UNIVERSITY OF GLASGOW

THE DETERMINATION OF THE THERMAL CONSTANTS OF NON-METALLIC

INCLUSIONS IN STEEL

THESIS PRESENTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN THE FACULTY OF SCIENCE   (APPLIED CHEMISTRY -

METALLURGICAL SIDE)

BY

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Part I.

INTRODUCTION.

In each of the principal methods of making steel, i.e. Bessemer, Open Hearth, or Electric, the impurities are removed from the charge by a process of oxidation at exceedingly high temperatures. With the exception of the Bessemer process, the transfer of the oxygen takes place through the slag. In the case of the Bessemer process, air is blown through the molten metal. In all cases, the laws of physical chemistry can be applied. McCance (Proc. Far. Soc. 1918) was among the first to realise this, and has shown how the constituents of the slag are partitioned between the slag and the molten steel in the same way as any solute is partitioned between two solvents. He also shows how the removal of carbon can be explained on physical chemical grounds, by the application of rates of reaction to the balanced reaction

$$C + FeO = CO + Fe$$

In the same paper, McCance showed how the Nernst Heat Theorem could be applied to the steel bath, and in the general discussion held in 1925, by the Faraday Society and the Iron and Steel Institute, on "The Physical Chemistry of Steel-making Processes" he showed further applications of the Nernst Heat Theorem to the Steel bath, with special attention to deoxidation. The paucity of high temperature data was a severe drawback.

In his Presidential Address to the West of Scotland Iron and Steel Institute, Vol.XLI, Part 1. Oct. 1933-34, McCance has again shown the importance of physical chemistry in understanding the behaviour of both Acid and Basic Open Hearth Processes.

Herty has, in America, also worked on the Physical Chemistry of steel making, and has recently grouped many of his publications together in "The Physical Chemistry of Steel Making" (Carnegie Institute of /

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of Technology and Mining and Metallurgical Advisory
Boards).   The very nature of the steel making process
with its boil etc. means that during the process there
must be a mechanical admixture of the slag and molten
metal.   Even without the products of the oxidation
produced in the metal itself, there are thus non-metallic
particles in the bath.   Deoxidation products add to the
number of non-metallics, and a further source is from
the refractory materials of the furnace parts with which
the molten steel comes in contact at the various stages
of the process.   Benedicks and Löfquist in their
admirable book, "Non-Metallic inclusions in Iron and
Steel", Chapman and Hall, 1930, have differentiated
between two types of inclusions -- first "Slag inclusions
due to reactions taking place in the molten and solidifying
metal, may be called native slag particles", and sedond
"Mechanically admixed slag inclusions, and reaction
products between these and the native slags.   These will
be called foreign slag particles."

It seems to the present author that the best place
to study the nature of slag inclusions is not in the steel
in which they occur but in the nature of the slag which
was responsible for that steel.

The number of inclusions occurring in the solidi-
fied steel is dependent on two factors.   First the
ability of these inclusions to rise in the ingot mould and
secondly, on the nature of those inclusions which appear,
as a necessary consequence of the solidification, due to
differential crystallisation etc. and the abilities of
these latter inclusions to rise also.   Within limits, the
rising velocity of an inclusion is given by Stokes' Law.

$$U = \frac{2g \times r^2 (d' - d)}{9n}$$

where   U = final rising velocity of a certain grain,

r = equivalent radius of this (the radius of
an /

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<blockquote>
r = equivalent radius of this (the radius of
an assumed spherical grain with identical
rising velocity.)

d = density of the grain

d' = density of the steel

n = coefficient of viscosity of the molten metal

g = acceleration due to gravity.
</blockquote>

The dominant factor is, thus, the size of the particle and
the factors influencing the size are the surface tension,
the viscosity, the melting point, the temperature of the
slag substance, as well as the presence of foreign slag
and the formation of gas. Measurement of the surface
tension and the viscosity with relation to temperature
will depend for their starting point on that temperature
at which the slag melts. The melting points of the slag
substances becomes therefore probably the most important
thermal constant. As is well known, the melting point
is a function of the constitution of slag, expressed in
the case of a binary slag by the liquidus, and in the case
of a ternary slag by the liquidus surface of the solid
model, representing the ternary system.

Before the measurement of the other thermal con-
stants of the slags can be attempted, it becomes necessary
to determine these functions for the various combinations
of substances which go to form slags and non-metallic
inclusions.

A consideration of the charge in a steel furnace
shows that, neglecting sulphur and phosphorus, the principal
elements which are present are iron, carbon, manganese, and
silicon. Refining in the bath is by a process of
oxidation by which the elements carbon, manganese and
silicon are reduced to small limits. As a consequence of
this oxidation there is in solution in the molten steel at
the end of the process certain quantities of the oxides of
these /

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these elements.   These are removed wholly or partially from the steel by the use of deoxidising agents such as ferromanganese, ferrosilicon, or aluminium, and the oxides of these latter elements appear as deoxidation products dispersed throughout the bath.   Thus, there may now be in the bath, oxides of iron and manganese, and combinations of these - silica, either by itself or in combination with the oxides of iron and manganese, singly, or together.   Alumina may appear alone or in combination with the oxides of iron, manganese, and silicon, singly, in pairs, or together.

These deoxidation products are known to form the most dangerous of the slag inclusions, and, as it was pointed out above, the most important thermal constant is, from the standpoint of rising velocity, the melting point. It becomes necessary therefore to make a study of the combinations of these substances, starting from the binary systems, then to the ternary systems, quaternary systems, and systems with greater numbers of components.   We may group the oxides together, following this method, as follows:

Binary Systems.	Ternary Systems	Group
$FeO-MnO$, $FeO-SiO_2$, $MnO-SiO_2$	$FeO-MnO-SiO_2$	1
$FeO-MnO$, $FeO-Al_2O_3$, $MnO-Al_2O_3$	$FeO-MnO-Al_2O_3$	2
$FeO-Al_2O_3$, $FeO-SiO_2$, $Al_2O_3-SiO_2$,	$FeO-SiO_2-Al_2O_3$	3
$MnO-SiO_2$, $MnO-Al_2O_3$, $Al_2O_3-SiO_2$,	$MnO-SiO_2-Al_2O_3$	4

The quaternaries and systems of more components can be studied on this basis.

The work described in parts, II, III, IV, V, VI, of this thesis deals with Group 2. i.e. the principal deoxidation products of aluminium, and the thermal diagrams are found for the binary systems $MnO-Al_2O_3$, $FeO-Al_2O_3$, and for the ternary system $FeO-MnO-Al_2O_3$.

The other groups have received and are receiving the
attention of other research workers.

From the standpoint of hot fabrication of steel,
it is of interest to know if an inclusion will yield with
the application of a deforming force, and so help to give
the directional properties associated with worked metals.
A hard unyielding inclusion acts as a stress raiser.   The
behaviour of the inclusion during fabrication will depend,
in the first instance, on its softening point, which will
be dependent on the solidus of the system to which the
inclusion belongs.   We could not expect an inclusion
which had a solidus temperature far above the hot working
temperature to deform with the metal.   The work about to
be described gives useful data which can be applied to the
behaviour of these inclusions during working.

As stated above, any applications of physical
chemistry to steel making, suffers from the lack of high
temperature data.   Among the other data required for the
application of the Nernst Heat Theorem to the steel bath,
are the specific heats of the reacting substances.   The
specific heats of the slag are also of great importance
when a consideration is made of the thermal balance in the
furnace, e.g. in connection with the heat transfer from the
gases to the metal.   Work is in progress to develop a
method for the determination of this thermal constant, and
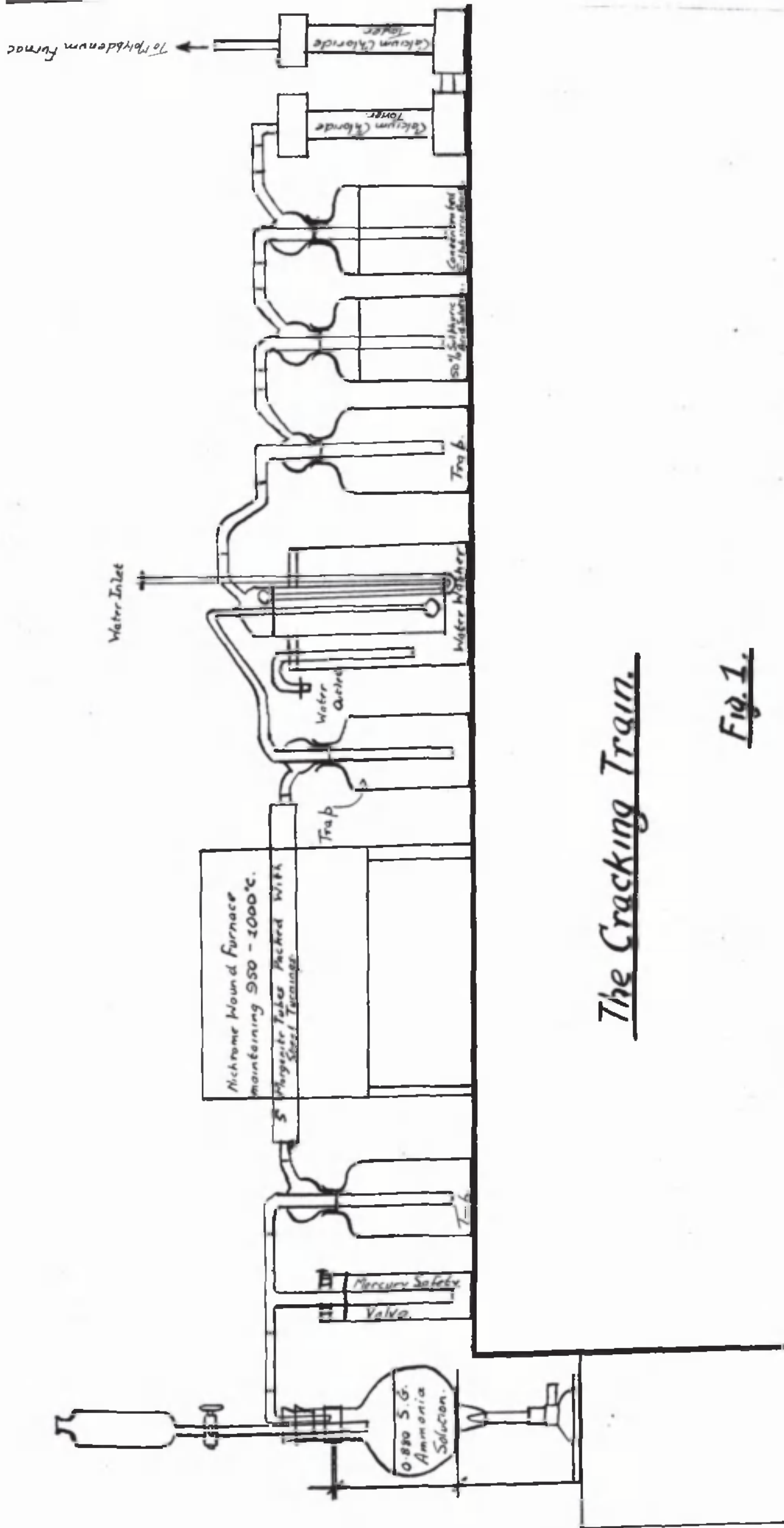the first stages of this work are described in part (VII).

Part (II).

APPARATUS AND TECHNIQUE.

The Cracking Train.

For high temperature work, molybdenum wire is the most convenient heating element, but it is necessary to maintain a neutral or reducing atmosphere around it during the heating, otherwise it is oxidised and lost. This may be done by means of hydrogen from a cylinder, or by "cracking" ammonia into nitrogen and hydrogen. The latter method was found to be more economical. A line diagram of the "cracking" train is shown in fig. (1).

A two litre flask was filled to about two thirds of its capacity with ammonia (0.880 S.G.), and fitted with a bung carrying a dropping funnel, and delivery tube. The dropping funnel allowed ammonia to be added, if necessary, near the end of a run, and a plentiful stream of gas was thus kept up while the molybdenum was cooling. The ammonia was driven off by applying a small bunsen flame to the flask and passed over a mercury safety valve, to a trap, which was an empty bottle, fitted with a Drechsel top as shown. All of the bottles were of the same type. Should the ammonia be driven off too quickly, the gas forced down the mercury in the valve and bubbled off. The trap was included to prevent any water which might be driven over, from entering the Morganite tubes. These Morganite tubes were five in number, connected with rubber and glass tubing so that the gas entered at one end and left at the other. They were contained in a Nichrome wound furnace, which passed 5-6 amperes at 125 volts. It was usual to run two of these furnaces in series from the 250 volts mains, and they maintained a temperature of $950^{\circ}C-1000^{\circ}C$. which was the temperature found by experience to be best for the cracking. The Morganite tubes were one inch internal diameter and thirty inches long. They were

The Cracking Train.

Fig. 1.

To Molybdenum Furnace ←

Calcium Chloride Tower

Calcium Chloride Tower

Concentrated Sulphuric Acid Solution

50% Sulphuric Acid Solution

Trap

Water Inlet

Water Outlet

Water Washer

Nichrome Wound Furnace maintaining 950 – 1000°C.

Silica Tube Packed With Steel Turnings

Trap

Trap

Calcium Chloride Tower

Mercury Safety Valve.

Gas

0.880 S.G. Ammonia Solution

To Molybdenum Furnace ←

packed with steel turnings, and loosely plugged with asbestos at the ends. Another trap was placed at the other side of the furnace, to prevent any water, which might be sucked back, from entering the Morganite tubes and cracking them. The residual ammonia was removed by passing the gas through a water washer, the design of which is shown in the sketch. The gas was led down to the bottom of the inner chamber, and rising through the water there, passed out through the top. The washer was of such a design, that the water in the inner chamber could be changed continuously, or periodically.

After the wash bottle, another trap was provided, which prevented any water passing over from the washer from reaching the sulphuric acid, contained in the next two bottles. The first was a 50% sulphuric acid solution, and the other was concentrated sulphuric acid. The first dissolved out any residual ammonia as ammonium sulphate, and the concentrated acid removed water vapour from the gases. The calcium chloride towers which completed the train, removed the last of the water vapour, and also any sulphuric acid spray. The "cracked" gas was then passed into the furnace. The tubing of the train was of as wide a bore as possible, and all connections made gastight. It is essential to maintain a positive pressure inside the furnace of about $\frac{1}{4} - \frac{1}{2}$ inch of water and this was verified by sealing a water manometer into the lid of the furnace.

The Large Molybdenum Furnace.

A sketch of the furnace is given in fig.(2), from which the construction may be clearly seen. It consisted of a cylindrical steel casing, 16 inches in diameter, by 16 inches in height, standing on three stout steel legs 16 inches high. The casing was provided with a detachable steel lid, with a central hole to allow the top of the furnace tube to come through, and be held in place by

To Nitrogen Cylinders

To pump and Manometer

Tungsten

Molybdenum

"Pythagoras" Tube

Alundum Seal
(See Text)

Lead

Silica Tube

Mains Terminal

Steel Furnace
Casing.

Alundum Sheath

Crucible Container

Asbestos Lagging.

Alundum Stool

Furnace Tube and
Winding.

Tube to keep "Pythagoras"
central.

Alundum
Stool

Train Gas
Distributor

Mains.
Terminal

Lead
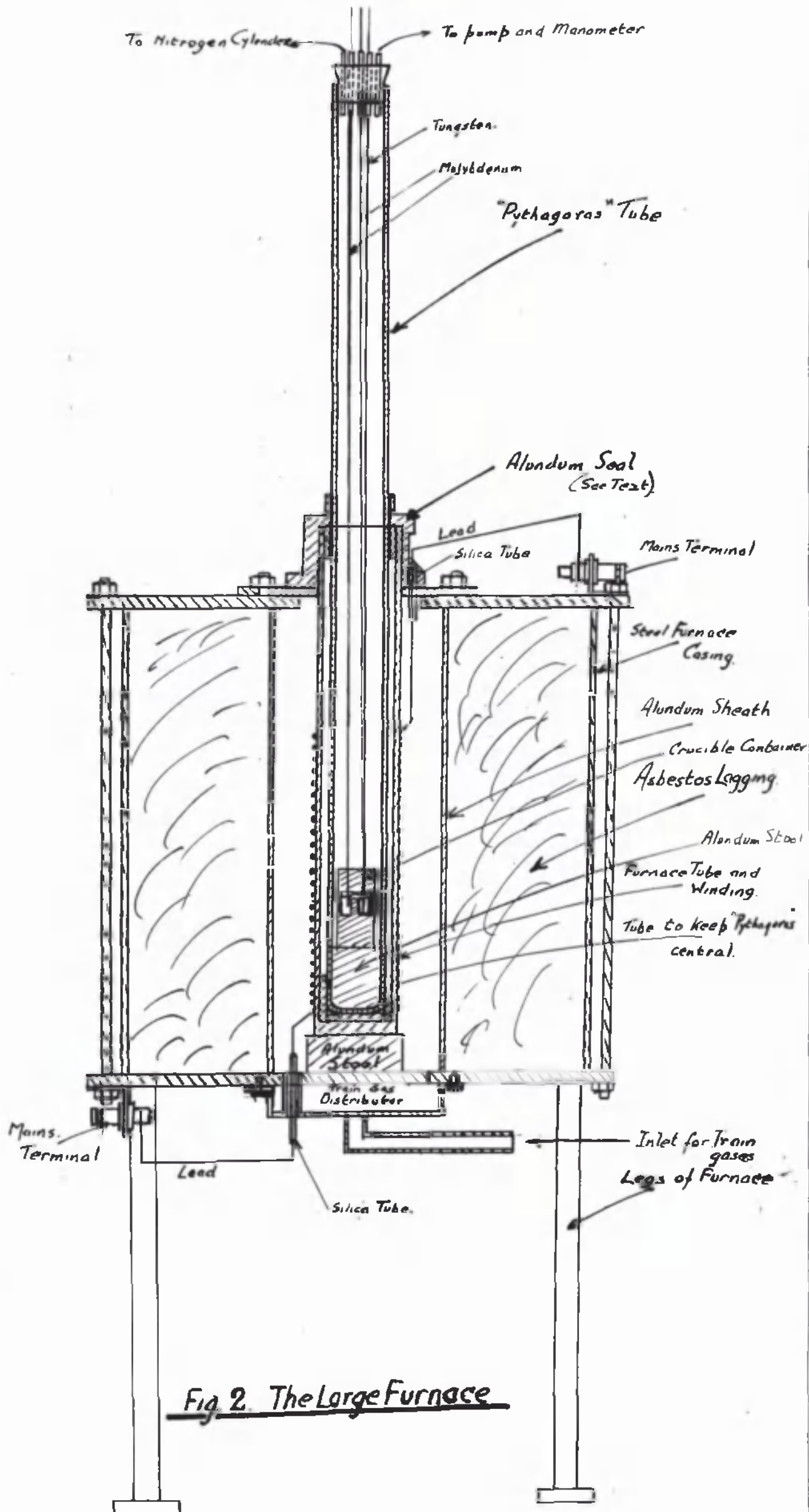
Silica Tube.

