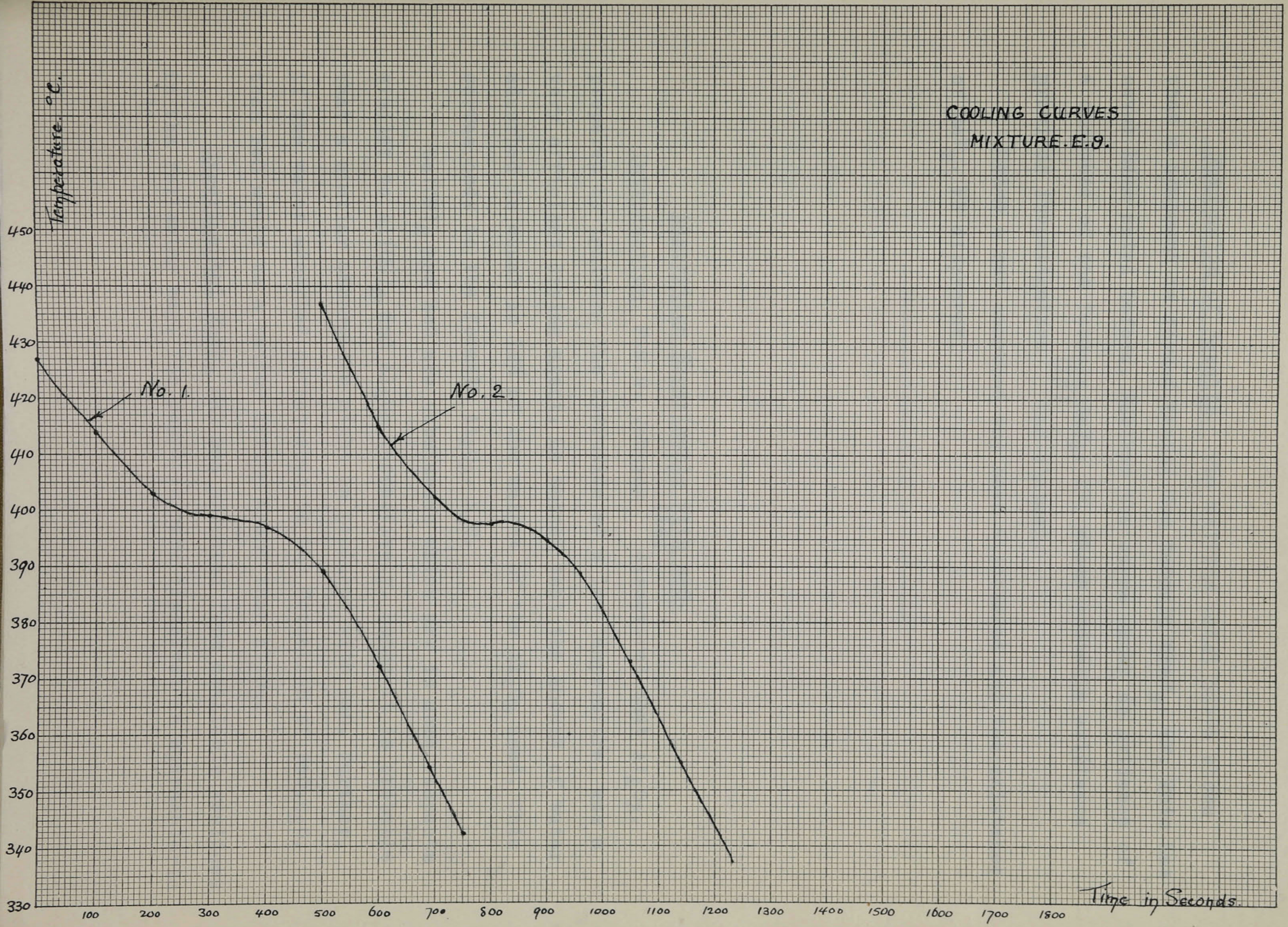

COOLING CURVES
MIXTURE. E.6.
Temperature. °C.
No. 1.
No. 2.
Time in Seconds.
410
400
390
380
370
360
350
340
330
320
310
300
290
280
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800



COOLING CURVES
MIXTURE. E. 7.



COOLING CURVES
MIXTURE. E.8.


COOLING CURVES
MIXTURE. E. 9.
Temperature. °C.
450
440
430
420
410
400
390
380
370
360
350
340
330
No. 1.
No. 2.
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
Time in Seconds.

Discussion of Results. The melting point curve shows that a compound is formed having the formula $2BeF_2 . KF$. This has never been noted before. Further the curve shows no evidence of a compound of the formula $BeF_2 . KF$, whose probable existence previous investigators (13) had claimed.

Hence a new compound has been discovered and the existence of $BeF_2 . KF$ disproved.

Adsorption Experiments with BeO.

Introduction. F.M.G. Johnson (14) discovered that Al_2O_3, prepared by igniting the hydroxide at a low temperature, was a very efficient drying agent. He showed that the amount of water adsorbed is equal to 18% of the weight of the Al_2O_3 used. This corresponds to the formula $Al_2O_3 . H_2O$.

$Be(OH)_2$ and BeO are substances which are in some respects similar to $Al(OH)_3$ and Al_2O_3 respectively. Hence it is probable that a similar adsorption might be produced with BeO. Further, if the water adsorbed corresponds to the formation of BeO,H_2O, then BeO would be a better drying agent than Al_2O_3.

Experimental Work. BeO was prepared from available residues in the following way. The residues were dissolved in hydrochloric acid and the beryllium precipitated with ammonia. The beryllium hydroxide was filtered off, and dissolved again in hydrochloric acid and filtered. This operation was repeated several times. Finally the beryllium hydroxide was removed from the filter and stirred up with a large quantity of hot distilled water and filtered. This operation was repeated until the filtrate gave only a slight trace of cloudiness with $AgNO_3$ solution. The beryllium hydroxide was removed from the filter and dried at 110°.C.

The adsorption by BeO for the vapours of several liquids was examined. The method employed by Johnson was used, which is briefly as follows. A stream of air is bubbled through the liquid, to be examined, so slowly that the air is saturated with the vapour. This saturated air is then passed through a U-tube containing the BeO. At intervals, the stream of air is discontinued and both the bottle containing the liquid and the U-tube of BeO weighed. From these weighings the total amount of vapour adsorbed by the BeO can be determined. To ensure that the air is pure, it is drawn in series through - a KOH wash-bottle, a concentrated H_2SO_4 wash-bottle, a P_2O_5 tube, the liquid under examination, and finally the U-tube of BeO.