Inlet for Train
gases

Legs of Furnace

Fig. 2. The Large Furnace

cement.   The furnace unit consisted of three tubes, which were inserted with the lid removed.   These were :-

1.   An outer sleeve or sheath of alundum to prevent heat losses, and also to prevent the asbestos lagging from slagging with the alundum covering of the heating element.

2.   The furnace tube.

3.   An inner tube.

(a).   In the case of work being done in the train gases this inner tube was a recessed alundum tube as shown in fig.(3), which was an easy sliding fit into the furnace, and was covered with molybdenum sheeting, the function of which is described later.   This sheeting or grid had to be recessed in this inner tube otherwise its proximity to the furnace winding caused the latter to arc across to the grid, with consequent loss of the furnace.

(b).   In the case of work being done in a controlled atmosphere, this inner tube was of "Pythagoras", a proprietary brand of refractory, capable of withstanding temperatures of $1400-1450^{\circ}C$ when evacuated, and $1650^{\circ}C - 1700^{\circ}C$ when working with atmospheric pressure inside.

Fig.(2) shows the "Pythagoras" tube in the furnace, The "Pythagoras" tube was closed at one end and open at the other.   It was ninety centimetres long, fifty millimetres internal diameter, and sixty millimetres outside diameter. There was a clearance of about one and a half centimetres all around the "Pythagoras" tube, this allowing ample room for the grid, which was sheathed round the Pythagoras tube near the bottom, and bound to it with molybdenum wire.

"Pythagoras" tubes are costly, and it was found that they had a longer life if certain precautions were taken.

To Differential Galvanometer

Mo

To Differential

Dual purpose Molybdenum (See Text).

hr. Molybdenum Wire of Differential Thermocouple

Tungsten Thermocouple Element.

Alundum Top for Furnace Tube

Furnace Tube (Alundum).

Alundum Sheath.

Asbestos Lagging

Molybdenum Grid.

Recessed Alundum Grid Holder.

Alundum Stool.

Alundum Stool.

Furnace Casing.

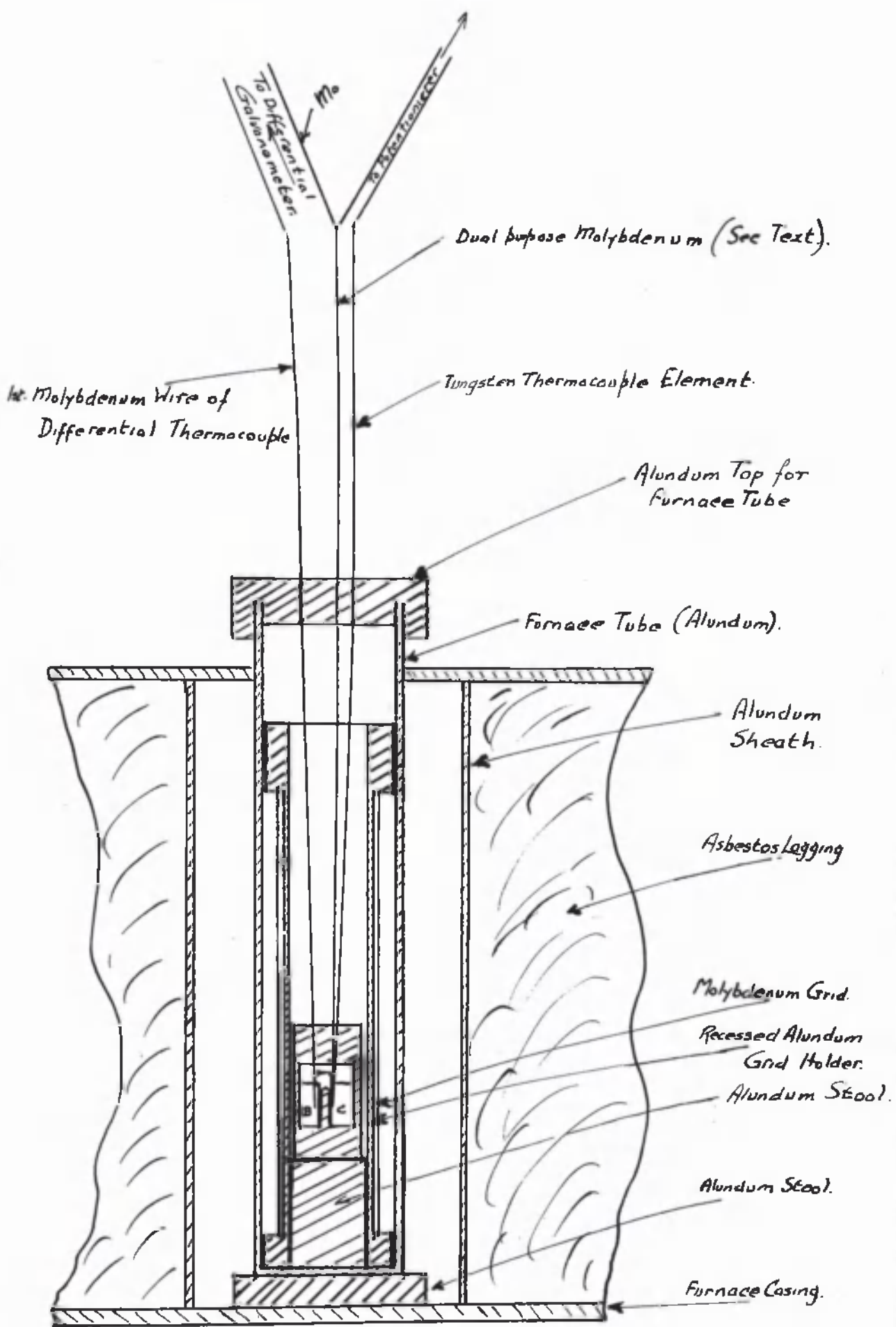Fig. 3. Recessed Alundum Grid Holder.

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(1)   The weak part of a "Pythagoras" tube was its rounded
bottom.   It was essential that this should be kept
well away from the hot zone of the furnace.

(2)   The "Pythagoras" tube must be central in the
furnace, otherwise the grid caused an arc from the
furnace winding.   This was done by providing a hollow
tube of alundum, about an inch and a half in length,
which was a sliding fit into the furnace tube, and
into which the Pythagoras tube fitted easily enough to
allow for the expansions of each on heating.   This
tube was placed at the very bottom of the furnace
tube.

(3)   A satisfactory method of sealing the furnace was
necessary, and the following was found to be the
safest.   As shown in fig.(2), the seal was essen-
tially made of two alundum tubes, one which fitted
into the furnace tube and was about five inches in
length.   The Pythagoras tube was a sliding fit into
this tube.   The other tube fitted over the furnace
tube, and was equal in length to that amount of the
furnace tube which protruded from the lid of the
furnace.   When these two tubes were joined concen-
trically by alundum, a recessed seal was obtained
which could slide over the furnace tube, and provide,
at the same time, an inner tube which kept the
Pythagoras central.   The small space between the
Pythagoras tube and this inner tube was packed with
asbestos, and the bottom of the outer tube was luted
to the lid of the furnace casing.

(4)   When work was being done at the high temperatures,
a counterbalanced system was provided whereby the
"Pythagoras" tube was suspended in position inside
the furnace, so that no weight was supported by the
tube itself.   If this were not done the Pythagoras

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tube sagged under its own weight, whenever the temperature was such that the refractory, of which it was made, became plastic.

The resistance of a molybdenum furnace such as has been described, was approximately one ohm at room temperature, and about eight or nine ohms at $1600^{\circ}C$.

These furnaces usually have a hot zone, which is about one third of the way up the winding and extends over about two inches. It made all the difference to successful operation, if the melt were not in the hot zone of the furnace. Sometimes, by merely raising or lowering the melt an inch in the furnace an additional $200^{\circ}C$ could be obtained, as well as a better heating rate.

Occasionally work had to be done, which required an even distribution of temperature along the tube, for practically the whole of its length. To obtain this a "differential" system of winding was tried. No calculations of heat distribution were attempted, but very successful results were obtained by spacing the wire at the centre of the former, slightly less than five to the inch, and working to slightly more than five to the inch at the ends.

The train gases were always allowed to run for some time before switching on the current. Then a small current of about ten amperes was passed through for about ten minutes, and then as the temperature rose the current was increased slowly, so that when the temperature was about $600^{\circ}C$ the current was about twenty amperes. A furnace lasted much longer if carefully treated, i.e. if no sudden shocks of current were sent through it. It was advisable to heat slowly through the temperature range about $600^{\circ}C$, as this range seemed to be the optimum range for the ignition of the train gases, and a slight explosion resulted from too rapid heating. A series of these small explosions invariably resulted in the cracking of the top

Part (11)

of the furnace tube.

In the case of work being done in the train gases, the "pythagoras" tube was dispensed with, and the top of the furnace was closed with a grooved disc of baked alundum with the necessary holes for the insertion of the thermocouple wires, the groove in the disc being made to fit the top of the furnace tube. (see Fig.3).

Design and construction of a small high temperature furnace.

It was decided to find some other type of furnace. if possible less costly to build, and which could be raised to a higher temperature, without involving the loss of a large Molybdenum furnace and Pythagoras tube if failure occurred. For some of the work, there had to be a controlled atmosphere in the working space of the furnace, and so the use of Pythagoras tubes had to be continued, as this is the only available refractory capable of retaining a given atmosphere, when heated to a high temperature. It was quite by chance that some smaller bore tubes were found to be more resistant than the usual 50mm. type, and so the design of a small furnace became possible. It was necessary to use smaller furnace tubes and this meant the use of much thinner wire, in order to get the required resistance of wire wound round the thinner section of these. This wire was only a fraction of the cost of the thicker wire, mentioned below. Even though such a furnace failed, it was a simple matter to have a replacement at short notice, the time required to make the necessary parts, being much less than with the larger furnaces.

To get the necessary amount of heat it was necessary to make the furnace a doubly wound furnace. The diameter of the molybdenum wire used was 0.25 mm. and the length calculated to give a minimum temperature of $1500^{\circ}C$ with a maximum current of six amperes at two fifty volts was 13.5 feet.

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The length of each solenoid was seven inches, the inside one being more closely wound. The actual furnace tubes were made, as described below, of baked alundum cement. Fifteen feet of wire were used, the extra length being to allow the leads to be made of doubly stranded wire.

At first, a molybdenum grid was not incorporated in the design, for it was thought that a small current of six amperes would not cause the unstable behaviour of the thermocouple experienced in tube furnaces at high temperatures. During the first heat of the furnace, without a grid, the thermocouple behaved erratically when the temperature reached about $1200^{\circ}C$-$1400^{\circ}C$ even when the current was only a fraction of an ampere, although it was not affected when no current was flowing. The furnace was used for some time, simply as a melting furnace, and then a molybdenum grid was sheathed around the Pythagoras tube.

The section of the Pythagores tube was only 0.8 inches, so that the working space was very limited, and to economise space the thin molybdenum wire was used with some tungsten wire of the same diameter as the thermocouple elements. At first the melt was simply hung inside, by means of the thermocouple wires, with no other support at all. The disadvantage here, was the fragility of the heated molybdenum and tungsten wires, and their brittleness at the high temperature. Even so, it was found that the crucible stayed in position throughout the run, but the slightest touch broke the wire, and the melt had to be withdrawn from the bottom of the furnace. A much more serious disadvantage was that no precautions could be taken to ensure that the crucible was upright in the furnace. As sometimes happened, the crucible was tilted, and when the melt fused, the liquid ran out and slagged a hole in the Pythagoras tube. Even though the space was limited, some means had to be devised to support the melt, and to

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provide some material to absorb the liquid should the
latter "boil" over, and in this way prevent the destruction
of the Pythagoras tube.   Finally a container-support was
made of the design shown in fig.(4a).   This was intended
to allow of heating and cooling curves being done in the
small furnace.   The mass of this component had to be as
small as possible due to its large heat capacity.   Acting
as a reservoir of heat, it markedly slowed up the cooling.
To diminish this effect, it was made hollow.   This enabled
the differential lead to be brought down the inside, and
out from the bottom of the furnace.

In fig. (4a), $\underline{A}$ is the container made of two hollow
tubes of alundum, joined with a little alundum cement.   The
upper and larger tube was about two and a half inches long,
and was an easy fit into the Pythagoras tube.   The bottom
tube was about a third of this in section, and about six
inches long.   A plug of alundum $\underline{P}$ as shown, was provided to
insulate the blank from the crucible.

The Furnace.

A section through the furnace is shown in fig.(5).
The outside frame was of asbestos sheeting braced with
steel.   The diagram is in the proper proportions roughly
half size.   There were five tubes altogether, viz:-
1. An outer one of alundum, to keep the asbestos from
slagging the hot parts of the next tube which was
2. A "Pythagoras" tube of the 50 mm. size which was 18-20
inches long and contained the furnace proper.
3. and 4. Two elements were provided in order to concentrate
the heat at the centre of the furnace.
5. Another "Pythagoras" tube of section 0.8 inches, which
passed through bungs in the outer Pythagoras tube, and
formed the innermost tube of the unit.   This Pythagoras
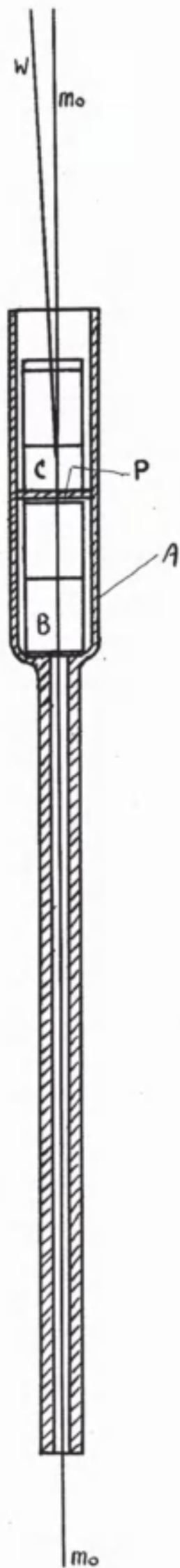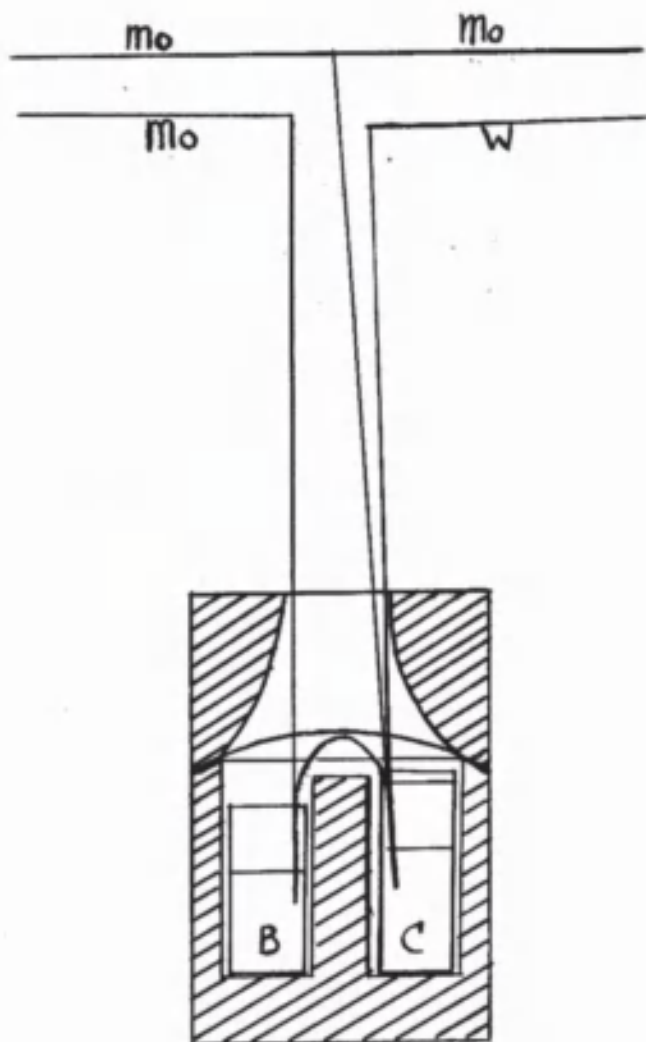tube was provided with one-holed rubber stoppers through

W

Mo

C

P

A

B

Mo

Fig. 4 a.

Mo   Mo

Mo   W

B   C

Fig. 4 b.

Crucible and Blank Containers.

a. For Small Furnace

b. For Large Furnace.

which passed T-pieces.   The side limbs of the T-pieces were
attached to the pump at one end of the furnace, and to the
cylinder of nitrogen or other gas at the other.   The thermo-
couple connections were taken out of the straight limbs of
the T-pieces.

Since the bungs were of rubber, they were protected
from the heat of the furnace by means of water cooling
circuits.   These were four in number, at both ends of the
inner tube and at both ends of the outer tube.   The water
coolers were of copper tubing, the one which went round
the outer "Pythagoras" tube being of a slightly larger
section than that going round the inner, because of the
greater section round which the former had to be bent.
The leads of the furnace were of doubly stranded molybdenum
wire, and were attached to stout nichrome wires, which were
led through the bungs and insulated from the water coolers
by means of mica sheeting.   Since the windings were of
molybdenum, the furnace was connected to an ammonia crack-
ing train, which maintained an atmosphere of nitrogen and
hydrogen around the furnace, while the windings were hot.
The gases from the train were passed in through a glass
tube in the bottom bung, and an outlet was provided at
the top.

The furnace was used in a slightly different form
when it did not matter whether the atmosphere was hydrogen
or not.   In this form, the inner Pythagoras was dispensed
with, and the whole design of the furnace had consequently
to be altered.   A line diagram is given of the essential
parts in figs. (6a) and (6b).   Temperatures in the
neighbourhood of 1800°C were easily obtained with the
furnace in this form, for the absence of Pythagoras in the
hot zone meant that the furnace could be used at its
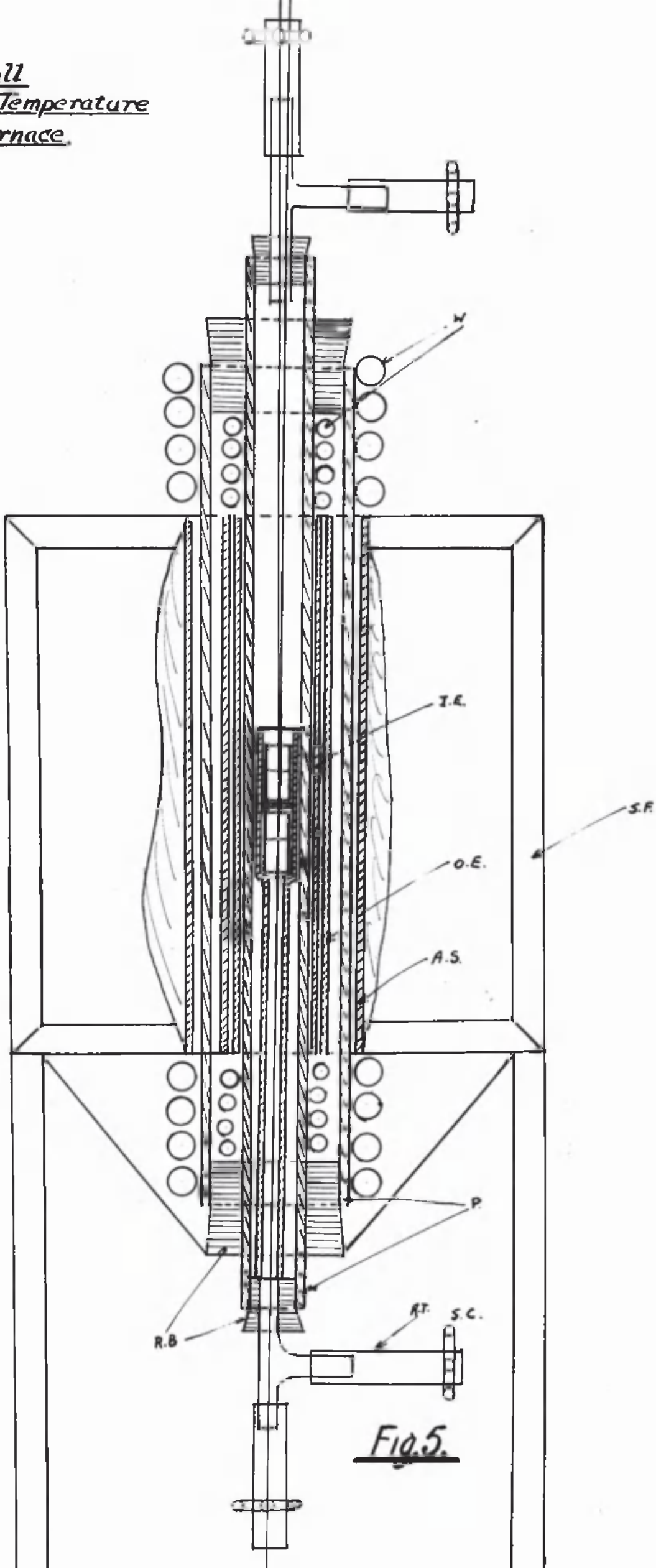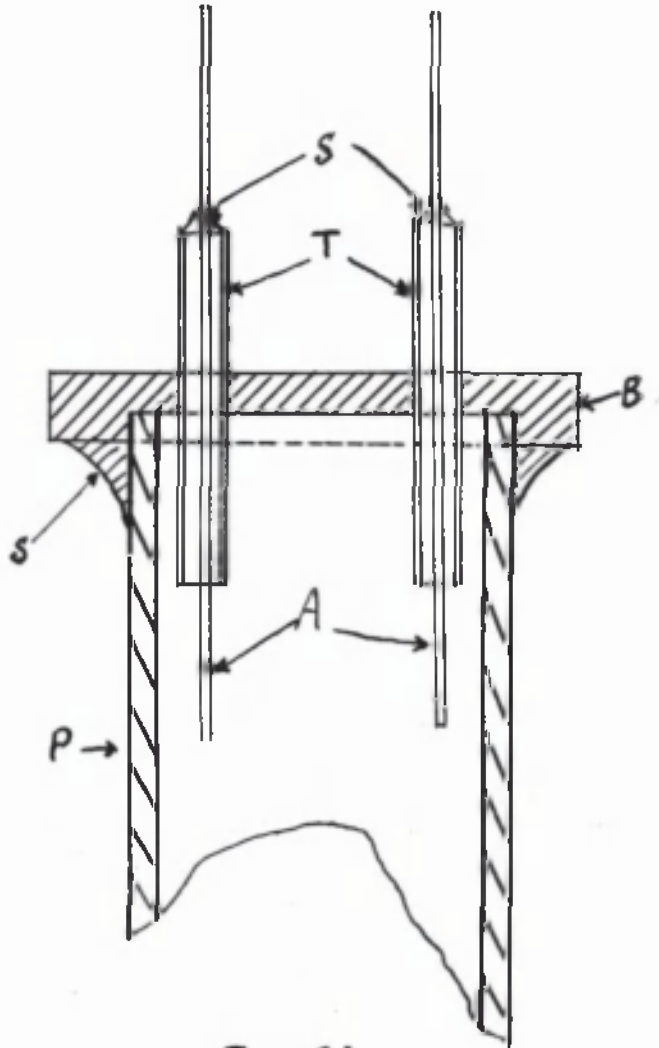maximum.

The Small
High Temperature
Furnace.

Fig.5.

S

T

B

S

A

P →

Fig. 6b.

The "Pythagoras" tube "P" in
Fig. 6a. fits into the rubber
bung of the large "Pythagoras"
tube.

A

p

Fig. 6a.

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KEY TO DIAGRAMS OF THE SMALL FURNACE.

Alundum parts are shaded thus

Pythagoras parts are shaded thus

Asbestos parts are shaded thus

Fig. (4a)

A - the container

P - the alundum plug

W - tungsten wire

Mo - molybdenum wire

Fig. (6a)

A - alundum

P - Pythagoras

This fits into the furnace, and takes the part of the inner Pythagoras tube: the alundum does not quite come up to the top of the furnace.

Fig.(5)

W - the water coolers

SF - steel frame

P - Pythagoras

AS - alundum sleeve

OE - outer element

IE - inner element

RT - rubber pressure tubing

SC - screw clips

RB - rubber bungs

Inlet and outlet for the train gases are in the bigger bungs, but are not shown, nor are the leads from the elements of the furnace, nor the mica insulating sheets.

Fig.(6b)

B - top of furnace made of alundum

S - seals of alundum

P - Pythagoras

T - $^{3}/16"$ bore silica sheaths

A - stout nichrome wires

These wires were attached to the leads from the heating element at one end and at the other to the mains leads by means of two-way terminals.   The train gases were introduced at the bottom of the furnace, as before and diffused through the top, no opening being provided for them.

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Heating and Cooling Curves in the Small Furnace.

Thermal curves were tried in this furnace with
very little success.   The method of taking differential
curves will be described later, and as is then noted, the
theoretical curve of a differential thermocouple e.m.f. is
a straight line.   This is true, only so long as the blank
and crucible are heating at the same rate, since they are
chosen to have approximately the same thermal capacity.
Otherwise this is true only when there is no temperature
difference between them.   Due to the small section of the
furnace, it was necessary to have the blank and the crucible
one under the other, and each was very near the heating
element.   Most of tube furnaces have what may be called a
"hot spot".   This is the part of the furnace which reaches
the highest temperature.   It occurs about one third of the
way up the furnace, but does not extend very far.   As
noted above, with the large furnaces an additional 200°C
have been obtained by raising or lowering the melt an inch
higher or lower in the furnace, as the case may be.   The
same effect exists in the smaller furnaces.   It will be
seen therefore, that when the thermocouple system stretches
over about two and a quarter inches, uniform heating of the
blank and crucible becomes impossible and the difference in
heating rates of these becomes so great that the "drift"
produced in the thermoelectric e.m.f. curve vitiates the
whole work.

To even up the heating rates of the blank and
specimen, winding the furnace in a differential manner was
tried, but without success.

With such a small section of furnace, the effect of
many faults is accentuated, faults which would not matter
very much in the bigger furnaces where the section is
large, e.g., variation in the thickness of the walls of the
furnace, and slight variation in the distance between two
consecutive turns of the furnace winding.   The idea of

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taking differential curves in the small furnace had
finally to be given up.

Method of making a furnace tube.

A steel pipe of outside diameter about a quarter of
an inch less than the inside diameter of the required
furnace tube, was covered with five layers of wet brown
paper, about two inches greater in breadth than the required
length of furnace tube.   A mixture of six parts of Norton's
563 alundum cement to one part of Norton's 562 was made
plastic with water and the whole surface of the paper was
covered with this paste to a uniform depth of about a
quarter of an inch.   This was dried by placing before a
muffle furnace, and when dried was dressed down to size by
rubbing with coarse emery cloth.   Experience had shown
that thirty nine feet of 0.04 inch diameter molybdenum wire
were best for the heating element.   Forty two feet of
white string of about twice this diameter were wound round
the alundum tube, allowing five turns to the inch, and
beginning about one inch from one end of the tube, this end
being finally the bottom of the furnace.   The string was
covered with a slurry of the alundum cement and water, and
the tube again dried before the muffle furnace.   It was
then placed in a large Nichrome wound drum furnace, and
heated to about $1000^{o}C$ until the paper and string were
burned away.   When cool the tube could be easily slipped
off from the steel former.   The top surface was rubbed off,
and the grooves where the string had been were thus exposed.
The ash of the string was carefully removed.

Molybdenum wire is always covered with graphite
from the dies during the drawing.   This was cleaned off,
and thirty nine feet of it were wound on to the tube into
the grooves prepared for it.   The leads to the furnace
were made of heavy Nichrome wire and these were attached
to the ends of the winding by means of molybdenum wire.

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The winding was kept in place on the tube by binding wires of molybdenum round it at the ends of the former. The winding was now covered with a coating of alundum, and the bottom sealed with an alundum disc, luted with alundum paste. The whole tube was thoroughly dried before the muffle furnace. The same technique was used for every size of furnace tube, the diameters of the steel pipe and of the wire being varied according to requirements. Sheaths were made in the same manner, only in this case neither string nor wire were needed.

Use of Tungsten-Molybdenum Thermocouples in Nitrogen.

It has been found that the thermal curves were never as smooth in nitrogen as when the thermocouple was used in hydrogen or in a vacuum. There was never any doubt about the large thermal arrests, but a curve taken in nitrogen had many small "wriggles", which made the search for small arrests very difficult. The extraneous deviations had no constancy, and so when a small deviation appeared on several curves in succession, this was taken as evidence of a small arrest.

At first this behaviour in nitrogen was taken as being due to the small residual amount of oxygen in commercial nitrogen oxidising the couple point at the high temperature. After steps had been taken to remove this by passage over heated copper turnings, no improvement was found, so that the cause had to be sought elsewhere. A search was made of the literature for information as to the action of nitrogen on molybdenum and tungsten.

Action of Nitrogen on Molybdenum and Tungsten.

Mellor in his "Treatise on Inorganic Chemistry" reports that molybdenum will absorb nitrogen at low pressures and high temperatures. I. Zschukoff (Ann. Inst. Anal. Phys. Chim., 3, 14, 1926) reports a slight reaction of molybdenum with nitrogen at $1000^{\circ}C$. Other workers including

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H. Moissan, did not find any reaction below 1200°C.
H. Moissan states that there is no reaction between
nitrogen and tungsten at red heat, while Sieverts and
Bergner claim no reaction up to 1500°C.   Mellor says
that nitrogen does not at any temperature react percept-
ibly with tungsten.   On the other hand Smithells and
Rooksby, (J.C.S. 1882, 1927) proved the formation of a
solid dinitride of tungsten, on an incandescent filament
of that metal in nitrogen, indicating that it might have
formed as a consequence of the electronic evaporation of
the metal into the atmosphere of nitrogen.

There is a decided paucity of data on this point
in the literature, and the author considers that the
explanation of the "wriggles" in a curve taken in nitrogen
lies in the possible formation of nitrides of molybdenum
and tungsten, these latter being probably unstable.   In
this way, the formation and decomposition of these would
cause, small extraneous e.m.fs. to be set up in the
thermocouple, giving at one time a small deflection of
the galvanometer to one side and at another a small
deflection to the other side, dependent on whether the
solid nitride was being formed or being decomposed.
This point will be cleared up, however, when the chemistry
of the nitrides of molybdenum and tungsten has been more completely
worked out.

The Calibration of the Thermocouple.

In general, molybdenum-tungsten thermocouples
have a neutral temperature of about 600°C, and a reversal
temperature of about 1200°C.

The couple was standardised against a standard
chromel-alumel couple up to temperatures of about 800°C.
This was done in an atmosphere of hydrogen, the only
reason being to keep the conditions as much as possible
the same throughout the calibration.   The couple was
standardised above this by taking the melting point of a

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  piece of copper in hydrogen. A heating curve of a piece
of pure iron was taken in hydrogen right up to melting,
and the values for the $\delta-\delta$ change and for the melting
point were noted. For this purpose, a differential thermo-
couple was attached to a piece of iron, in the manner
described below. The thermocouple point was placed in
a small piece of silica sheathing, luted at one end with a
small quantity of alundum cement, and a hole was drilled
in the iron specimen to take this piece of silica sheath-
ing. The iron was embedded in alundum cement in the hole
for it in the container. The heating was done in hydrogen
so as to prevent any ferrous oxide from forming because
the latter readily fluxes the alundum, causing it to run,
and so endangering the furnace. The values for the
thermal e.m.f. at these known temperatures were then
plotted on squared paper and the approximately parabolic
curve obtained by drawing a smooth curve through the
experimental points.

  It was noted during the work that the thermal
e.m.f. at the neutral point varied slightly during the
life of the couple.

  Although all molybdenum-tungsten couples have
approximately the same thermoelectric power, each batch
of wires had their own neutral point and reversal temper-
ature. A separate calibration had to be done for each
new couple. If a melt was done at different times with
different couples it was found that the same temperatures
were shown for the same arrests, although, of course, the
actual value of the e.m.f. at these points was not the
same. Melts which were done with both a platinum-
platinum-10%rhodium couple and a molybdenum-tungsten
couple gave agreeing results.

  The diameter of the thermocouple wires used in
most of the work was 0.635 mm. for the molybdenum and
0.4 mm. for the tungsten.

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It was necessary to incorporate a grid or sheath of molybdenum, round the "Pythagoras" or recessed tube to render the couple stable at temperatures above 1200°C.

The taking of a curve.

Each of the constituents was ground separately before weighing and then the appropriate weights were ground together in an agate and well mixed. The crucible which was a piece of molybdenum rod with a hole drilled in it, was filled with the mixture and this was well pressed down, to lessen the risk of a "boil-over" during melting, due to entrapped air escaping. The dimensions of the crucible were one inch long and 0.4 inch in diameter, fitted with a closely fitting lid of molybdenum. In each case two grams of the melt were prepared although the crucible held only about three-quarters of this amount, dependent on the specific volumes of the constituents. The crucible and blank were connected, and the whole placed in the furnace as described below. The top of the furnace was luted up with alundum, and the external connections made as shown in figs.(2), (3), and (7).

As a rule three heating and two cooling curves were taken on the one run. Differential galvanometer and time readings were taken, the times and differential scale being read at every 0.02 millivolts of the molybdenum-tungsten thermocouple, i.e. about every 5°C. The times were taken so that an inverse rate curve could be plotted but due to the smallness of the melt it was rarely that the inverse rate curve showed anything. The times were taken also as a guide as to how the furnace was heating, for as will be seen later the rates of heating and cooling have an important effect on the shape of the curve shown by the differential thermocouple. Curves were taken of a melt until satisfaction was obtained, and when a system was drawn up tentatively, confirmatory melts chosen at random

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were done.

The measurement of temperature.