For the first four experiments the BeO was prepared from the supply of beryllium hydroxide by igniting at a red heat to constant weight, and the four liquids water, ethyl alcohol, methyl alcohol and ether were tested. In the fifth experiment the beryllium hydroxide was dried at 300° C. to constant weight.

and water was again used. Thus we can compare the adsorption of water for BeO prepared by 3 different heat treatments.

In the following pages tables of the results obtained are given. Also curves are drawn, showing tha total amount of liquid passing through the U-tube per gram of BeO as abscissae, and the corresponding amount of liquid adsorbed per gram of BeO as ordinates. For comparison the curve of perfect adsorption is also given.

In the following tables :-

A = The no. of grams of vapour passed through the BeO between consecutive weighings.

B = The total no. of grams of vapour passed through the BeO.

C = The total no. of grams passed through the BeO per gram of BeO.

D = The no. of grams of vapour adsorbed by the BeO between consecutive weighings.

E = The total no. of grams of vapour adsorbed by the BeO.

F = The total no. of grams of vapour adsorbed by the BeO per gram of BeO.

EXPERIMENT NO.I. WATER.

0.8842 grams of BeO were used.

A	B	C	D	E	F
.0I03	.0I03	.0II7	.0I00	.0I00	.0I33
.0262	.0365	.04I3	.0I75	.0275	.03II
.0203	.0568	.0643	.0I8I	.0456	.05I7
.0443	.I0II	.II48	.0272	.0728	.0824
.0884	.I895	.2I43	.0336	.I064	.I206
.0902	.2797	.3I63	.0208	.I272	.I44I
.09I4	.37II	.4I97	.0I62	.I434	.I622
.0588	.4299	.4862	.0090	.I524	.I728
.0728	.5027	.5684	.0I00	.I624	.I840
.I45I	.6478	.7324	.0I76	.I800	.204I
.I86I	.8339	.9430	.0I78	.I978	.2237
.3I86	I.I525	I.303	.0294	.2272	.2569
.4904	I.6429	I.858	.0320	.2592	.293I
.2I82	I.86II	2.I04	.0I39	.273I	.3089

EXPERIMENT NO.2. ETHYL ALCOHOL.

I.60I8 grams of BeO were used.

A	B	C	D	E	F
.04I7	.04I7	.0260	.0403	.0403	.0252
.0266	.0683	.0426	.0247	.0650	.0406
.0296	.0979	.06II	.0279	.0929	.0580
.0339	.I3I8	.0823	.0I86	.III5	.0696
.02I4	.I532	.0957	.0042	.II57	.072I
.0290	.I822	.II38	.0050	.I207	.0753
.0258	.2080	.I300	.0034	.I24I	.0775
.0469	.2549	.I592	.0048	.I289	.0805
.2I38	.4687	.2926	.0200	.I489	.0930
.I859	.6546	.4087	.0I38	.I627	.I0I6
.I639	.8I85	.5III	.0I28	.I755	.I096
.2337	I.0522	.6567	.0I70	.I925	.I20I
.3260	I.3782	.8602	.0I94	.2III	.I3I8
.3772	I.7554	I.096	.0206	.2325	.I452
.4688	2.2242	I.389	.02I4	.2539	.I585
.4654	2.6896	I.680	.0I36	.2675	.I670
.7206	3.4I02	2.I29	.0I65	.2840	.I773

EXPERIMENT NO.3. **METHYL ALCOHOL**

I.7636 grams of BeO were used.

A	B	C	D	E	F
.040I	.040I	.0228	.0384	.0384	.02I9
.0592	.0993	.0566	.0539	.0923	.0526
.0370	.I363	.0774	.0I67	.I090	.06I8
.08I0	.2I73	.I232	.02I4	.I304	.0740
.2284	.4457	.2527	.0368	.I672	.0948
.4896	.9353	.5303	.0450	.2I22	.I203
.45I6	I.3869	.7865	.0292	.24I4	.I369
.49I6	I.8785	I.065	.0238	.2652	.I503
.5376	2.4I62	I.370	.0224	.2876	.I63I
.8880.	3.304I	I.874	.0320	.3I96	.I8I2
.8272	4.I3I3	2.343	.0I82	.3378	.I9I5
I.0486	5.I799	2.937	.0I66	.3544	.2009

EXPERIMENT NO.4, (first time done) **ETHER .**

I.7520 grams of BeO were used.

A	B	C	D	E	F
.0884	.0884	.0505	.0638	.0638	.0365
.I370	.2254	.I286	.0670	.I308	.0745
.II02	.3356	.I9I5	-.0024	.I284	.0733
.0972	.4328	.247I	-.00I0	.I274	.0726

EXPERIMENT NO.4. (second time done) ETHER.

I.7520 grams of BeO were used.

A	B	C	D	E	F
.II69	.II69	.0666	.0669	.0669	.0382
.0965	.2I34	.I2I8	.04I5	.I084	.06I8
.0266	.2400	.I370	-.0004	.I080	.06I6
.2428	.4828	.2755	.0224	.I304	.0744
.3696	.8524	.4865	-.0048	.I256	.07I6

EXPERIMENT NO.5. WATER.