The temperatures were measured by the molybdenum-
tungsten thermocouple, and evolutions and absorptions of
heat were noticed by the differential method using as a
blank (i.e. a body showing no thermal changes) an empty
molybdenum crucible packed with molybdenum scrap.   A
section through the crucible diameter is shown in fig(4b),
the construction of the container and the connections being
obvious from the sketch.   In general, a differential
thermocouple involves two thermocouples.   One is a
straightforward thermocouple which at any instant measures
the temperature of the specimen under examination and the
other is a thermocouple, the differential, whose two
junctions are attached one to the specimen and the other to
the blank.   In the work being described, a tungsten bridge
was used between the crucible and the blank, and the
differential thermocouple was completed by taking off two
molybdenum leads from the ends of the tungsten.   It will
be seen that from the crucible, or specimen there were four
leads, viz:- the molybdenum and the tungsten of the thermo-
couple, which were led through the furnace to the potentio-
meter, the molybdenum of the differential which was led
to the differential galvanometer, and the tungsten of the
differential which was led to the blank.   From the blank
there was also a molybdenum wire which was led to the
other terminal of the differential galvanometer.   From
the crucible there were thus two molybdenum wires, the
points of which at the crucible were at the same temper-
ature, and of which the other ends at the cold junction
were also at the same temperature.   If these two were
joined no e.m.f. would be produced, and so it was possible
to dispense with one of them, and use one molybdenum wire
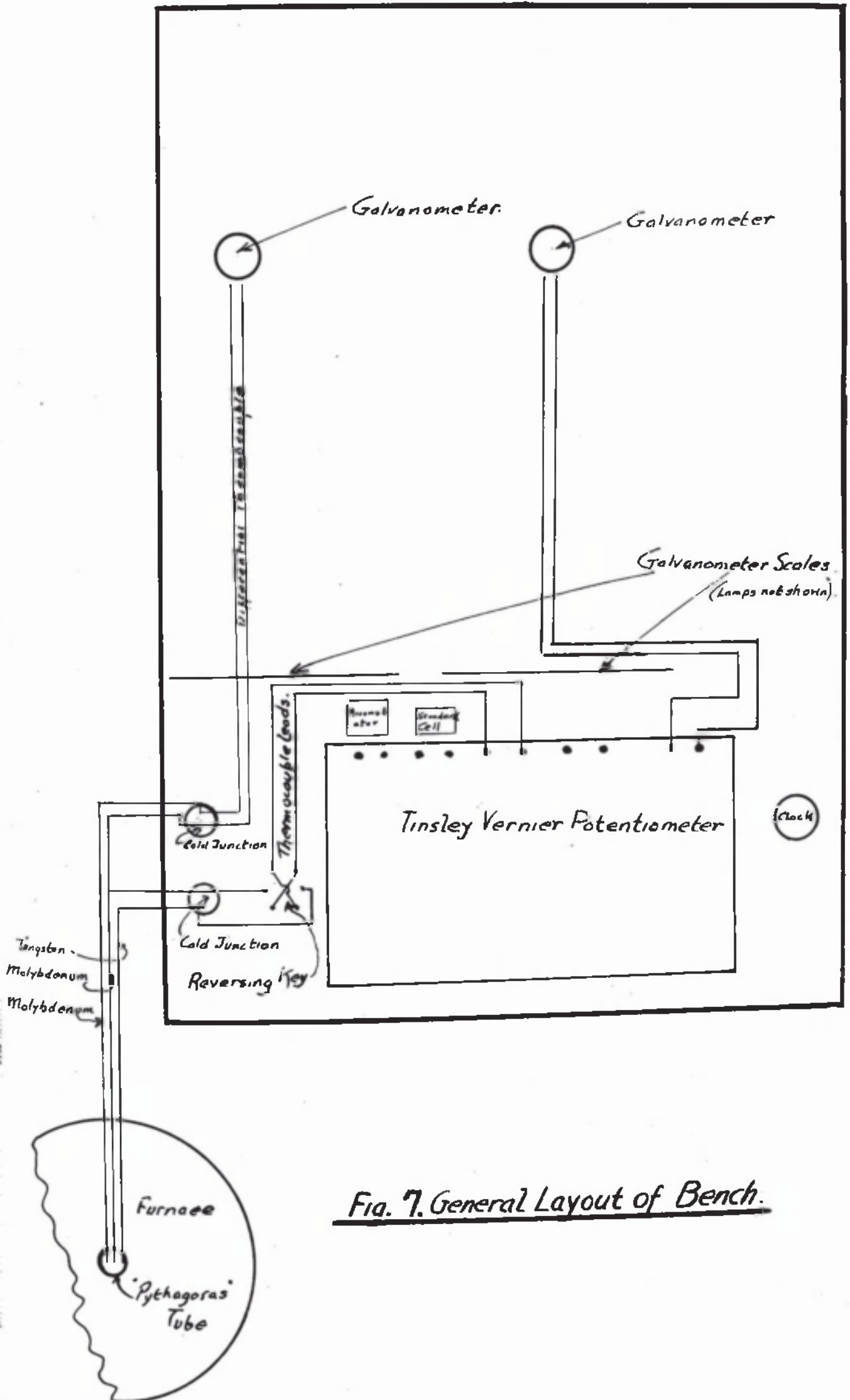from the crucible which performed the dual purpose of the
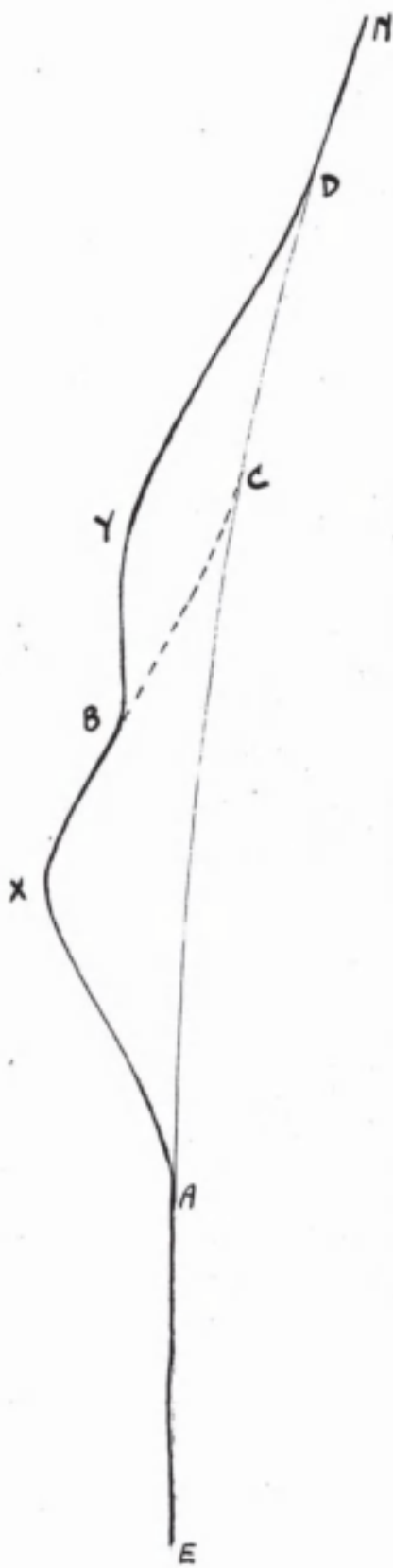
Fig. 7. General Layout of Bench.

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molybdenum of the thermocouple, and the second molybdenum of the differential. At some point outside the furnace, this lead was attached to a double lead as shown, one part of which was led to the potentiometer and the other to the differential galvanometer. The wires were always cleaned with emery before use and then the molybdenum was always wound round the tungsten, because the tungsten always broke if wound round the molybdenum. The couple points were bound to the crucible and blank by means of small pieces of molybdenum wire. The elements of the thermocouples were carefully sheathed with silica sheathing for insulation purposes and the lid of the container luted up with alundum cement. The container was then lowered into the furnace, or the Pythagoras tube, by means of a piece of string, on to a stool which was of such a height as to bring the crucible into the hottest zone of the furnace. The string was then removed. A line diagram fig.(7) is given of the general layout of the apparatus. A reversing key was necessary, to maintain a unidirectional e.m.f. applied to the potentiometer, when the thermocouple reversed.

The interpretation of the differential curves.

Provided that the blank and the crucible are arranged to have the same thermal capacity, then if they are heating at the same rate, at any instant they will be at the same temperature. Under these conditions no electromotive force will be produced in the differential thermocouple, and so the graph of the differential galvanometer scale reading will be a straight line parallel to the zero axis. Due to differences in thermal capacity, heating rates etc., between the specimen and the blank a small temperature difference usually exists between these two, and so the galvanometer spot experiences a constant, but small, drift.

Suppose that the normal heating curve is EACD in fig. (8) and at the temperature corresponding to A a

Fig. 8. Theoretical Differential Curve.

Axis labels:
- Vertical: Temperature Plotted As Thermocouple E.M.F.
- Horizontal: Differential Galvanometer Reading

change takes place in the specimen accompanied by an
absorption of heat.   This means that the specimen tends
to remain stationary in temperature or heats at a much
slower rate.   The blank continues to heat and a differ-
ence in temperature between the blank and the specimen
results, which causes a deflection in the galvanometer.
The temperature difference and with it the e.m.f. and the
galvanometer deflection, reach a maximum and then the
crucible heats at a much quicker rate to overtake the
blank in temperature.   As it does so, the e.m.f. diminishes
until it is finally zero when the temperatures are normal.
The curve will now have reached the normal heating curve
at some point C.   If another change takes place as the
crucible is overtaking the blank, say at temperature B,
then the same thing happens again, and so the curve now
follows the path EAXBYDN.

Differential curves may be misleading, if due
attention is not paid to the effects of the rates of
heating.   (Applying to the work being described).

Effect of slow heating (say 20-30 secs. per 0.02 mv.)

When a change takes place with slow heating, the
blank continues to heat slowly, and the difference in
temperature, produced, is not marked.   Thus the deflection
of the galvanometer is less and the magnitude of the point
smaller.   With too slow a heating rate, small changes may
escape notice.

Effect of rapid heating (about 5-7 secs. per 0.02 mv.)

With rapid heating, the lag of the crucible is
greater, and so the magnitude of the point or arrest
appears greater, often being much exaggerated.   Due to
the difference of temperature, existing at the conclusion
of the change, being greater, the crucible heats more
rapidly to overtake the blank, and so the curve tries to
get back to the normal curve quicker, and if another
change takes place the break caused in the curve is

usually very emphatic. If this curve is then compared with a corresponding curve taken at a slower rate, the latter usually gives a truer indication of the temperature of the arrest. With the thermocouple system used in this work, the thermocouple point is really the crucible itself, as the point of the couple is bound to the outside of it. Too rapid heating, means that this may be at an appreciably higher temperature than the actual melt, and an arrest may, on this account, appear high in temperature on heating and low on cooling. Slight differences of ± 5 Centigrade degrees have been found occasionally, due entirely to differences in heating rates,

If energy is supplied, due to heating slightly faster than it is absorbed by a change, then the temperature of the crucible will continue to rise, although more slowly, and the point will appear to stretch over a range of temperature.

It was found that differences in rates of heating least affected the temperature at which a change began. The temperature at which the change seemed to reach a maximum and the temperature at which the differential curve returned to the normal curve were dependent on the rate of heating. In every case the first point of deviation from the normal curve has been taken as the temperature of the arrest.

Second heats were usually faster than the first, and it was possible to reach higher temperatures than in the first heat. This was because the lagging of the furnace was saturated with heat, and any loss of heat took place principally by radiation, while on the first heat the lagging absorbed a great amount.

Second and third heats were more reliable than first heats because homogeneity was only obtained after melting the mixture. Evidence was sometimes obtained, on a first heat, of the heat of formation of a compound shown in the form of a point to the opposite side of the normal curve.

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Effect of Liquation.

In the case of a melt which had a fairly low eutectic and fairly high liquidus, the tendency was, on the first heat, especially with fairly rapid heating, for the eutectic to form and run to the bottom of the crucible, leaving the almost pure substance "high and dry". This was especially the case when the constituents were high melting substances. The result of this liquation was that the liquidus seemed high, because a higher temperature was necessary to melt the substance left after the eutectic had run away. After melting on the first heat the melt was usually superheated a little, and then soaked for some time at the high temperature. Invariably on the second heat the liquidus appeared at a lower temperature than on the first heat. The first heat was rarely as smooth a curve as the second or the third heats. The reason for this is probably due to the fact that even though the melt was ground as finely as possible, the state of subdivision was still relatively large. When melting began, the melting process would continue by particles of the mixture falling into the newly melted liquid. Each particle falling into the liquid would chill it slightly so causing the "wriggles" by which a first heat was usually characterised. The eutectic showed on the first heat, and was the lowest point. If on the second heat there appeared a deviation below this, then this was due to something which was consequent on the first melting, e.g. the formation of a compound, in which case the new point on the heating curve was probably related to this compound and this formed a point of special interest in the further study of the system.

Cooling Curves.

The rate of heating has been shown to play a large part in the form of the heating curves. It plays a larger part in the form of the cooling curves. In general what

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has been noted about the effects of rates of heating with
respect to the heating curves is also true of the cooling
curves. With fairly rapid cooling, super-cooling was
pronounced, and the amount of this supercooling often
decided the appearance or non-appearance of other points.
For example, a frequent type of heating curve was one which
showed three points viz. eutectic, peritectic and liquidus.
Depending on the rate of cooling, this curve might show one,
two, or three points. With slow cooling, say twenty
seconds per 0.02 mv. the three points usually would appear,
each being a little lower than the corresponding heating
points. With a rate of cooling of say ten to fifteen
seconds per 0.02 mv. sometimes only two points appeared,
the liquidus being depressed to below the peritectic
temperature, but not so far as the eutectic, so that the
liquidus and peritectic appeared together as one point,
followed at a lower temperature by the eutectic. With a
rate of cooling of say five seconds per 0.02 mv. only one
point sometimes appeared. The liquidus in this case had
been depressed to such an extent that the three points
appeared together. This fusion of points was common in
cases when the temperatures of the arrests were not widely
separated. In no case was the supercooling so great that
the points were completely suppressed, i.e. in no case were
the melts glassy, as was occasionally found with systems
containing silica.

Equilibrium in the Melts.

The ability of non-metallic slag forming substances
to react and diffuse seems to be much less than that of
metallic substances. In this way the coring of solid
solutions is very pronounced with these systems. Also
when a peritectic reaction takes place it was not uncommon
to find a metastable state existing in the melts, i.e. the
binary melts frequently showed three phases showing that
the reaction had not been completed. As will be seen in

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the FeO-Al$_2$O$_3$ system this was even more pronounced when a reaction took place in the solid state.   In each of the systems the melts were examined microscopically and as the melts were not always homogeneous, a representative number of fields was examined and so the average nature of the melt determined.

Preparation of the melts for photography.

The hardness of the melts was such that they could neither be sawn nor filed.   In the MnO-Al$_2$O$_3$ system the melts were chipped and ground.   In the FeO-Al$_2$O$_3$ system and the ternary system the melts could not be chipped without destroying the melt.   In these cases the molybdenum crucible was sawn longitudinally round the melt and one half removed.   This could be done easily without damaging the melt.   The latter was then ground down to about a third of its diameter.   The method of grinding these melts was to rub them on a steel plate covered with powdered carborundum and water paste.   In this way it was found that the surface could be taken down without the loss of any of the constituents by being torn out.   The next stage was grinding with putty powder on a glass plate. The melt was then further ground by rubbing on Hubert's O, OO, OOO paper in the usual way and then finished off with a wet selvyt using diamantine (140 mesh) abrasive powder.

The melts were always examined in the unetched condition before etching.   In general the etching reagent was dilute hydrochloric acid solution, the strength being varied as required.

Observations Made During the Work.

The nature of the solidified melts was always examined and observations made on the following properties. 1. Colour. 2. Fluidity (this could only be observed very qualitatively, e.g. if a cracked crucible was used, it was

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possible to see if the melt had run through the crack or not.)   3. Surface tension, i.e. whether the melt had a high surface tension like mercury or a low surface tension like water.   4. Hardness; wherever possible this was tested by Moh's Scale.   5. Crystal habit, this was examined macroscopically.   6. Brittleness.

PART III.

PREPARATION AND NATURE OF THE MATERIALS USED.

Preparation of Ferrous Oxide.

      Ferrous oxide was prepared from the purest ferrous oxalate in the following way: An alundum container closed at one end, about eight inches long, and about an inch and a half in diameter was filled to about an inch from the top with ferrous oxalate, and the top plugged loosely with asbestos. A chromel-alumel thermocouple was tied to the tube which was then placed in a Pythagoras tube, stoppered at both ends, and contained in a Nichrome wound furnace. From one end of the Pythagoras tube the thermocouple connections were taken to a millivoltmeter and from the other end connections were made to a manometer and to a Cenco Hyvac Pump. The tube was evacuated, and the temperature was raised slowly to $700^{\circ}C$, with the pump evacuating the evolved gases all the time. The manometer level had a maximum fall of about one and half inches. The temperature was kept constant at $700^{\circ}C$ with the pump running until the tube was wholly evacuated again, as shown by the level of the manometer. The note of the pump was a good qualitative guide to the process, for when the pump was withdrawing gases its note was flattened, and as the tube became more completely evacuated the note sharpened again. Usually about two hours at $700^{\circ}C$ was sufficient to complete the decomposition of the oxalate, and then the temperature was raised fairly rapidly with the pump still running, to $1000^{\circ}C$ to partially sinter the material. This had the effect of causing the same mass to expose a less surface, and hence lessened the tendency to oxidation. The mass was cooled from $1000^{\circ}C$ with the pump still running. If this latter heating to $1000^{\circ}C$ was omitted, and the material cooled from $700^{\circ}C$, on exposure to air, it was pyrophoric. Under these conditions of preparation, the yellow oxalate

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was changed to a black material which was weakly magnetic, and which gave on analysis an iron content of 76-77%.

The Nature of FeO.

There are grave doubts as to whether there exists a compound with the composition FeO. Benedicks ("Non-metallic Inclusions in Iron and Steel", Chapman and Hall, 1930) has given a diagram for the system FeO, based mainly on the work of Rosenhain, Tritton, and Hanson (J.I.S.I. 1924 (11)), in which the compound FeO exists over a range of temperature and is capable of dissolving small amounts of iron and oxygen. This compound undergoes a solid change at 570°C decomposing on cooling into αFe with a very small amount of oxygen in solution, and magnetite. At 1370°C this compound undergoes a peritectic reaction giving γ Fe with a small amount of oxygen dissolved in it, and liquid FeO, finally all becoming liquid at some temperature between 1450°C and 1500°C. Also in Benedicks' diagram the γ-δFe change exists from the liquidus at about 77% Fe right across to 100% Fe.

Mathewson, Spire, and Milligan (Trans. Amer. Soc. Steel Treat. 1931, 19, 66) do not show a compound FeO, but show a eutectic between magnetite and a solid solution richer in iron than magnetite but not so rich in iron as FeO. The eutectic temperature is about 1170°C and the solution undergoes a eutectoid change at about 565°C into αFe and magnetite. The solid solution undergoes a peritectic reaction at about 1370°C into γFe and liquid FeO.

Jette and Foote (Am. Inst. Min. Met. Eng. Iron and Steel Division, 1933, 105, 276) showed by X-ray examination that the compound FeO had no real existence but that there was a single phase field in the FeO system stretching from about 75.7% Fe to 76.7% Fe and this had the common salt type of lattice. Experimental work by R. Schenk, and
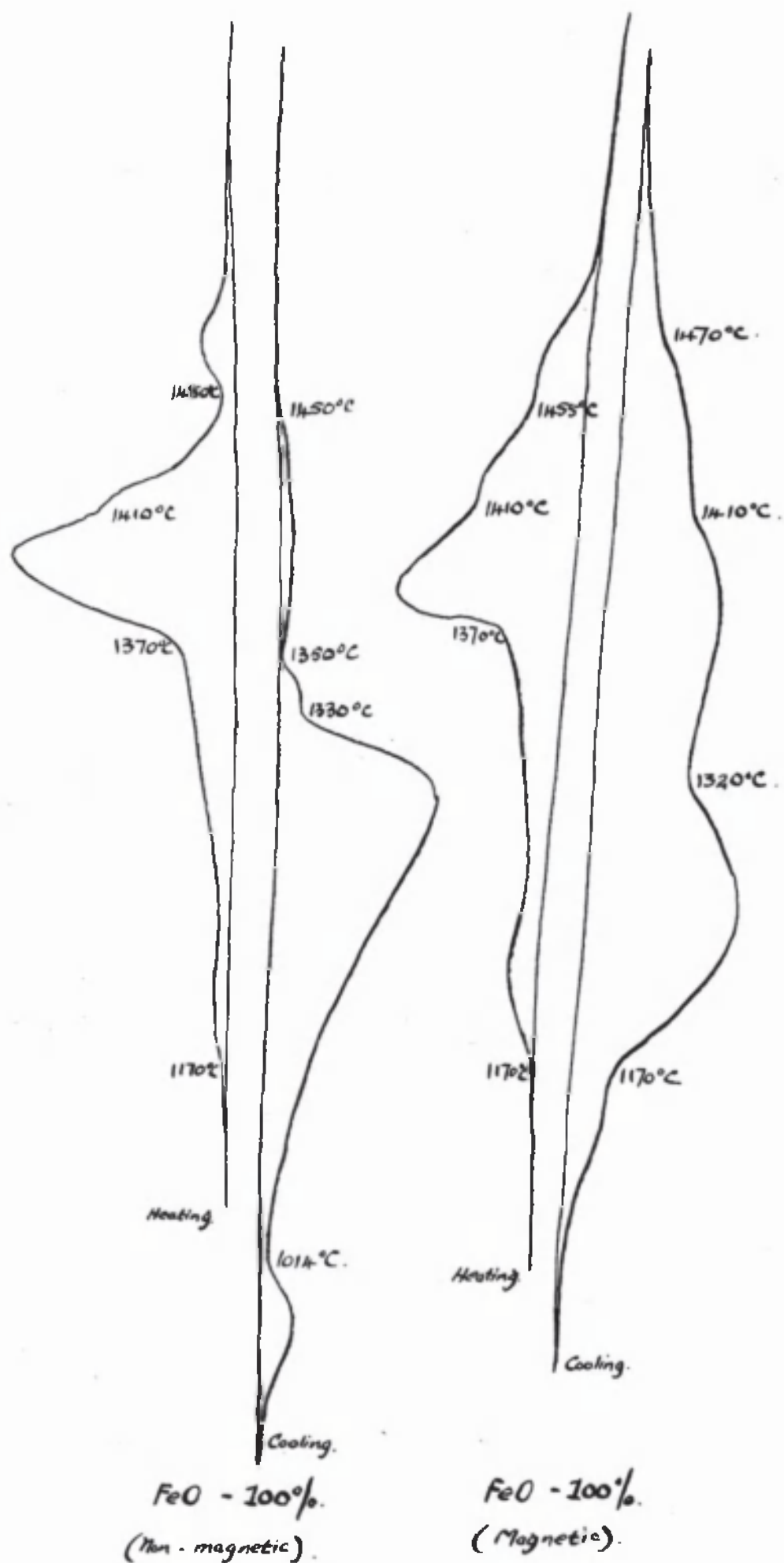
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Dingman (Z. Anorg. Chem. 1927, 166, 113, and 1928, 171, 239) tended to show that the compound FeO had no real existence.