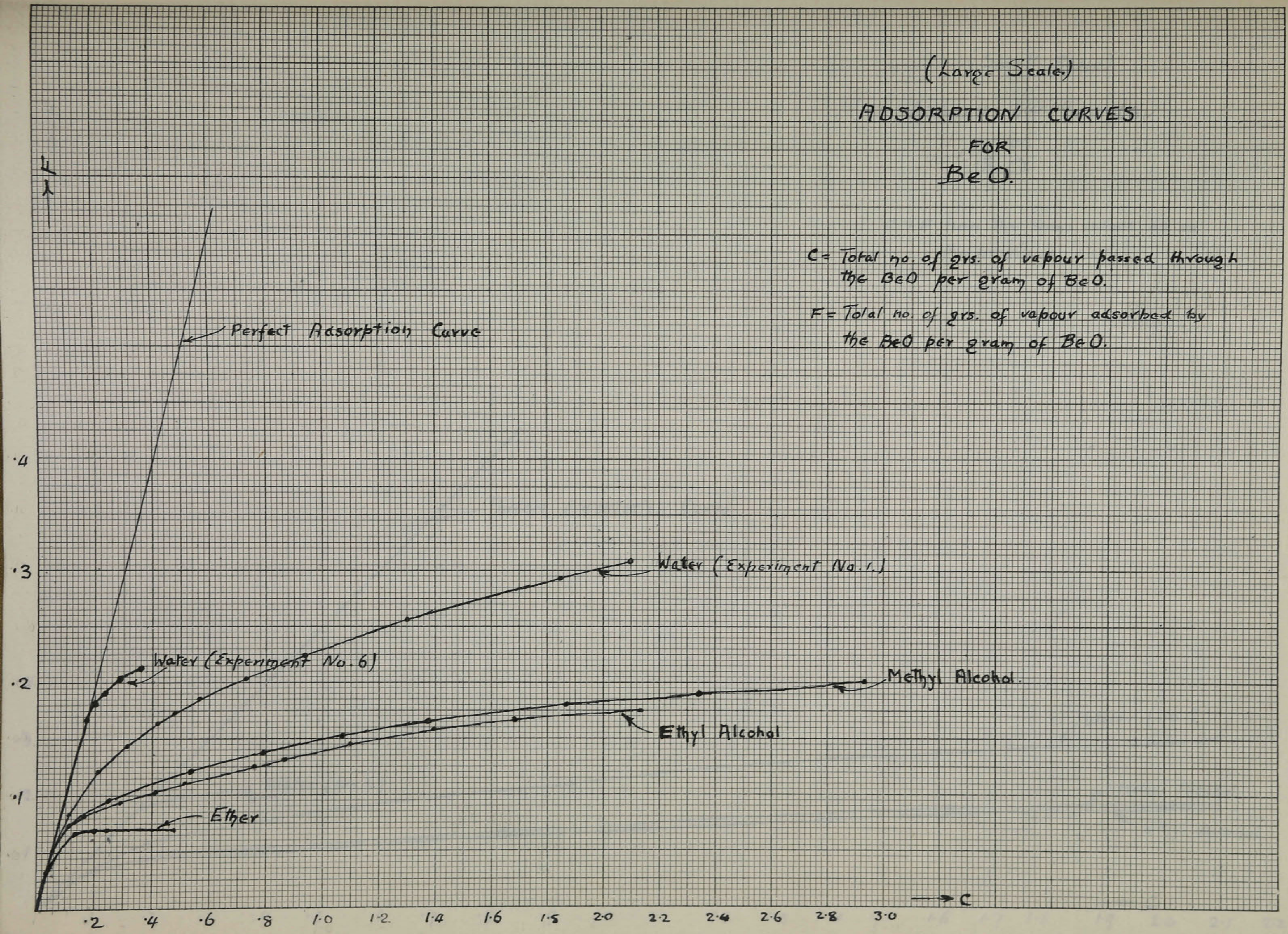
I.2760 grams of BeO were used.

A	B	C	D	E	F
.0046	.0046	.0036	.0046	.0046	.0036
.0060	.0I06	.0083	.0058	.0I04	.0082
.0225	.033I	.0260	.0204	.0308	.0252
.0I39	.0470	.0369	.0I32	.0440	.0345
.0346	.08I6	.064I	.0352	.0792	.062I
.03I6	.II32	.0889	.0324	.III6	.0875
.03I8	.I450	.II37	.0346	.I462	.II47
.0344	.I794	.I406	.0358	.I820	.I427
.03I0	2 .3I04	.I649	.0274	.2094	.I64I
.0270	.2374	.I86I	.0I68	.2262	.I773

EXPERIMENT NO.6. WATER.

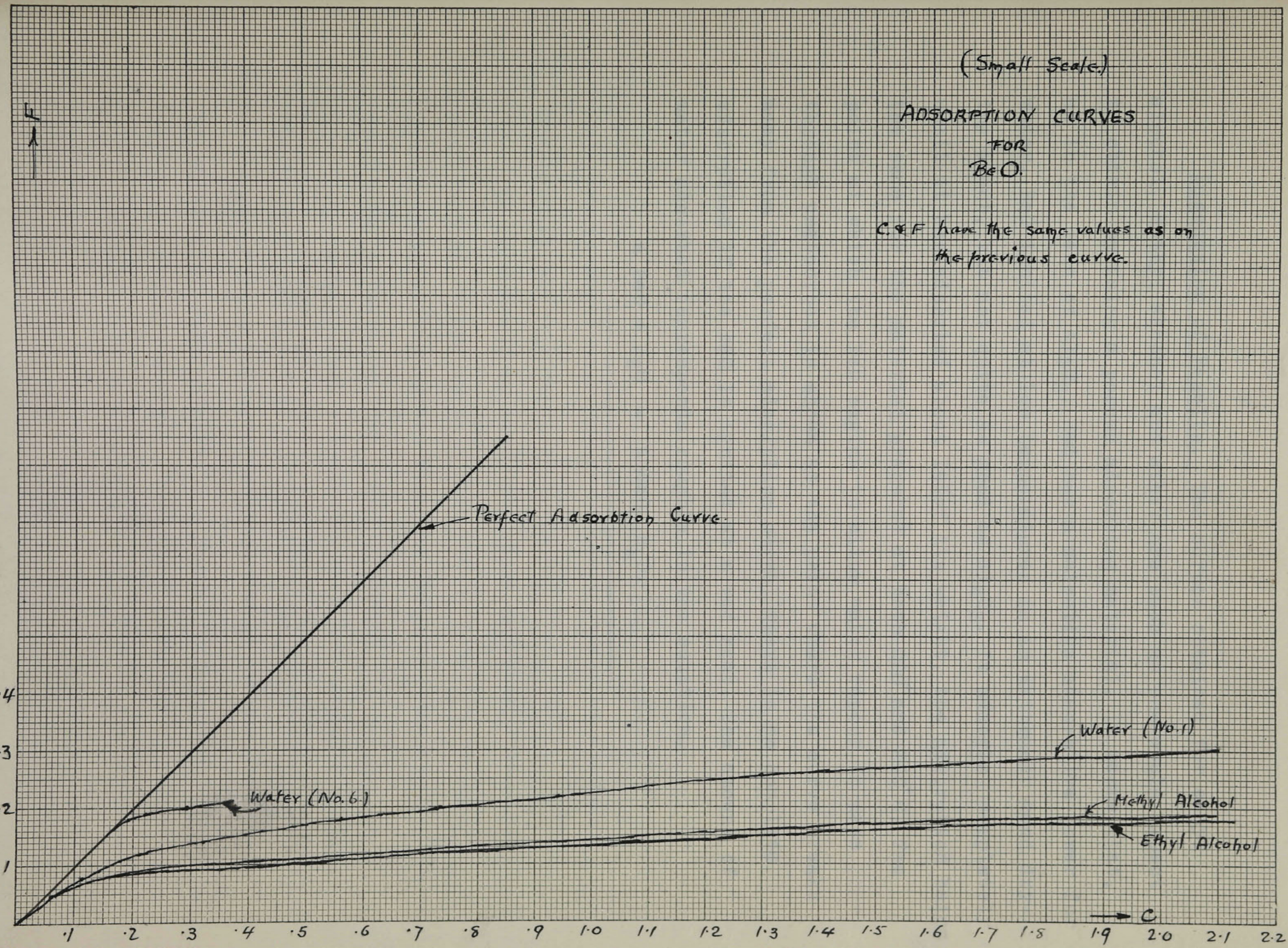
I.I468 grams of BeO were used.