Thus it would appear that no such compound as FeO exists, but that the oxide phase richest in iron is a solid solution of approximately 75-77% Fe.   This phase has been called Wüstite, and there is general agreement in the literature that Wüstite decomposes at a temperature of about $570^{\circ}C$ into a eutectoid of metallic α Fe and magnetite, Fe_3O_4.   There is disagreement, however, as to its behaviour near its melting point.

Before proceeding to a system containing this complex substance, it was necessary to understand what thermal points would occur due to it.   The oxide as prepared, would be expected to be magnetic, due to the occurrence of α Fe and magnetite, caused by the eutectoid and also due to any Fe_3O_4 caused by a richness in oxygen. Even with approximately constant conditions of preparation the magnetic nature varied.   Sometimes it was weakly magnetic, other times more strongly magnetic, and very seldom non-magnetic, as tested by a magnet.

An X-ray examination of prepared FeO showed that it had a cubic space lattice of the NaCl type with parameter 4.30 Å.U.   A faint line was identified as due to the 4 4 0 plane of the Fe_3O_4 crystal lattice.   After fusion, lines due to Fe_3O_4 were more pronounced, reflections of the α and β radiations used appearing from the 4 4 0 plane and of the α radiation from the 2 2 2 plane of the Fe_3O_4.   Some of the more magnetic FeO was separated from the less magnetic and heating and cooling curves were done on the two lots.   The curves are reproduced in fig. (9).   In each lot a point at $1170^{\circ}C$ was obtained, this being more pronounced in the more magnetic material. In each case there was a large arrest at $1370^{\circ}C$, followed

1415°C
1450°C
1410°C
1370°C
1360°C
1330°C
1170°C
Heating.
1014°C.
Cooling.

1470°C.
1455°C
1410°C
1410°C.
1370°C
1320°C.
1170°C
1170°C
Heating.
Cooling.

FeO - 100%.
(Non - magnetic).

FeO - 100%.
(Magnetic).

Differential Heating and Cooling Curves
of Magnetic and Non-magnetic FeO

Fig. 9.

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by a small deflection at $1410^{O}C$, and another at $1480^{O}C$ or lower. The magnitude of the $1370^{O}C$ point suggested that this was the point at which most of the material became liquid i.e. the temperature of the peritectic reaction of FeO splitting up into γ Fe and liquid FeO. The small arrest at $1410^{O}C$ has been interpreted as due to the $\gamma-\delta$ point of the γ Fe raised due to the oxygen in solution. The arrest which occurs at $1450^{O}C - 1480^{O}C$ has been taken as the liquidus point. This agrees with the work of Mathewson, Spire, and Milligan rather than with that of Jette and Foote or Benedicks.

Some FeO was melted in platinum and some in molybdenum. While the platinum absorbed Fe from the melt the molybdenum did not react. Molybdenum was therefore used for crucibles. Even so, there was no material difference in the nature of the heating curves even in platinum. Many samples of FeO have been melted and curves taken. The following may be taken as the points due to it:

$1170^{O}C$ this point increases in magnitude with increase in the Fe_3O_4 content of the oxide.

$1370^{O}C$ peritectic dissociation of Wüstite.

$1410^{O}C$ $\gamma-\delta$ point of the Fe formed by the above peritectic.

$1450-1480^{O}C$ Liquidus which is dependent on the content of Fe_3O_4.

These points are influenced by rates of heating as described in part (11).

Some analyses of the material are now given:

FeO as FeO compound should have 77.73% Fe^{++}

(i) FeO, as prepared, but magnetic

Total iron $=$ 74.5%

(ii) FeO, as prepared, "non-magnetic"

(a) Total iron 77.5%

(b) Total iron 76.3%

Part (III)

"Non-magnetic" FeO always analysed 76-77. 5% total
iron.

(iii) FeO as prepared, non-magnetic, then melted in
vacuo in platinum.

Total iron   74.3%

(iv) FeO as prepared, non-magnetic, melted in vacuo
in molybdenum

Total iron $\pm$ 76.7%

When various batches of FeO were used in the systems,
thermal arrests could be repeated, and no difference could
be detected micrographically, between two melts of the
same composition but with different batches of FeO.

Within the limits of our conditions of preparation,
we obtain a substance which is not FeO compound, but an
alloy of iron and oxygen containing about 76-77% Fe.   We
know the thermal nature of this substance, and although we
name our systems FeO-X, it would be probably more correct
to name them Wüstite-X etc.   Since $1370^{\circ}C$ is the temper-
ature at which most of the material melts, this has been
taken as the melting point of the material in the systems.
It is to be noted that it is the temperature of a peri-
tectic reaction, which is necessarily a constant temperature
over a large range of oxygen compositions.   Thus within
limits it may be said that the purity of the FeO used is a
matter of little moment, since it has been shown that the
only point to be influenced in temperature by its compos-
ition is its liquidus, and also that the micrographs of
the melts containing different lots of FeO, show no change.

Although the $570^{\circ}C$ point does not influence the
work which is carried out at temperatures much above this,
thermal curves carried out at this temperature with a
chromel-alumel couple, confirmed the existence of a thermal
change.   A curve is reproduced, fig. (20).

Low Temperature Heating Curve
of FeO.
Taken With Chromel-Alumel
Differential Thermocouple.

682°C.

570°C

Fig. 10

The Preparation and Nature of MnO.

To prepare MnO, an alundum container about one and a half inches in diameter and about eight inches long, was filled to about one inch from the top with the purest manganese oxalate.   The tube was plugged loosely with asbestos, and a base metal couple tied to the side of it. This was heated slowly to about 650-700°C, in an evacuated "Pythagoras" tube, the evolved gases being withdrawn all the time by an Edwards' Hyvac Pump.   When the manometer attached to the tube, showed that all of the gases had been evolved the temperature was raised to 1000°C to partially sinter the mass.   As with FeO, if this were not done the material was pyrophoric on exposure to the air. On cooling from 1000°C, the MnO was obtained as an olive green powder.   The pump was kept running all through the preparation.   If correct conditions were not obtained during the preparation, the colour of the product was not olive green.   The slightest trace of MnO_2 caused a darkening of the colour, and this darkening became more pronounced the more impure became the oxide.   The colour test was so sensitive and the green colour so characteristic of the pure oxide that the colour alone could be relied upon as a test of the purity.   It was found that, if the heating to 1000°C after the gases had been completely evacuated, as well as the cooling from 1000°C, were done in a stream of hydrogen, the oxide was without fail pure MnO and a beautiful olive green in colour.

The Nature of MnO.

Unlike FeO, MnO at once shows by its colour the state of its purity.   It has an oxygen content of 22.5%. Benedicks in his book (loc. cit.) states that the allotropic transformation points are not known.   In all of the work, no thermal arrest has been found that could be taken as indicative of a transformation in the MnO.

Part (III)

The Alumina.

The alumina used was the purest anhydrous precipitated alumina obtainable.

These oxides were kept in a desiccator when not actually in use when making up melts.

PART IV.

THE SYSTEM MnO-Al$_2$O$_3$

Previous Work.

Until quite recently, the only way in which aluminium could find its way into the steel, was in the form of alumina, picked up as a foreign substance from the refractories of the various parts of the furnace which the charge came into contact, during the several parts of the steel making process.   The majority of such inclusions were usually large enough to rise in the molten metal with a velocity sufficiently high to be removed.   Nowadays the greater use of aluminium as an alloying agent and killing agent means that among non-metallic inclusions we must reckon the aluminates or spinels.   It is perhaps due to the recent nature of the use of aluminium that no work seems to have been done on this system, for an extensive search of the literature was fruitless.   The only mention was of some workers who had found that a certain mixture had softened at some high temperature, but no scientific study had been published.

The Experimental Work.

The technique of the experimental work has been described in Part (11).   Since MnO is not reducible by hydrogen, a "Pythagoras" tube was not required, and hence the large molybdenum was used in the form shown in fig.(3). Both MnO and Al$_2$O$_3$ are very high melting substances, and the small furnace was required to melt the more refractory melts.   It was used in the form shown in the figs. (6a.) (6b.).   This was necessary for the first melting, because the large furnace could not be taken so high with safety. After melting the melt was transferred to the large furnace and thermal curves taken even if the furnace could not melt it completely.   In this way, it was

Part IV.

possible to find the changes taking place below the liquidus, even although in some cases the liquidus itself could not be reached in the large furnace.

The technique of taking curves has been described in part (11). In this case the melts were chosen at intervals of five per cent of alumina. As a rule, three heating and two cooling curves were done, the first heat serving to melt the substances and render them homogeneous, the second and third as the heating curves proper.

Both MnO and Al_2O_3 showed great tendencies to resist solution and to cause the eutectic to liquate. When this happened, what looked like a perfectly good curve was vitiated. With the high MnO melts, the tendency was for the eutectic to run away, and leave the richer MnO mixture sitting up as a ball on one side of the crucible. The effect of this on a curve will be seen in the curve of 85/15 MnO/Al_2O_3. With the melts on the Al_2O_3 side of the eutectic the tendency was for the eutectic to run away from the melt but this was left as a plug in the shape of the crucible. This plug was loose and easily removed, leaving the crucible as clean as when new. The small furnace was particularly useful in melting these liquated melts for the fact that they were liquated meant that the top of them had a very high melting point, higher than could be reached with safety in the large furnace. Unless a melt was homogeneous when taken out of the furnace after the heating curves were taken, the run was repeated with the same composition until such was the case, each time, of course, going to a higher temperature. The method of dealing with one of these plugs was to turn it upside down, and add some more of the mixture, the idea being that the eutectic would run down and attack the undissolved constituent. This was done in the small furnace and was the most satisfactory method

Part IV.

of rendering these melts homogeneous.

The Actual Curves.

A selection of the actual curves is reproduced
in figs.(11), (12), (13), (14), (15), (16) with
appropriate remarks.

FIG.	MELT MnO/Al$_2$O$_3$	HEAT No.	REMARKS
-	100		MnO is so refractory that it was not attempted to melt it. This is discussed in the sequel.
-	95/05		This was one of the melts in which it was not possible to reach the liquidus. The curve is not reproduced but it showed the eutectic point.
-	90/10		Same remarks as with 95/05.
11	85/15	1	Shows the type of curve obtained on a first heat. Due to the liquation of the eutectic, the liquidus seems high. Note that the temperature scale is one half of that of the other curves. The curve shows two points. Eutectic 1520°C Liquidus 1640°C (high).
11	85/15	2	Shows the difference in the curve of the same melt after homogeneity has been obtained on melting. The points were taken from this curve. Eutectic 1520°C Liquidus 1613°C
12	80/20	2 3	(Show the difference to be obtained by (differing the heating rate. 3 was the faster. Curves show two points. Eutectic 1517°C Liquidus 1558°C
-	75/25		

Part IV.

75/25

Curves are not reproduced for this melt.
Due to bad effects of heating rates,
current changes, and the fact that the
furnace had just been repaired after a
failure, entirely different heating con-
ditions were obtained.   This meant that
the height of the melt in the furnace
was not correct, etc.,   Each curve in
itself was unsatisfactory, but taken all
together, the points due to the eutectic
and the liquidus could be traced on them
all.   These points fitted in with the
points of the other melts, so that this
melt was not repeated at the time.

> Eutectic 1520°C
>
> Liquidus 1538°C

14   70/30   2   Curve shows three points

3   Curve shows three points.

> Eutectic 1520°C
>
> Peritectic 1560°C
>
> Liquidus 1580°C

15   65/35   1   Curve shows three points

> Eutectic 1520°C
>
> Peritectic 1555°C
>
> Liquidus 1651°C

Liquidus is high due to liquation in the
melt.

15   65/35   2   Curve shows three points

> Eutectic 1514°C
>
> Peritectic 1550°C
>
> Liquidus 1620°C

Liquidus is now lower because of homo-
geneity in the melt.   Note that the
temperature scale is halved.

Part (IV)

16   60/40   2   Curve shows the eutectic and the peri-
tectic very well.   There is a large
solution range which gives the impression
of reaching a maximum, and for this melt
the liquidus was taken as the point in
which the curve joined the normal heating
curve.

        Eutectic $1520^{\circ}C$
        Peritectic $1555^{\circ}C$
        Liquidus $1645^{\circ}C$

16   60/40   3   Same remarks as 2.
        Eutectic $1520^{\circ}C$
        Peritectic $1560^{\circ}C$
        Liquidus $1645^{\circ}C$

      50/50   These curves are not reproduced.   Heat-
ing conditions were such that the drift
was so great that the curves could not
be reproduced on the small scale.   The
points are, however, used in the diagram.

Melts of a higher Al_2O_3 content than 50% could not be
melted on a first heat in the large furnace.   The
curves of these melts, however, as far as they were
taken, did not show a eutectic arrest, in fact as far
as the curve was taken no arrest appeared.   As far as
was possible they were melted in the small furnace and
again attempts were made to take thermal curves.   It
was not possible to melt them in the large furnace.
The first arrest was the peritectic change, i.e. the
eutectic did not stretch as far as these compositions
and this was later confirmed by the micrographic work.

The Cooling Curves.

11   85/15   This curve was one of the confirmatory
series.   The smallness of the arrests is
due to slow cooling.   The curve shows two
points

85 % MnO. 15% Al$_2$O$_3$.

1640°C.

1613°C

1560°C

1525°C.

1520°C.

1520°C.