A	B	C	D	E	F
.0I00	.0I00	.0087	.0I06	.0I06	.0925
.0I80	.0280	.0244	.0I60	.0266	.0232
.0I80	.0460	.0402	.0I70	.0436	.038I
.0366	.0826	.072I	.0375	.08II	.0709
.0482	.I308	.II4I	.0509	.I320	.II52
.0376	.I684	.I458	.0396	.I7I6	.I496
.0262	.I946	.I696	.02I7	.I933	.I677
.0340	.2286	.I993	.0I57	.2090	.I822
.0325	.26II	.2276	.0098	.2I88	.I907
.0669	.3280	.2860	.0I46	.2334	.2034
.0828	.4I08	.358I	.0I24	.2458	.2I43



C = Total no. of grs. of vapour passed through the BeO per gram of BeO.

F = Total no. of grs. of vapour adsorbed by the BeO per gram of BeO.



(Small Scale.)

ADSORPTION CURVES
FOR
BeO.

C & F have the same values as on the previous curve.

Discussion of Results. The curves obtained for ethyl alcohol, methyl alcohol and ether are such as one would expect to obtain by using a porous adsorbing material. It seems that, as in the case of Al_2O_3, BeO has a selective adsorbtive power for water. BeO ignited at low temperatures is an extremely good drying agent, but not quite so good as Al_2O_3. It adsorbs completely until it has adsorbed about 16% of its weight, the adsorption being the same for the material prepared at both 200° and 300° C. The point at which the BeO begins to allow water vapour to pass through unabsorbed is shown at the point where the curve breaks away from the perfect adsorption curve. There is no complete adsorption if the BeO is ignited at a red heat. The amount of water adsorbed corresponds roughly to the equation,

$$4\ BeO + H_2O = 4\ BeO.\ H_2O.$$

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 $BeCl_2$ vapour by heated tungsten filament.
3. The reduction of hydrated $Be(NO_3)_2$ in liquid ammonia.
4. The electrolysis of solutions of hydrated beryllium nitrate in liquid ammonia.

It is shown that impure metallic beryllium can be prepared by the reduction of $2BeF_2.NaF$ with metallic sodium.

It is shown that under the right conditions metallic beryllium of 99 per cent. purity can be obtained by the electrolysis of the double fluoride $BeF_2.NaF$. The correct conditions however have not been determined.

An investigation has been made on the products of the electrolysis of a liquid ammonia solution of hydrated beryllium nitrate and these products are observed to be identical with those obtained from the electrolysis of an ammonium nitrate solution in liquid ammonia.

Melting point curves have been obtained for mixtures of BeF_2 and NaF and mixtures of BeF_2 and KF for temperatures between 300 and 400 degrees C. The formation of the double fluorides BeF_2.NaF and $2BeF_2$.KF has been shown for the first time,and no evidence of the formation of the double fluoride BeF_2.KF has been obtained.

It is shown that BeO, prepared by dehydrating $Be(OH)_2$ at a low temperature, is a good desiccating agent, adsorbing almost as high a percentage of water vapour as Al_2O_3. The adsorption curves of BeO for several liquids are given.

References to the Experimental Work.

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2. Loc. cit., "I".

3. Comptes rend., Vol. I2I, p.496 (I895).

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5. J. Chem. Soc., Vol. 85, p. 603 (I904).

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8. J. Phys. Chem., Vol. I, p.707 (I896).

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IO. Ber., Vol.46, p. I604 (I9I3).

II. Ann. Chim. et phys., Vol. 30, p. 45 (I873).

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and Ann. Chim et phys., Vol. I6, p. 457 (I899).

I3. Loc. cit., "II" and "I2".

I4. J.A.C.S., Vol. 34, p. 9II (I9I2).

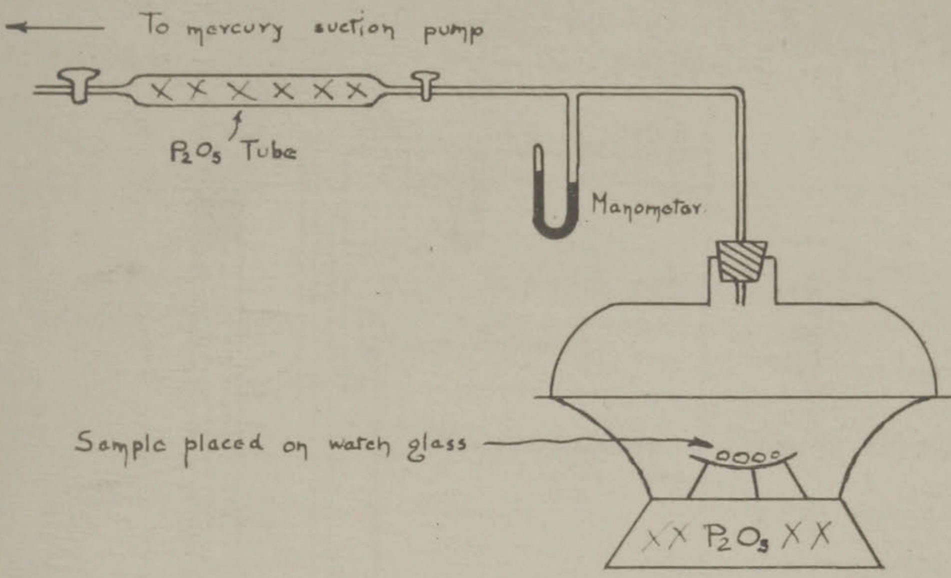

To mercury suction pump
P_2O_5 Tube
Manometer
Sample placed on watch glass
XX P_2O_5 XX

Fig.5.

Fig.1.

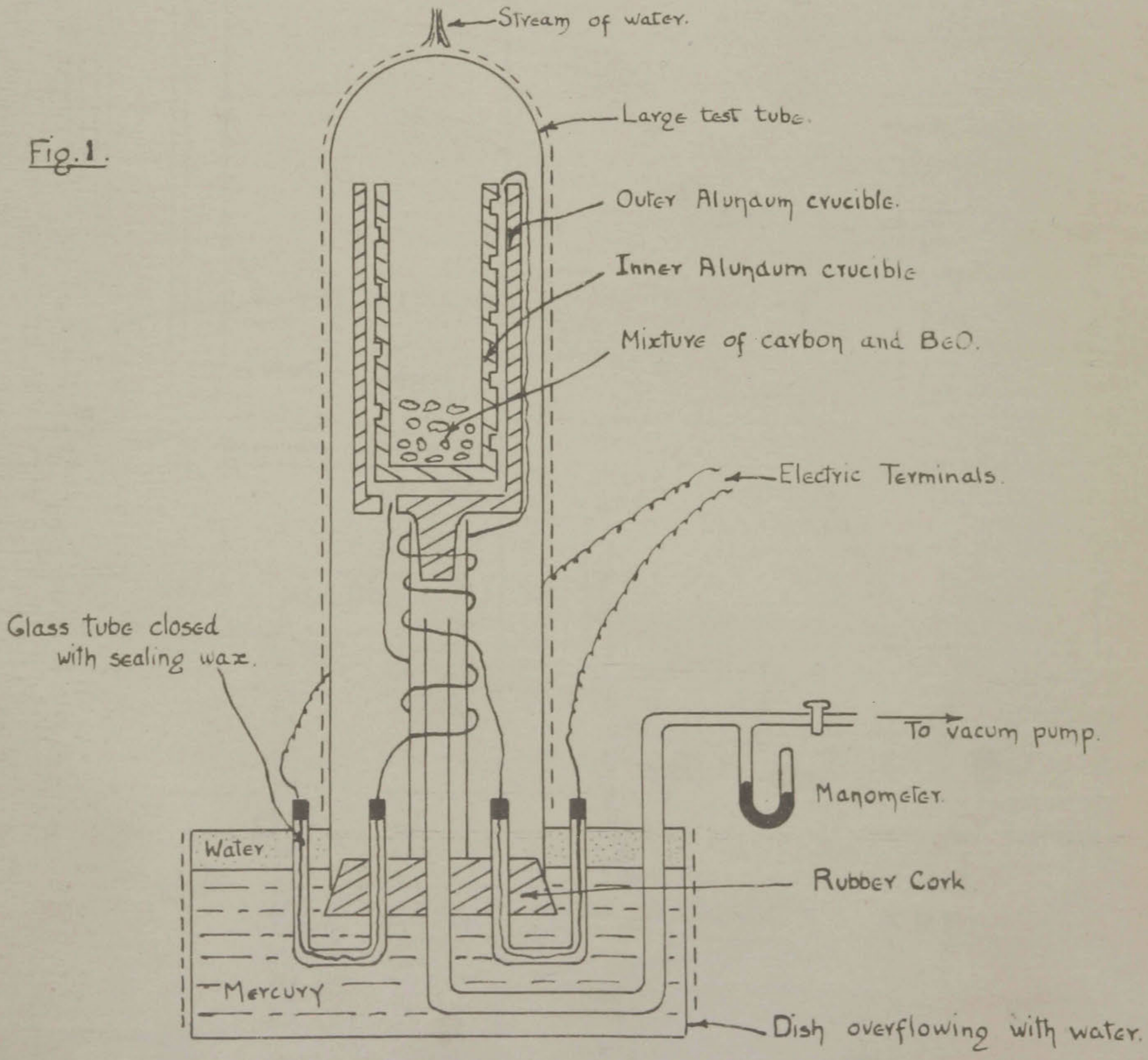

Stream of water.
Large test tube.
Outer Alundum crucible.
Inner Alundum crucible
Mixture of carbon and BeO.
Electric Terminals.
Glass tube closed with sealing wax.
To vacum pump.
Manometer.
Water.
Rubber Cork
Mercury
Dish overflowing with water.

Fig. 3.

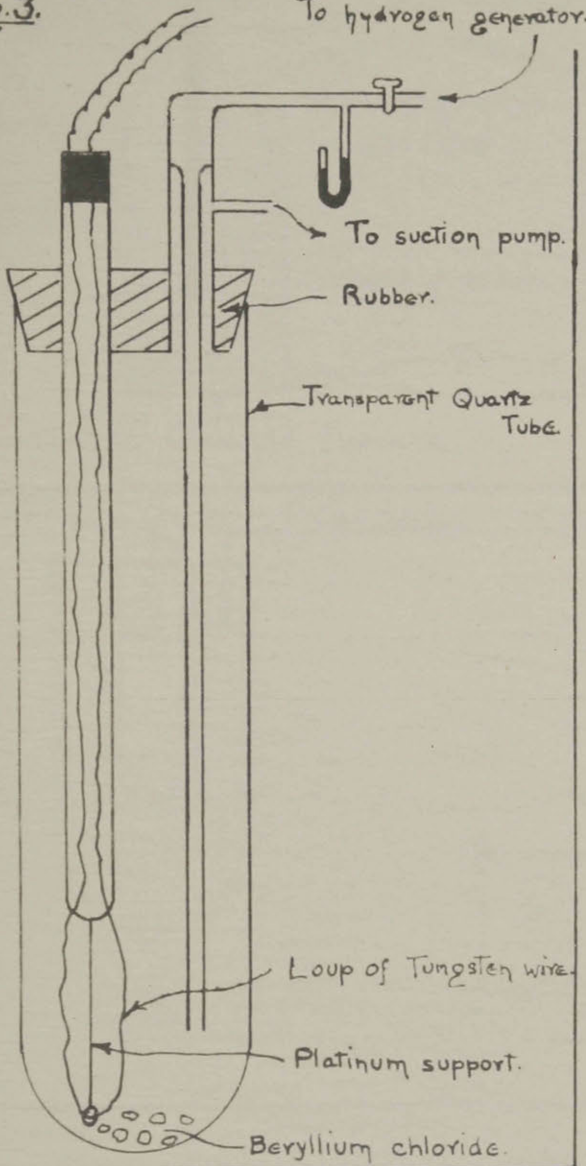


Fig. 8.