2

1
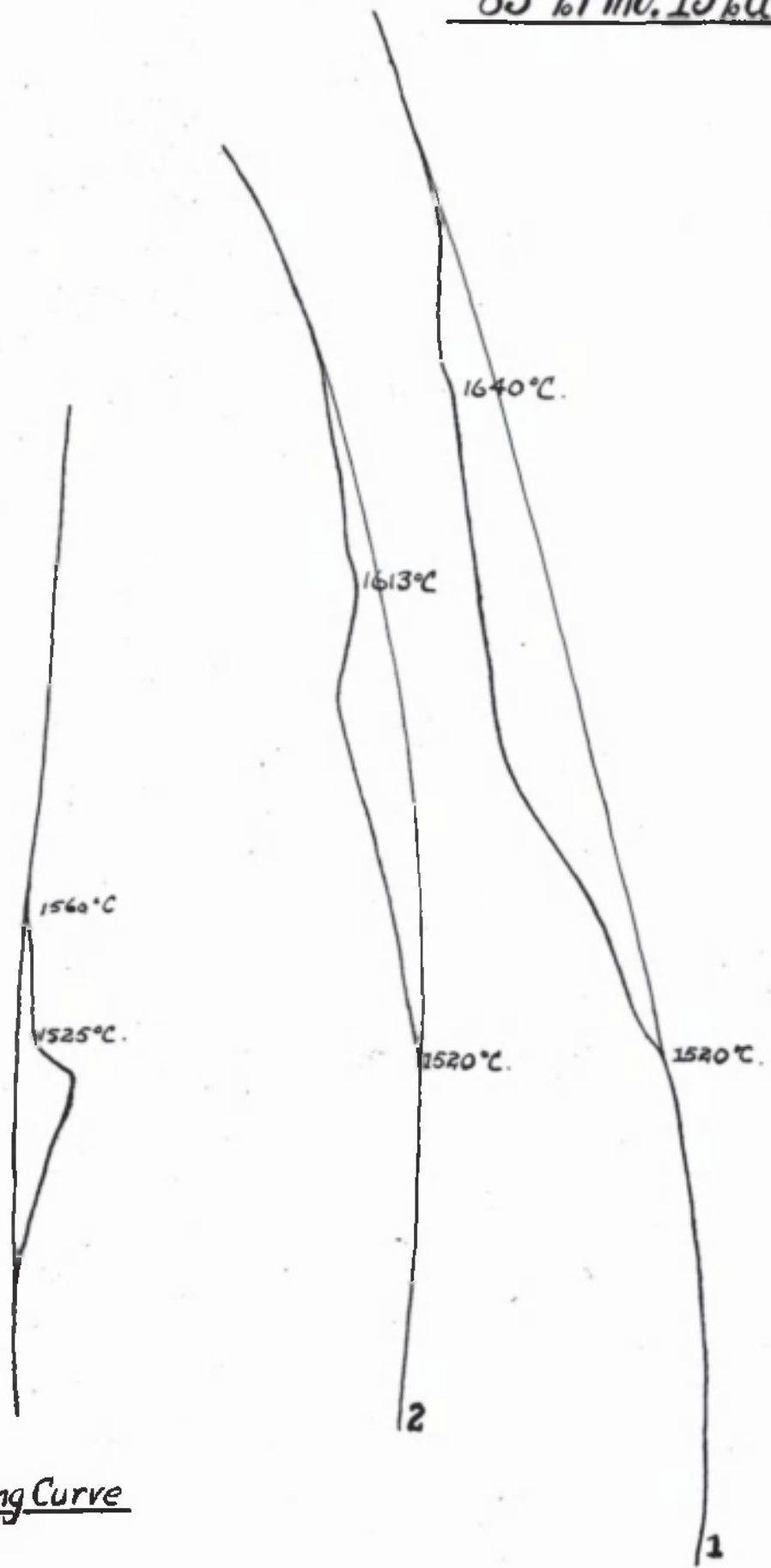
Cooling Curve

Heating Curves

Fig. 11

80% MnO. 20% Al₂O₃

$80\% \, MnO. \, 20\% \, Al_2O_3$

1558 °C

1558°C

1517°C   1517°C

Heating Curves
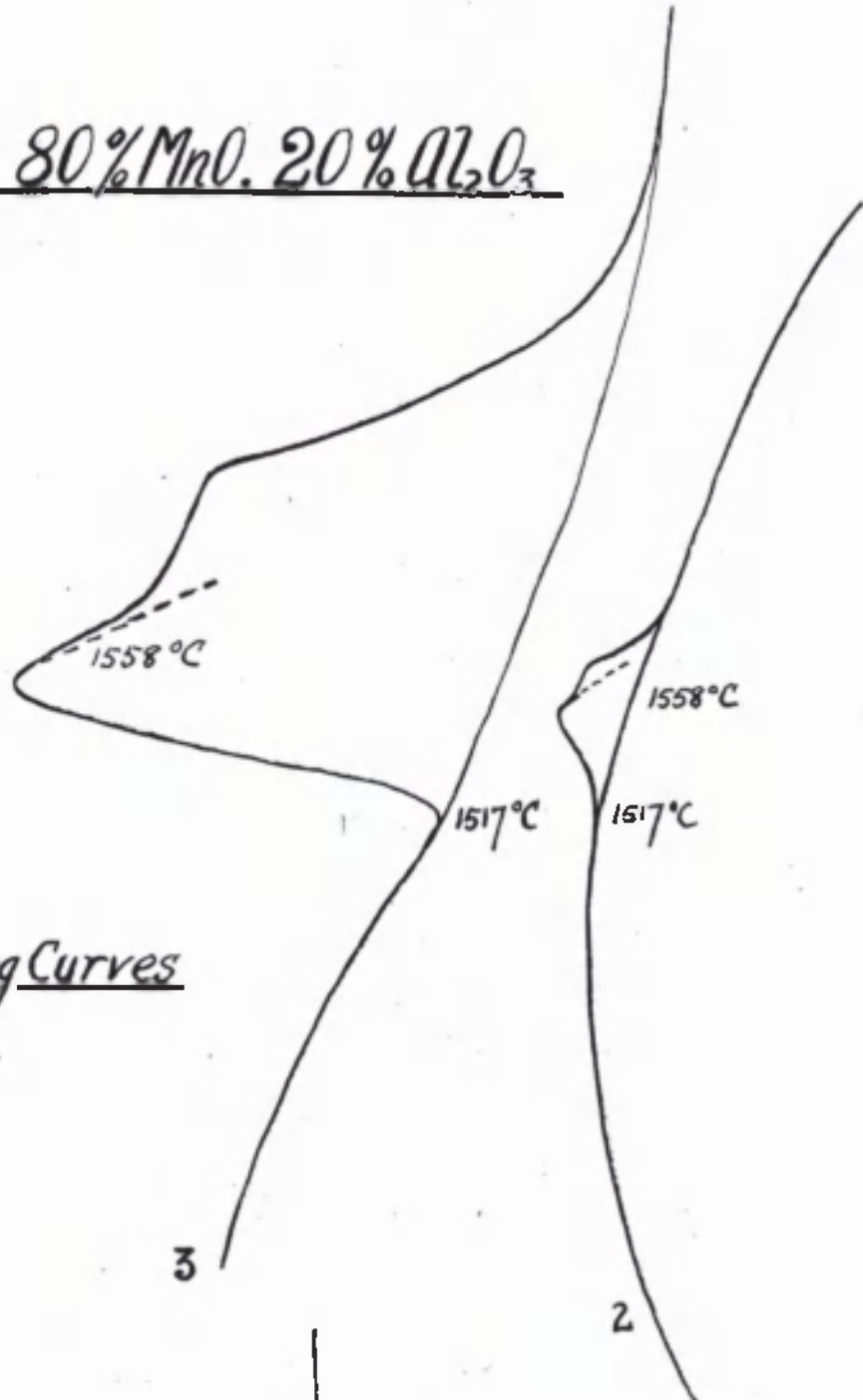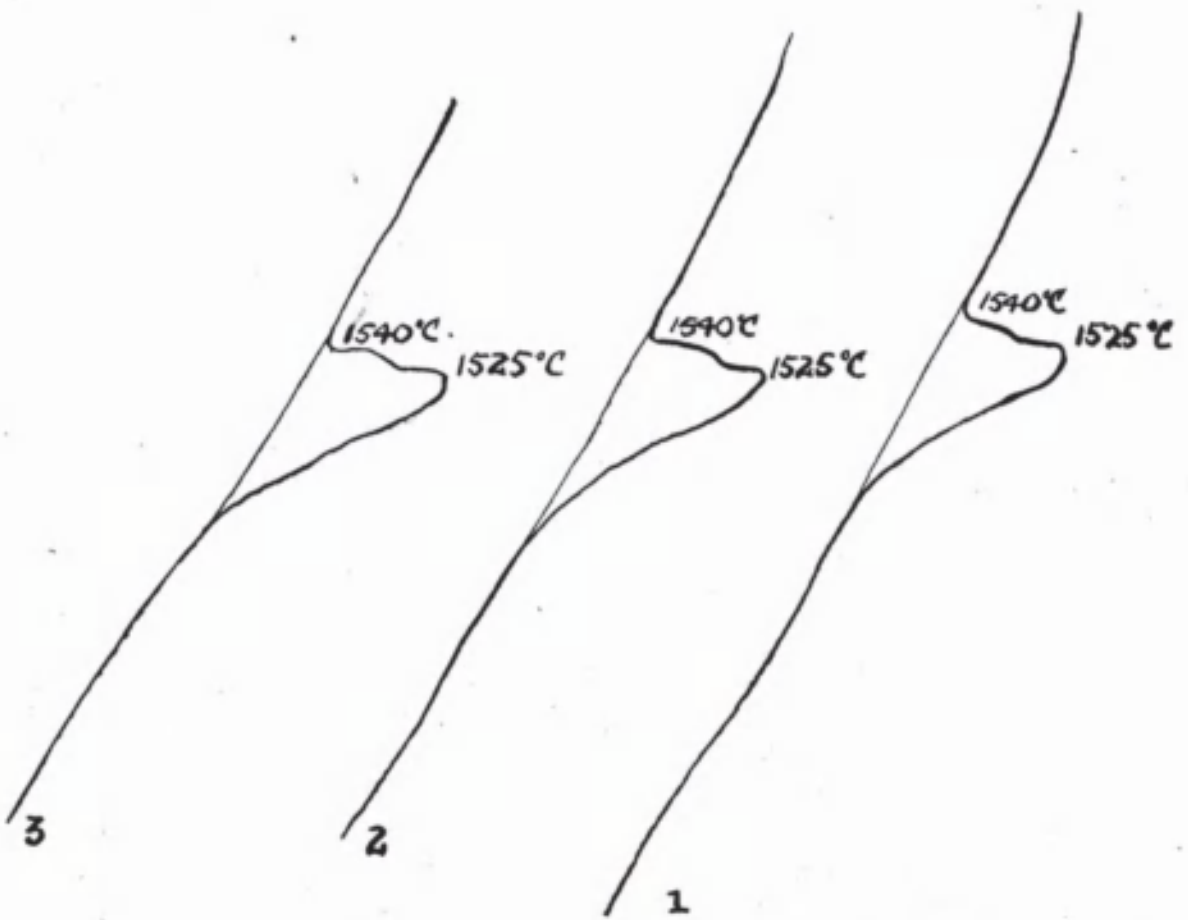
3   2

1550°C
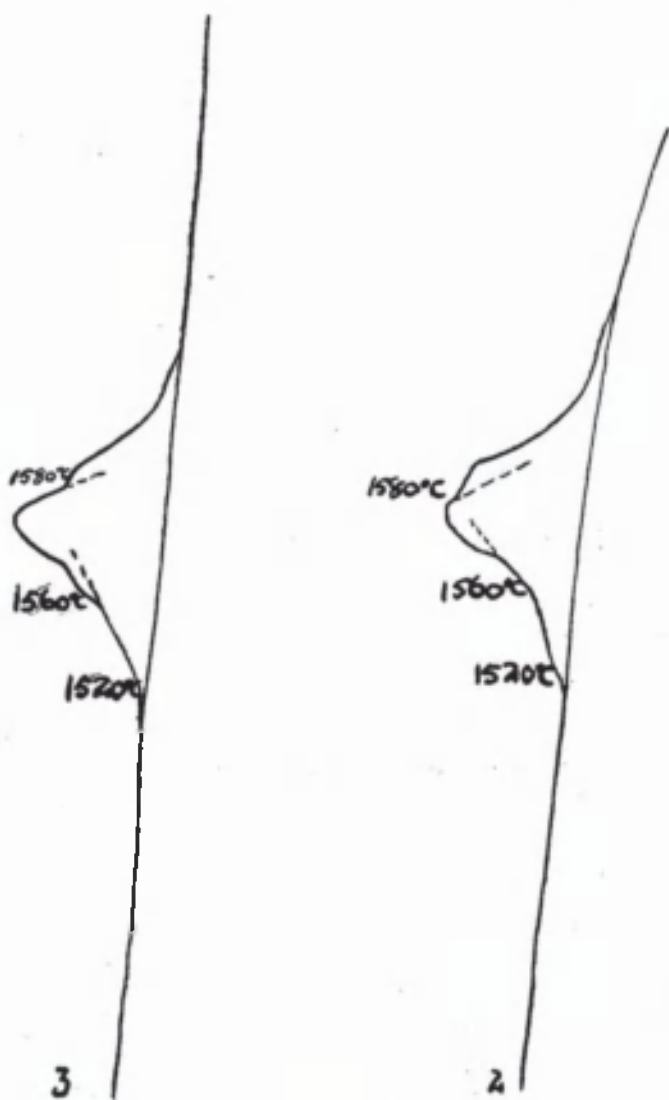
1520°C
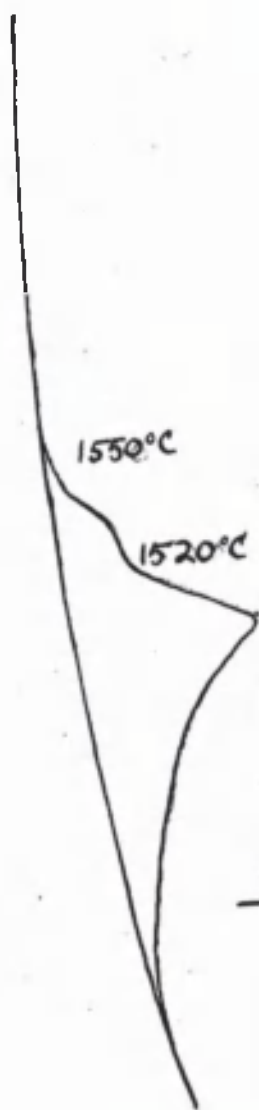
Cooling Curve

Fig.12
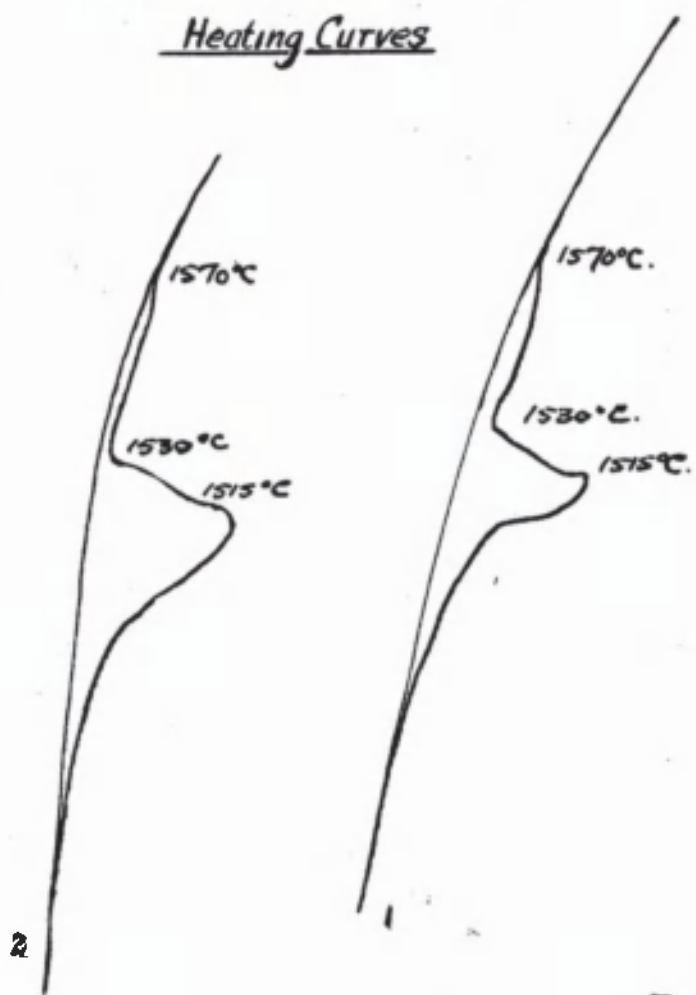
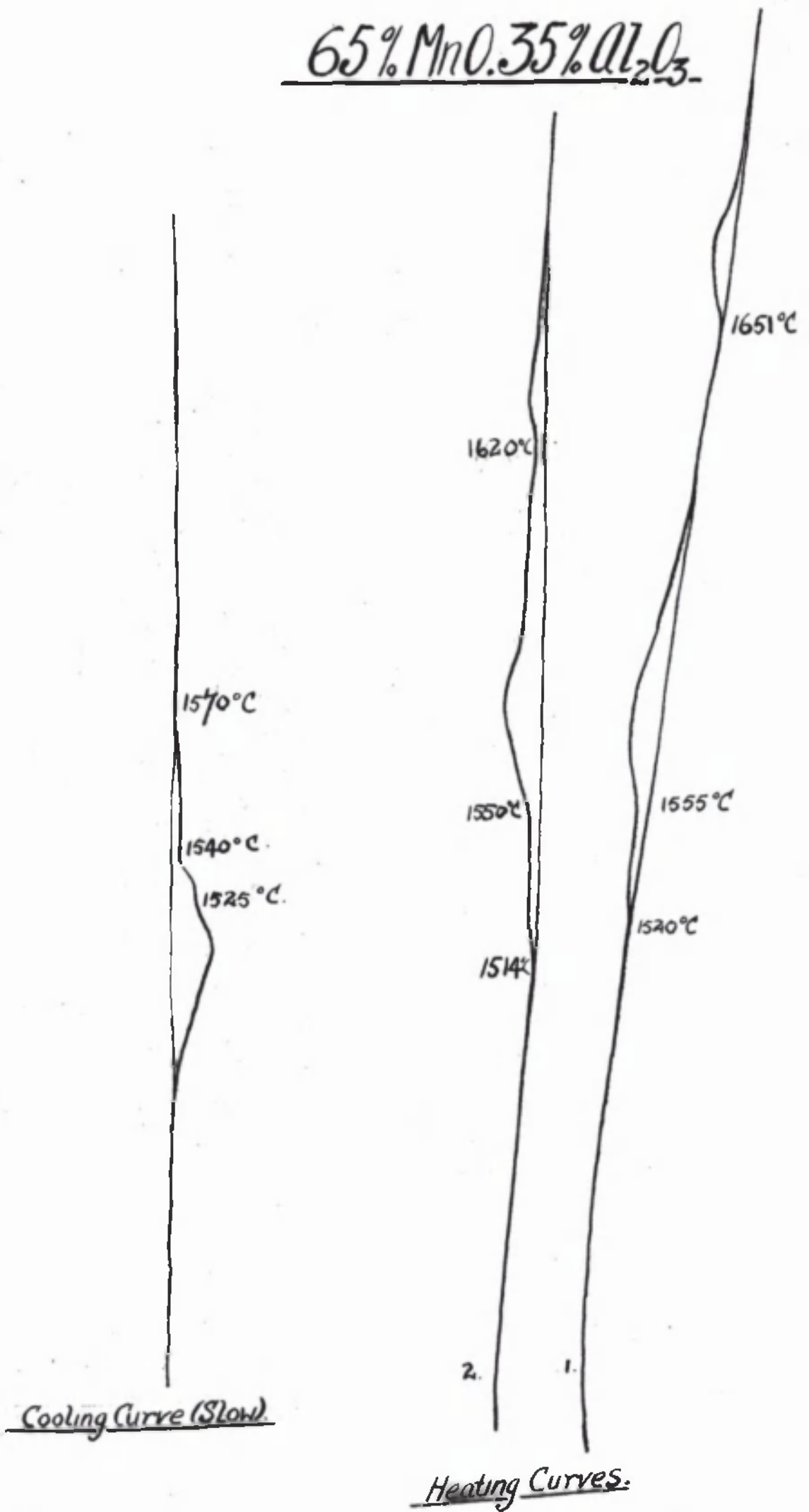## 75% MnO. 25% Al₂O₃

Cooling Curves

Fig. 13.

70% MnO. 30% Al₂O₃.

Heating Curves

Cooling Curves.

Fig. 14

65% MnO.35% Al₂O₃.

Cooling Curve (Slow).

Heating Curves.

Fig. 15

Note. Vertical temperature scale is halved.

$60\% \, MnO. \, 40\% \, Al_2O_3$

1645°C.

1645°C.

1560°C.

1555

1520°C.

1520

3.

2.

Heating Curves

1535°C

1540°C.

1520°C.

1517°C.

2.

1

Cooling Curves

Fig. 16

Part (IV)

<pre>
                     Liquidus   1560°C
                     Eutectic   1525°C
</pre>

12   80/20   One cooling curve is given, which shows two

points

<pre>
                     Liquidus   1550°C
                     Eutectic   ·1520°C
</pre>

It will be noticed that the liquidus in these

curves is depressed somewhat.   In the 80/20,

note the size of the eutectic arrest.

13   75/25   Three curves are reproduced.   They all show

two points very close together, these prac-

tically forming the one arrest.

<pre>
                     Liquidus   1540°C
                     Eutectic   1525°C.
</pre>

14   70/30   Shows three points

<pre>
                     Liquidus   1570°C
                     Peritectic   1530°C
                     Eutectic   1515°C
</pre>

15   65/35   Shows three points

<pre>
                     Liquidus   1570°C
                     Peritectic   1540°C
                     Eutectic   1525°C
</pre>

16   60/40   Only two points are shown by this curve.

The solution range is now very large, so that

gradual deposition may take place without an

actual arrest appearing on the curve.   On

the other hand supercooling may have taken

place, delaying the initial crystallisation so

long that it would be below the peritectic in

temperature, and these two points would thus

appear as one.

<pre>
        1.   Liquidus and peritectic   1540°C
              Eutectic   1517°C

        2.   Liquidus and peritectic   1535°C
              Eutectic   1520°C
</pre>

Part (IV)

The diagram was constructed from the heating curves, with confirmation from the cooling curves. As has been stated, it was not possible to take curves of melts higher in Al_2O_3 than 50%, but above this the diagram was constructed from the photographs taken of the melts. These melts above 50% Al_2O_3 were prepared in the small furnace.

The following points were noted during the work.

Colour of the melts.