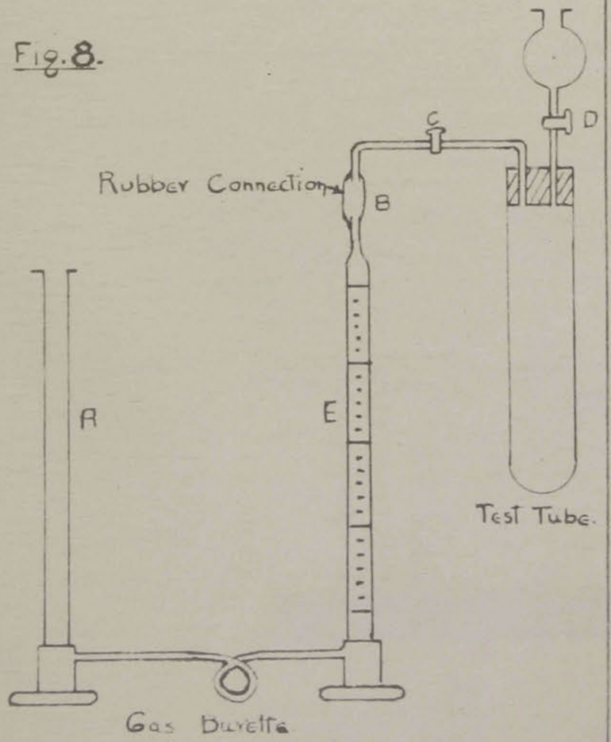
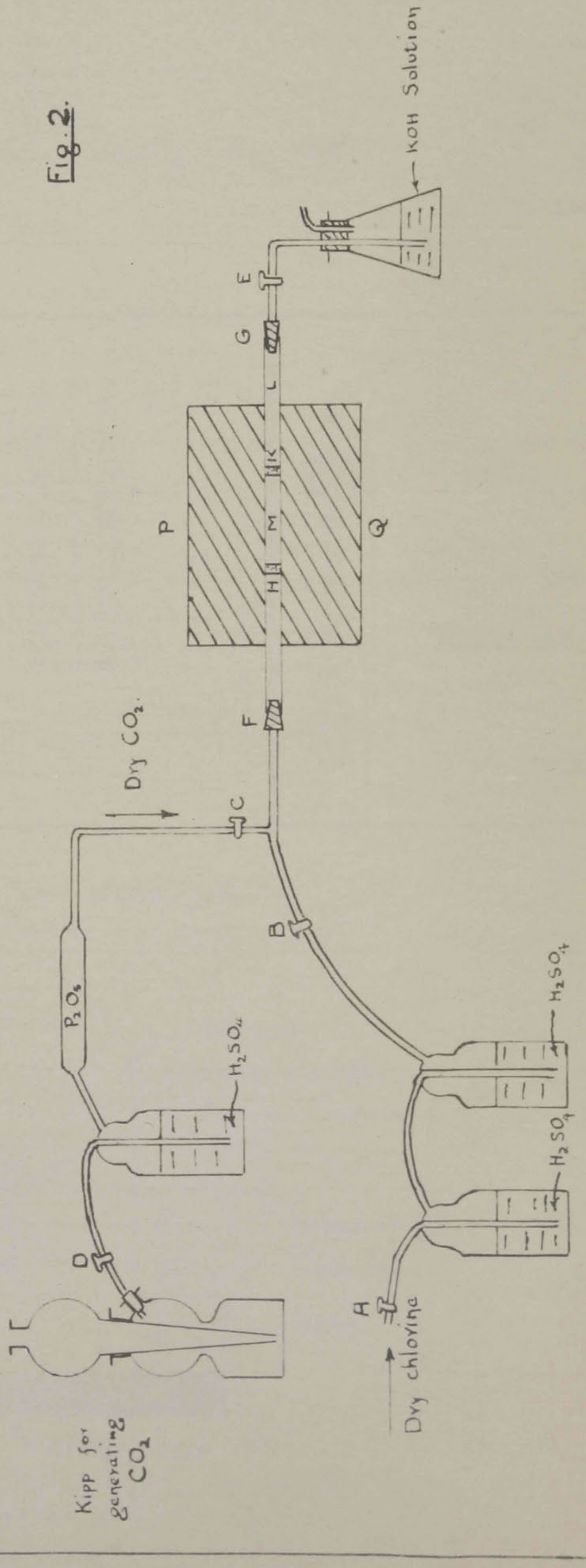


Fig. 2.



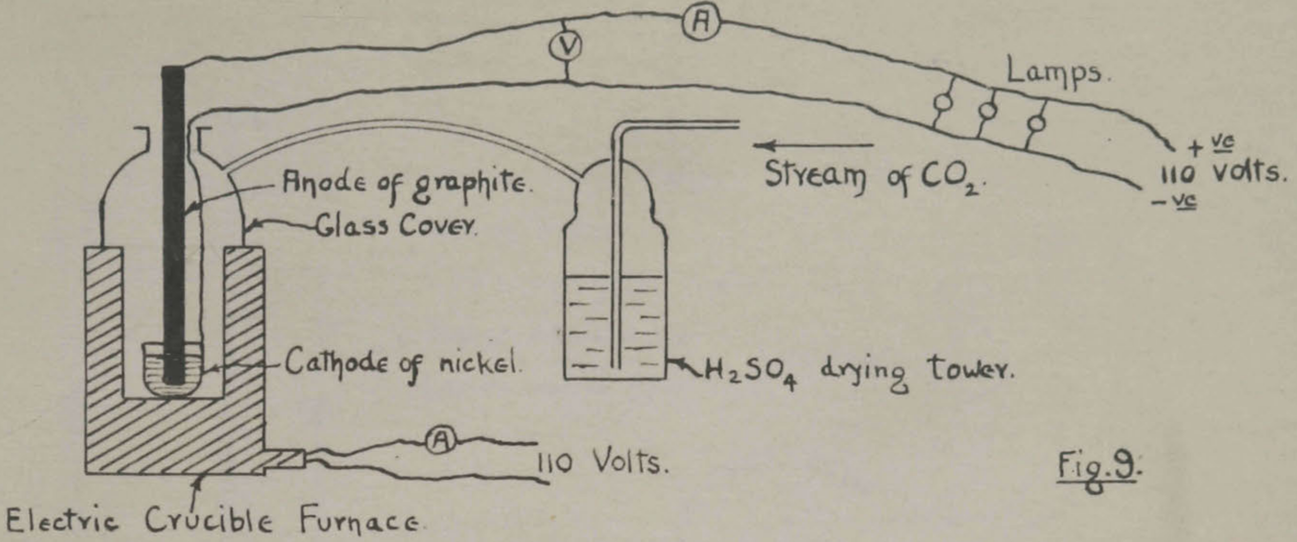


Fig. 9.

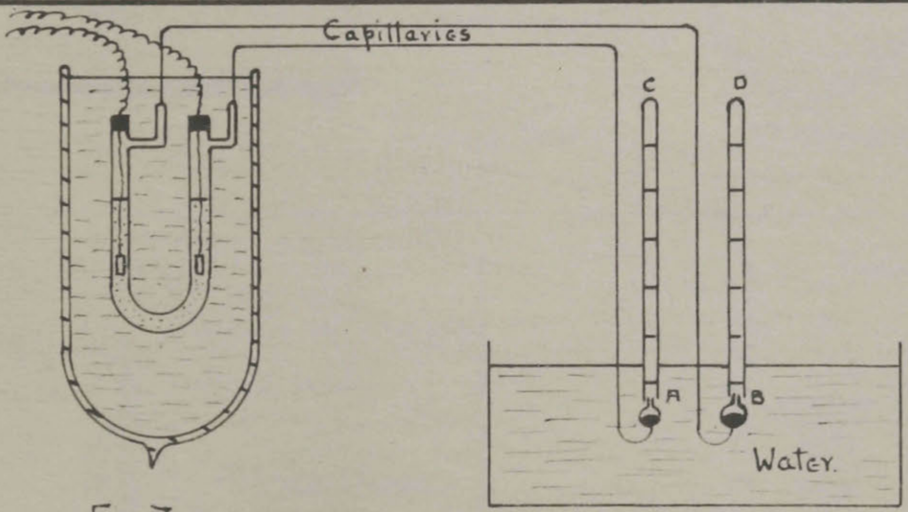


Fig. 7.

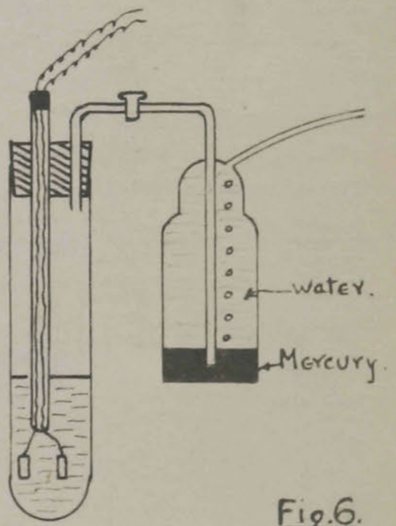


Fig. 6.

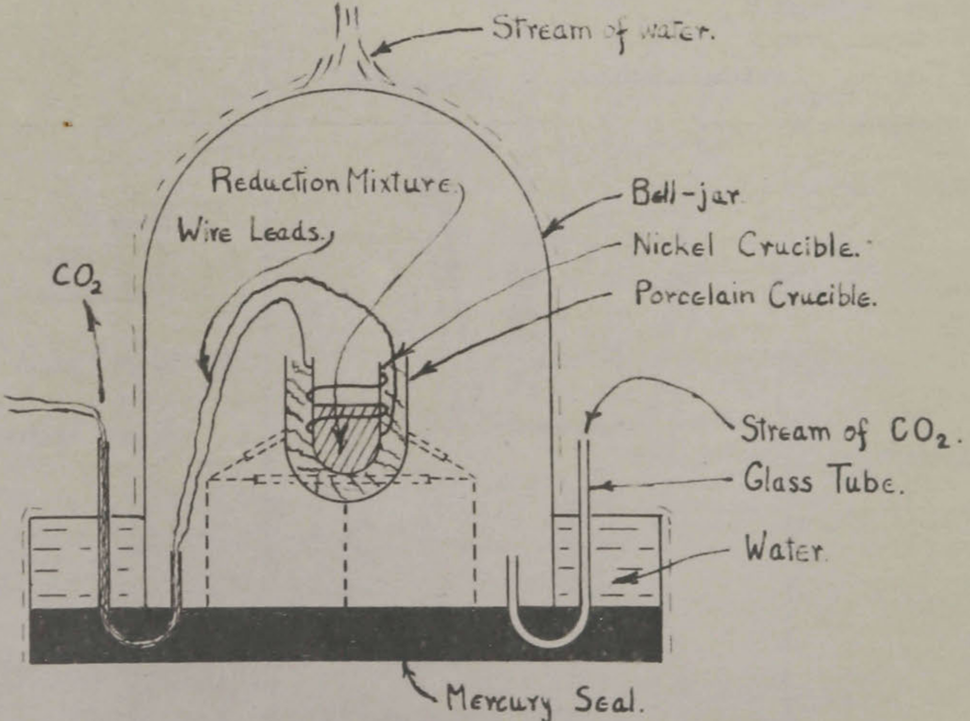


Fig. 4.