When a high MnO melt had not been completely molten it was blackish in colour, but when it had been completely molten it was olive green. On the other side of the eutectic, the melts, when they had not been completely molten, were olive green with yellow spots. When they had been completely molten they showed a transition in colour, from olive to emerald. The appearance of the deep emerald melts corresponded to the composition where the melts had only one phase, i.e. the solution of MnO in the spinel $MnO.Al_2O_3$. When this $MnO.Al_2O_3$ composition had been passed towards the Al_2O_3 side, the colour changed to amber, which is in all probability the colour of the pure spinel.

The Hardness of the Melts.

The solidified melts were of the nature of corundum, and even at the high MnO end were so hard that when a plane surface was presented they resisted a high speed tool steel drill. The melts were really torn out of the crucible rather than drilled out. At the high MnO end prolonged attack with concentrated hydrochloric acid served to loosen the material. The melts got harder as the Al_2O_3 content increased, until

Part (IV)

until it was impossible to saw the melts. To
enable these surfaces to be examined the melts were
chipped and then ground, as has been described in
Part (II), Page (28)

Surface Tension of the Melts.

The surface tension of the melts of the MnO-
Al_2O_3 system was low in that they climbed up the walls
of the crucible.

Other Characteristics of the Melts.

As the percentage of the spinel increased,
there was a corresponding increase in the contraction
suffered on solidification. A photograph of a 50/50
melt and crucible is given in which the contraction
cavity is well shown and also the beautiful hexagonal
plates of the spinel are clearly shown. The sections
were more difficult to polish as the percentage of the
spinel increased. With regard to the contraction
suffered on solidification, this property is said to
be characteristic of a stable substance and it became
so great in the melts rich in spinel that these came
out of the crucible as a fused plug leaving the latter
clean without any sign of erosion or corrosion.

Photographs of the System.

Each of the melts was sectioned, polished,
and examined microscopically. They were examined in
the unetched condition and then in the etched condition.
In many of these photographs were taken of several
fields. A selection of these micrographs is shown
in plates 1-16.

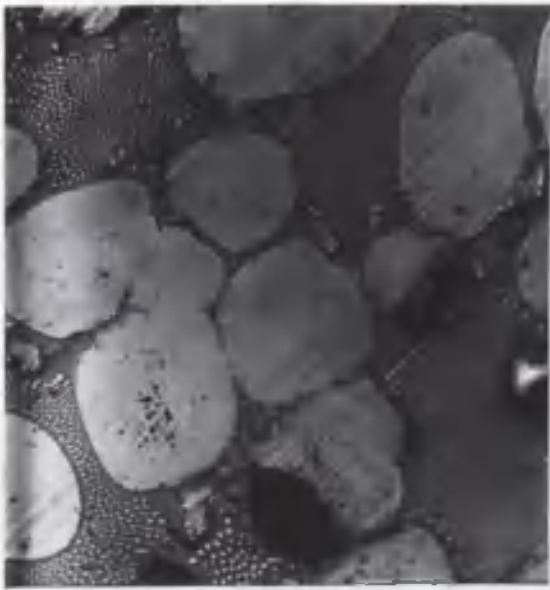| Plate.	Melt.	Remarks.
1	MnO/Al_2O_3 85 15	Primary MnO solid solution in a ground mass of eutectic of MnO solid solution and spinel solid solution. x 370 Etched 10% HCl in water.

PLATE 1

Etched 10% HCl   x 370

85%MnO/15% Al₂O₃

PLATE 2

Etched 10% HCl   x370
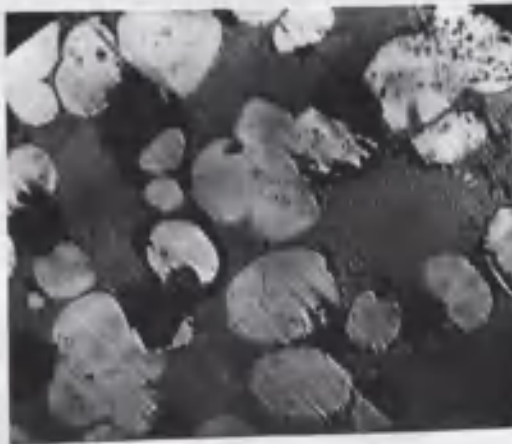
85% MnO / 15% Al₂O₃
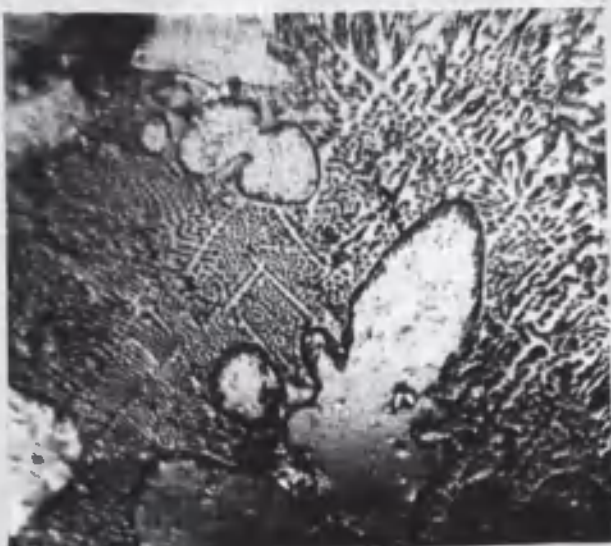

PLATE 3

Etched 10% HCl   x 200

85% MnO / 15% Al₂O₃

PLATE 4

Etched 10% HCl   x150

80 % MnO / 20 % Al₂O₃

PLATE 5

Etched 10% HCl   x 150

80%MnO / 20 % Al₂O₃

Part (II)

2	85	15	As in plate 1. x370 Etched 10% HCl in water.
3	85	15	As in plate 1, but magnification is x 200, as compared with x 370 in 1

        Etched 10 HCl in water.

4	80	20	Primary MnO solid solution in a ground mass of eutectic of MnO solid solution and spinel solid solution. Note the dendritic nature of the MnO solid solution. Note also that the eutectic is now conforming to a roughly triangular pattern.

        x 150 Etched 10% HCl in water

5	80	20	Another field of the same melt. Primary MnO solid solution in a ground mass of spinel solid solution-MnO solid solution eutectic. x 150

        Etched 10% HCl in water.

6	80	20	The same melt at a lower magnification. Remarks as in 4 and 5. Note the dendritic nature of the MnO solid solution primary. Only micrographic evidence of this solid solubility was obtained. x 118.

        Etched 10% HCl in water.

7	70	30	Almost every kind of eutectic pattern is shown by this melt. The eutectic is of a very finely divided nature. A plate of primary spinel solid solution is shown in a ground mass of spinel solid solution - MnO solid solution eutectic. Note the strong crystallisation habit of the primary spinel. This habit has been impressed on the eutectic.

PLATE 6

Etched 10% HCl   x118

80 % MnO / 20 % Al$_2$O$_3$

PLATE 7

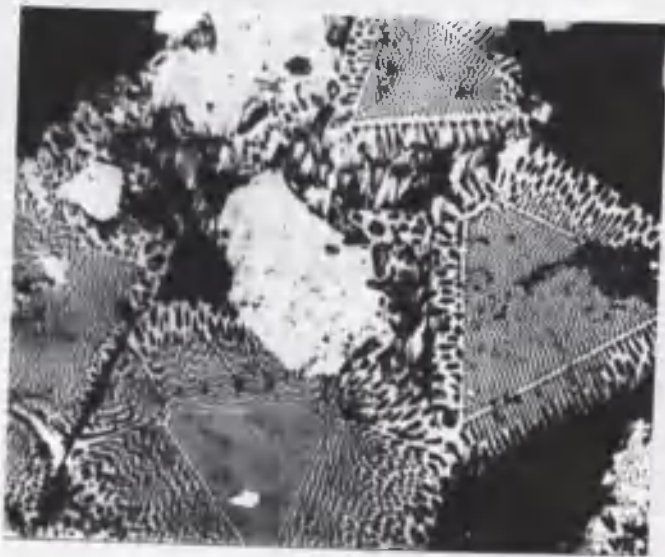Etched 10% HCl   x 145

70 % MnO / 30 % Al$_2$O$_3$

PLATE 8

70 % MnO / 30 % Al$_2$O$_3$

Etched 10 % HCl   x 145
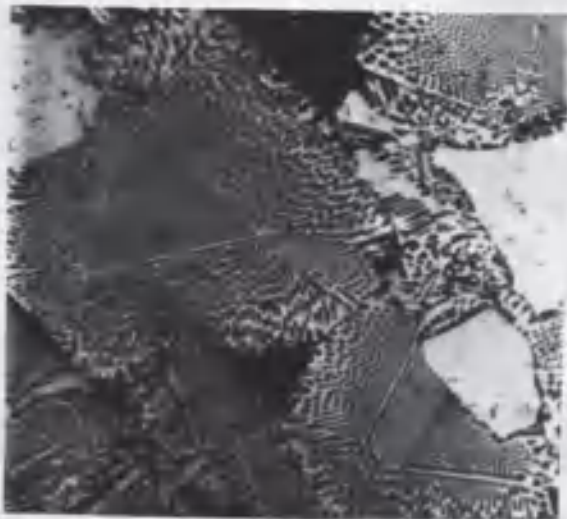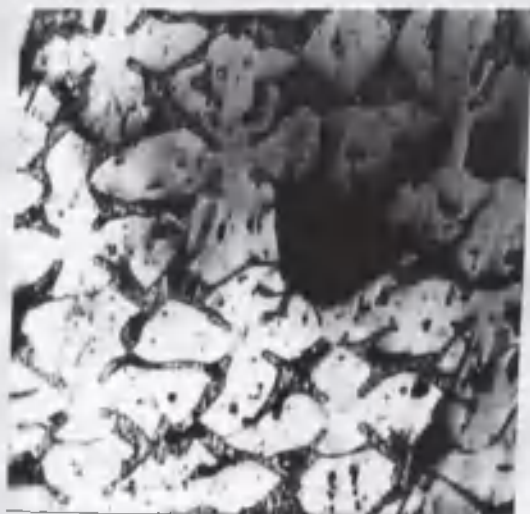

PLATE 9

Etched 10% HCl   x 145

70 % MnO / 30 % Al$_2$O$_3$

PLATE 10

Etched 10% HCl   x 192

57.75% MnO / 42.25% Al$_2$O$_3$

Part (IV)

This was the pattern which was first noticeable in the 80/20 melt. x 145

Etched 10% HCl in water.

8   70/30   Shows the same as plate 7.   Primary spinel solid solution in a ground mass of eutectic of MnO solid solution and spinel solid solution.   Note the beautiful nature of the eutectic. x 145.

Etched 10% HCl in water.

9   70/30   Remarks as in 7 and 8. x 145

Etched 10% HCl in water.

10   57.75/42
and   .25   Primary spinel solid solution with a small amount of eutectic of MnO solid
10a.   solution and spinel solid solution. Note the dendritic nature of the primary, and that due to the contraction suffered on solidification the eutectic in some cases has not been enough to fill the spaces in between the dendritics.

10 x 192
10a x 150

Etched 10% HCl in water.

11   50/50   Spinel solid solution with practically no eutectic.   Note the large contraction cavities. x 150

Etched 10% HCl in water.

12   50/50   As in plate 11. This is another field of the same melt. x 150

Etched 10% HCl in water.

13   50/50   This melt unprepared in any way shows

1. The large contraction cavity formed on solidification.

2. The beautiful crystals of the spinel projecting out into the "pipe".

The very strong crystal habit of the

PLATE 10a

57.75% MnO / 42.25% Al$_2$O$_3$
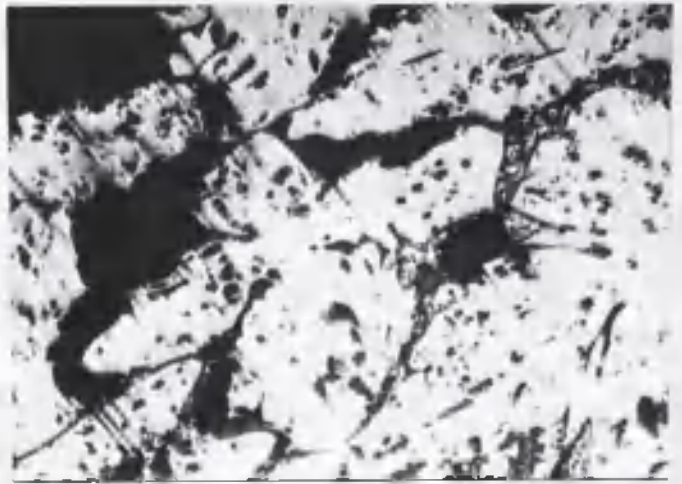
Etched 10% HCl   x150

PLATE 11

50 % MnO / 50 % Al$_2$O$_3$

Etched 10% HCl   x 150

PLATE 12

Etched 10% HCl   x 150

50 % MnO / 50 % Al$_2$O$_3$

PLATE 13

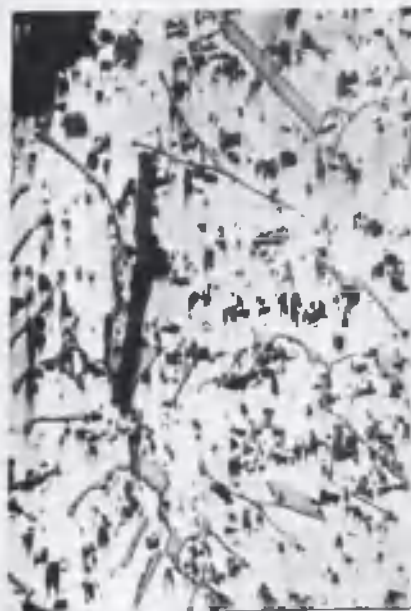Unprepared in any way

50 % MnO / 50 % Al$_2$O$_3$

PLATE 14

Etched 10% HCl   x 120

40 % MnO / 60 % Al$_2$O$_3$

Part (IV)

spinel is exemplified by these crystals.   x 4.5

The crucible was sawn round the melt and the latter fractured.

14   40/60   This melt which is over the composition of the spinel, shows no eutectic but Al_2O_3 as a primary phase in a ground mass of the spinel $MnO.Al_2O_3$.   The Al_2O_3 tends to appear as rhombs.   The MnO. Al_2O_3 spinel is of course the solid solution of MnO in the spinel.

x 120   Etched 10% HCl in water.

15   40/60   As in plate 14.   This is another field of the same melt.   x 120 Etched 10% HCl in water.

16   40/60   As in plates 14 and 15.   x 120 Etched 10% HCl in water.

The optical properties as far as was possible were also determined with the powdered melts.   The refractive indices were determined by the well known Becke immersion method using liquids of known refractive index, as described by Graham and Hay, Journal Roy. Tec. Coll. Vol.3, Pt.2.   The high refractive indices were found using selenium sulphur glasses as described by Merwin and Larsen (Am. Journ. Sc. 1912, 34, p.42).

Three phases were found in the melts:

1.   MnO solid solution of refractive index 2.16.

2. $MnO.Al_2O_3$ solid solution of refractive index 1.76 - 2.00

3.   In the 40/60 melt a phase was found of refractive index 1.66-1.74.

Phases 1. and 2. were isotropic, (both are cubic), phase 3 seemed also to be cubic, but this must
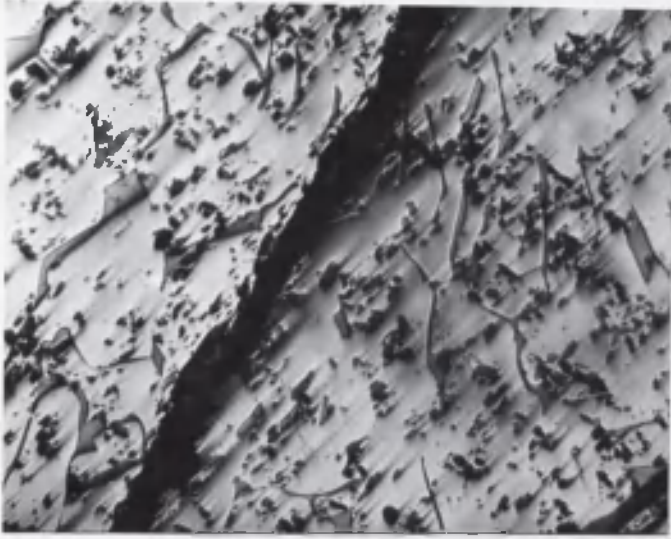
PLATE 15

Etched 10 % HCl   x 120

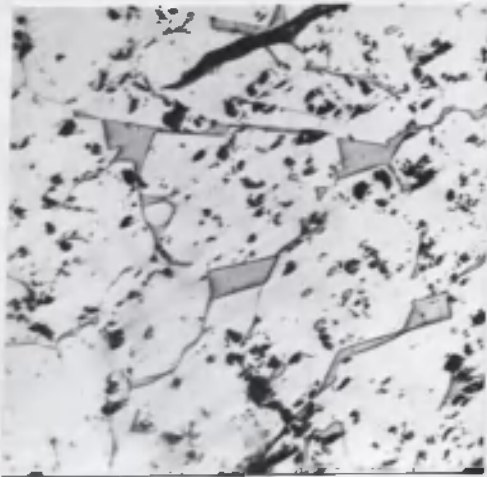40 % MnO / 60 % Al$_2$O$_3$

PLATE 16

Etched 10 % HCl   x 120

40 % MnO / 60 % Al$_2$O$_3$

Part (IV)

have been on a basal section, for corundum is hexagonal
or rhombohedral.

The Diagram.