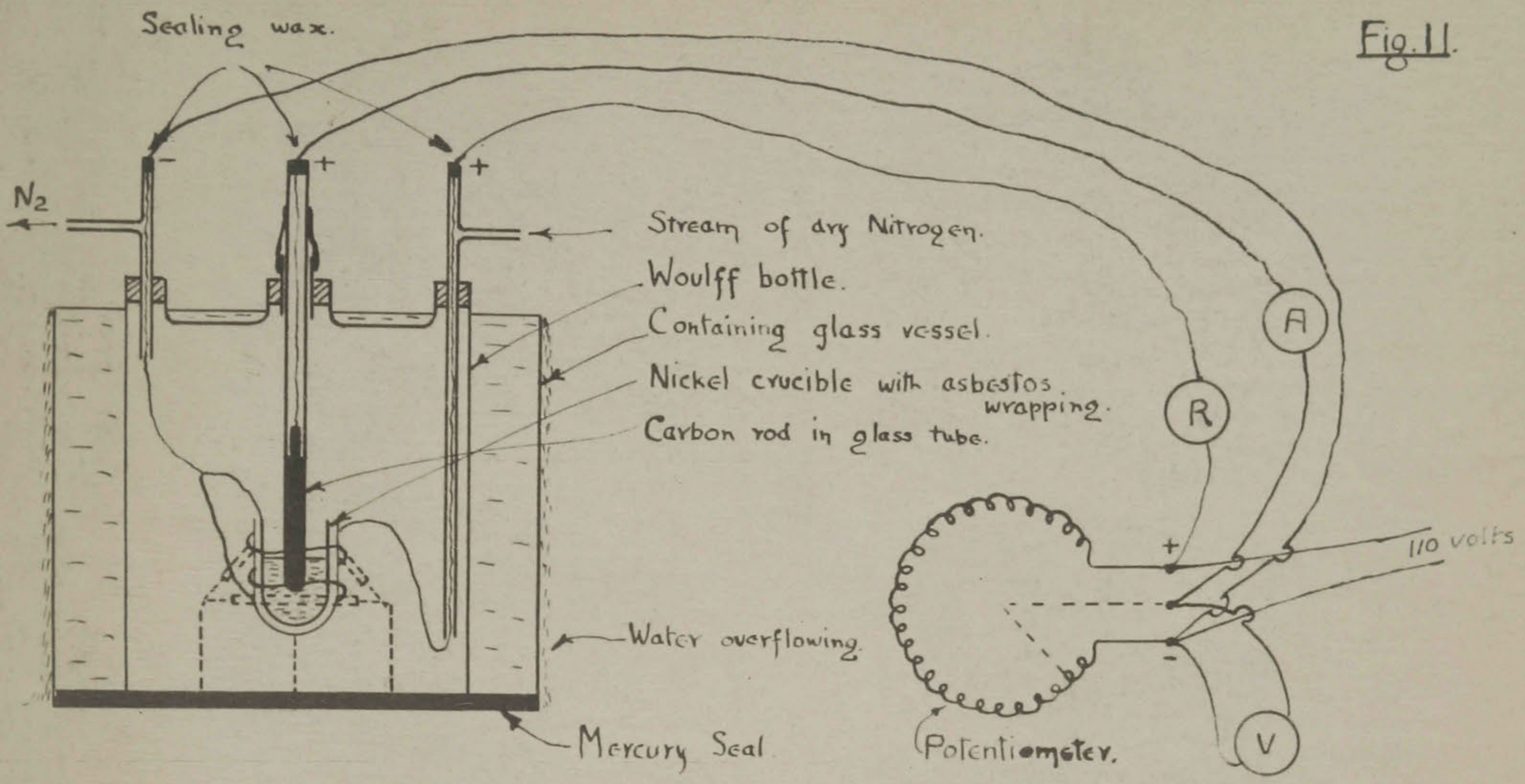


Fig. 11.

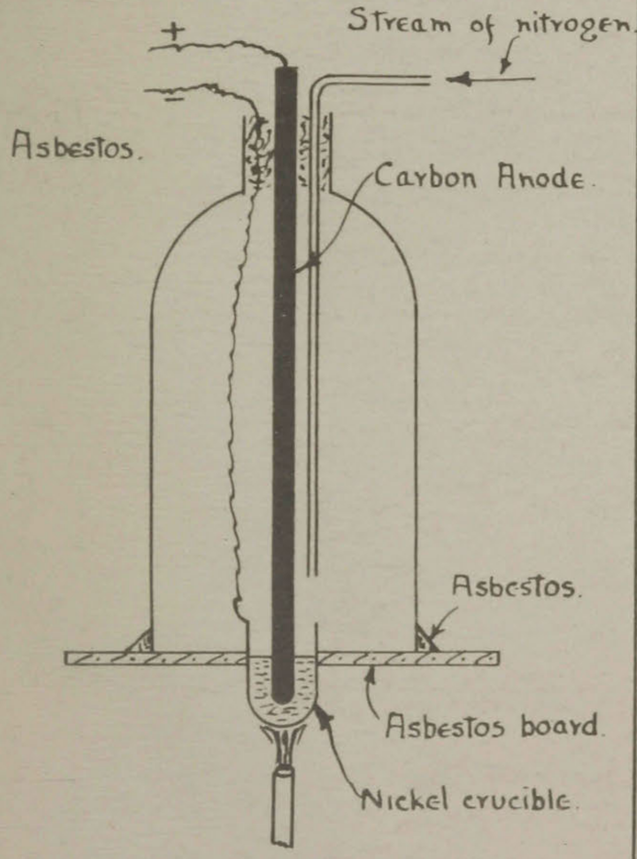


Fig. 10.

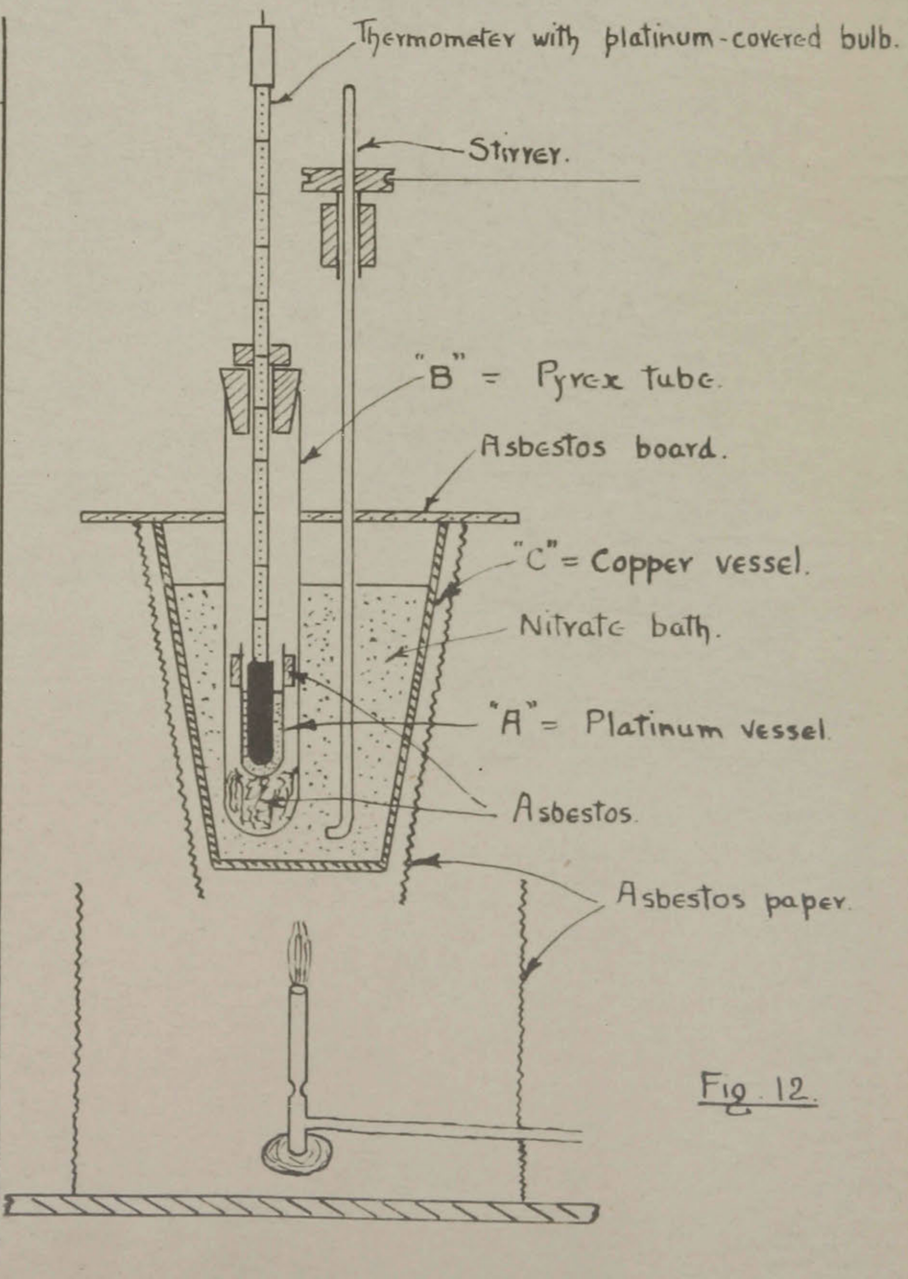


Fig. 12.