The diagram is as is shown in fig. (17).   The
melting point of MnO was not found experimentally.
The liquidus when extrapolated cuts the MnO axis at
1785°C and this is the figure found by White, Howat, and
Hay when they melted MnO. (Jour.Roy. Tec. Coll. Vol.3
Pt.2.)   The melting point of MnO is lowered by the
addition of Al_2O_3 from 1785°C to 1520°C at 23.5% Al_2O_3.
The liquidus then rises steeply until it is 1560°C at
about 26% Al_2O_3.   Above this it rises less steeply,
but linearly to the melting point of Al_2O_3 at 2050°C.
A slight solubility of Al_2O_3 in MnO has been postulated,
but no thermal indication of its extent has been found.
The only evidence of this, has been micrographic.
This solid solution is the α phase in the diagram.
One compound only has been found, at the composition
$MnO.Al_2O_3$.   This melts incongruently at 1560°C, giving
rise to a MnO richer liquid, and Al_2O_3.   Herty and
Judkins (unpublished thesis, Carnegie Institute of
Technology) suggest the existence of another compound
$MnO.2Al_2O_3$).   According to the results of the work
above described, no concrete evidence has been found for
the existence of such a compound.   The evidence for the
omission of such a compound is:

1. The liquidus on extrapolation cuts the 100% Al_2O_3
axis at 2050°C, the accepted melting point of Al_2O_3.
If a compound $MnO.2Al_2O_3$ existed, it would necessarily
melt incongruently, for if it did not it would form
another eutectic which would appear in the micrograph of
the 40/60 melt, as can be seen in plates 14, 15, 16,
this is not the case.   If then, the incongruent
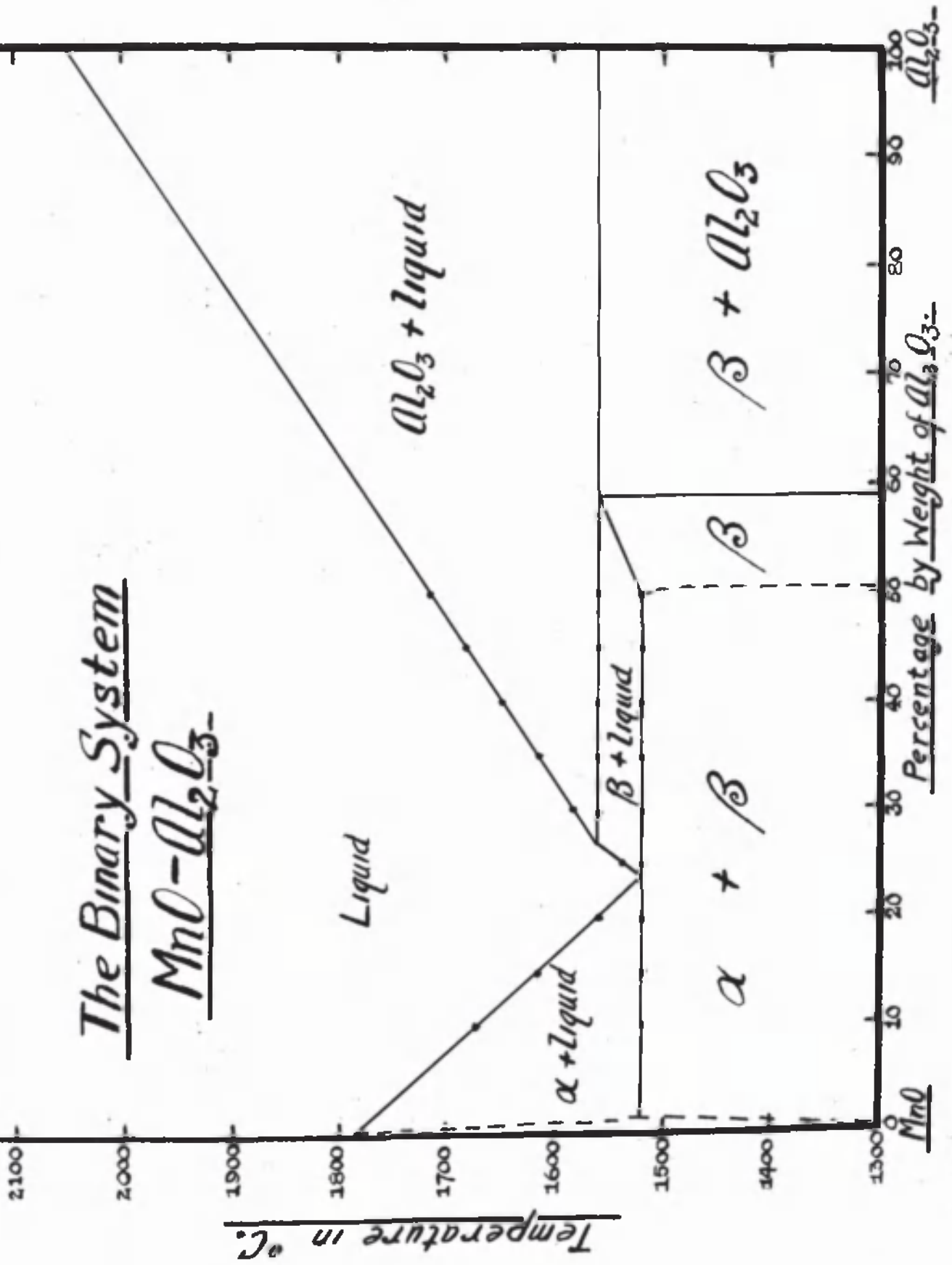melting did take place, an inflexion of the liquidus

The Binary System MnO–Al₂O₃.

Al₂O₃ + liquid

Liquid

β + liquid

α + liquid

α + β

β

β + Al₂O₃

MnO

Percentage by Weight of Al₂O₃.

Al₂O₃.

Temperature in °C.

Fig. 17.

would result, and the latter would no longer cut the
100% Al_2O_3 ^{axis} at $2050^{\circ}C$.

2.   Only on one curve was anything found which could be
attributed to the peritectic dissociation of another
compound, and this was on the curve of 60% MnO, 40%
Al_2O_3.   This has been explained as the energy change
due to the solution of Al_2O_3 reaching a maximum, and not
to the dissociation of another substance.

Even though the composition of $MnO.2Al_2O_3$ corres-
ponds to a borate, and since aluminium and boron are
congeners in the periodic system, it might be expected
that aluminium would form an analogous compound, yet no
place has been found for it, and therefore the system
has been made up with only one compound $MnO.Al_2O_3$.
Because no coring took place in the high Al_2O_3 phase,
the diagram has been completed without any solubility of
MnO in Al_2O_3, the latter probably being in the form of
corundum in the photographs.

What curves that were obtained after 50% Al_2O_3
did not show any eutectic arrest, and this fact together
with the evidence of the micrographs above 50% Al_2O_3
has enabled the diagram to be completed with a range of
solid solubility from about 50% - 59% of Al_2O_3 - the
β phase in the diagram.

PART (V)

THE SYSTEM FeO-Al$_2$O$_3$

Previous Work.

The only previous work which could be found on this system was that of Herty, (Metals and Alloys, Vol.1, No.18, Dec. 1930). The diagram which he suggests deals only with the section from 55-100% Al$_2$O$_3$. He proposes a eutectic between a compound FeO.2Al$_2$O$_3$ and some other phase which he does not name. His diagram is reproduced below in fig. (18). It is to be noted that the other phase of Herty's eutectic would necessarily be another compound since the eutectic temperature is higher than the melting point of FeO.

The Diagram as Found by the Work to be Described.

The diagram is as shown in fig. (19), and was constructed from a consideration of the thermal and micro-graphical data.

The melting point of FeO is lowered from 1370°C to 1305°C, by the addition of 5% of Al$_2$O$_3$. With further addition of Al$_2$O$_3$, the liquidus rises rapidly to 1440°C at 10% Al$_2$O$_3$, and then it rises less steeply but linearly to the melting point of Al$_2$O$_3$ at 2050°C. A slight solubility of Al$_2$O$_3$ in FeO has been found, to the extent of about 4% at the eutectic temperature 1305°C. This solubility decreases rapidly with falling temperature.

Two compounds have been identified on micrographi-cal evidence and thermal evidence has been found to support their formation. To these the compositions FeO.Al$_2$O$_3$, and 3 FeO.Al$_2$O$_3$ have been provisionally assigned chiefly on micrographical grounds. They show a resemblance to the spinels of the system MnO-Al$_2$O$_3$, and both have a very strongly crystalline habit. Evidence, micrographic and thermal, has been found to show that 3FeO.Al$_2$O$_3$ is formed
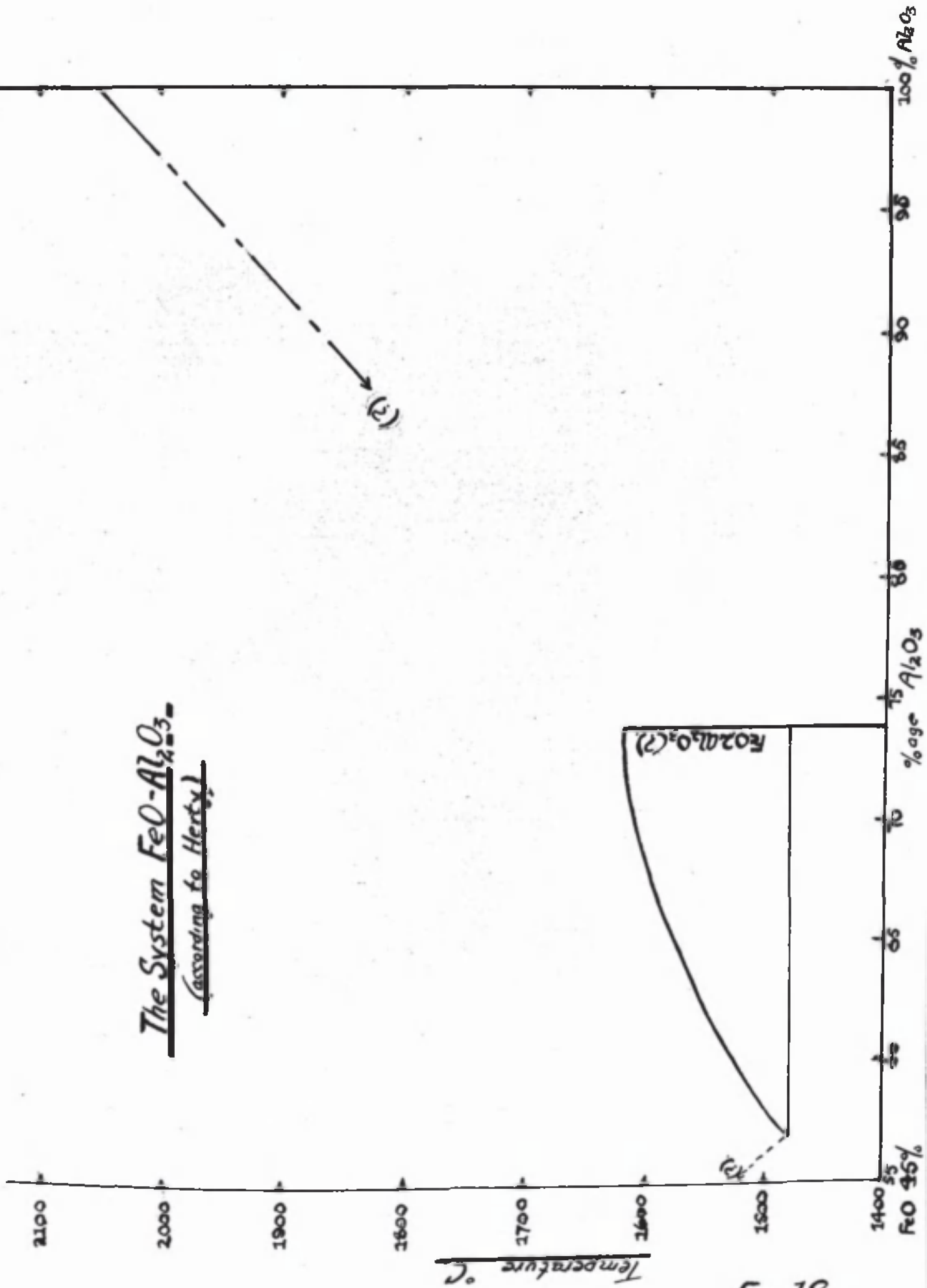
The System FeO-Al₂O₃
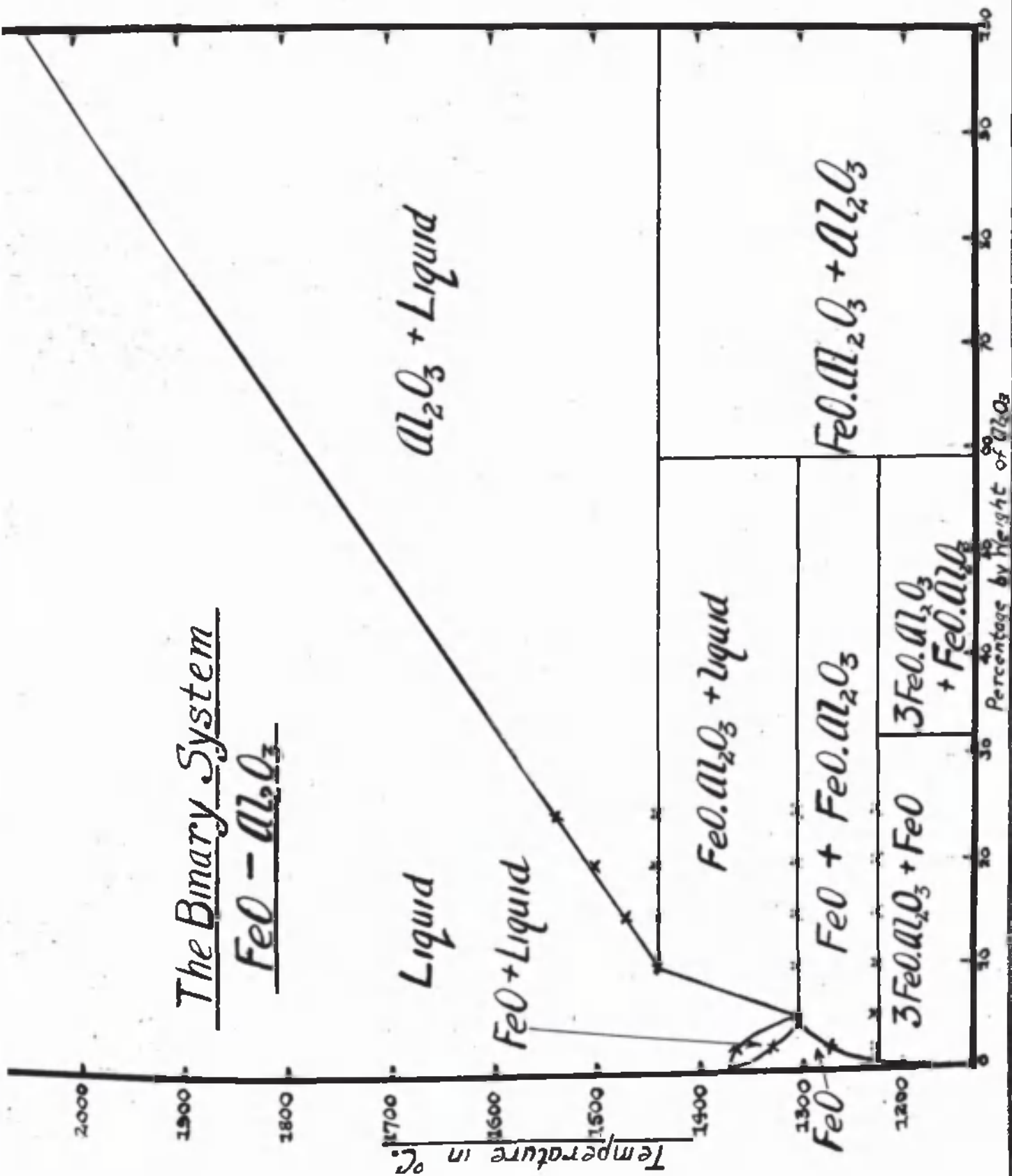
(according to Herty)

Fig. 18

The Binary System
FeO – Al₂O₃

Fig. 19.

Part V.

from FeO and $FeO.Al_2O_3$ at $1225^\circ C$. The reaction is very sluggish and requires considerable time to go to completion. Experimental evidence has been found to show the absence of a eutectic at the percentage shown by Herty. Also no compound $FeO.2Al_2O_3$ has been found. The liquidus on extrapolation cuts the 100% Al_2O_3 axis at $2050^\circ C$. This would not be possible if another compound $FeO.2Al_2O_3$ existed. Either it would form a eutectic on the high Al_2O_3 side or it would melt incongruently, producing an inflexion of the liquidus and so prevent its cutting the Al_2O_3 axis at $2050^\circ C$. The first case is only possible if the eutectic temperature is extremely high, say about $1800^\circ C$, for melts in this region were found to be infusible within the limits of temperature imposed by the Pythagoras, i.e. about $1650-1700^\circ C$. Bearing this in mind as well as the fact that the liquidus as found on extrapolation cuts the Al_2O_3 axis at the melting point of Al_2O_3, the diagram has been completed without this compound as shown.

Experimental Work.

The technique of the determination of the thermal curves has been described in Part (II). FeO is easily oxidisable and reducible, so that the work had to be done in a "Pythagoras" tube. It would have been preferable to have done the determinations in vacuo, but this was not practicable because of the collapse of the evacuated "Pythagoras" tubes at the high temperatures of $1450^\circ C$ and over. For that reason the work was done in nitrogen. A slight amount of residual oxygen in the commercial nitrogen attacked the thermocouple points, causing them to break off. The nitrogen was passed over copper turnings heated to about 900° C, and on thus removing the oxygen, the thermocouples stood up much better.

Procedure During a Run.

Because of the use of the "Pythagoras" tube the procedure is slightly different from that when no

Part V.

Pythagoras is used, so a typical run will be described in
detail.   The FeO and the Al_2O_3 were separately ground in
an agate mortar and their appropriate weights to make up a
two gram sample were then ground together and intimately
mixed, and placed in a Molybdenum crucible.   The thermo-
couple connections were made as described in Part (II), and
the assembly placed in the alundum container, which was
sealed with alundum cement.   This was carefully lowered
into the Pythagoras tube, care being taken to ensure that
the silica sheathing of the thermocouple elements completely
covered the wires.   An undiscovered short meant that the
run had to be repeated, because it was only when the
couples had been heated that this became evident, and of
course it was necessary to wait until the molybdenum was
cold before the tube could be opened, for inspection.   The
bung of the Pythagoras was sealed with a solution of
celluloid in amyl acetate, and the exit tubes were closed
with P.R. tubing and clipped with screw clips, then sealed
in the same way with the exception of the tubes leading to
the mercury gauge and to the pump.   The Pythagoras was
attached to the counterbalancing system which was in the
nature of a steelyard.   The space between the Pythagoras
and the alundum collar of the furnace was packed with
asbestos wool.   The tube was now evacuated, and the level
of the mercury in the gauge watched to see if the tube was
airtight.   This ascertained, the nitrogen copper train
was connected to a T-piece in the pump connection, and it
was then evacuated along with the tube and the vacuum
tested again.   When the train gases were passing freely
about the furnace, a small current was passed through the
furnace and the temperature was slowly raised to about
$600-700^{o}C$, with the pump running all the time, to evacuate
any gases evolved by either the alundum or the amyl
acetate.   The pump connection was then closed and the
vacuum was tested again.   The oxygen-free nitrogen was

Part V.

then passed in until it bubbled off through the mercury
in the manometer.   Its pressure was very slightly above
atmospheric.   During the heating the nitrogen bubbled off
through the mercury in the gauge, which was merely a glass
tube about thirty six inches long with one end immersed in
two or three inches of mercury in a container and with the
other end attached to the apparatus.

As was the general rule in the systems, three
heating and two cooling curves were done.   It was not
practicable to take thermal curves of mixtures containing
40% Al_2O_3 and over, because of the very high temperatures
required to melt them.   The small furnace was used as far
as was possible to melt the high melting mixtures.   It was
used in the form shown in fig. (V).   It was found that the
small Pythagoras tube stood up to higher temperatures than
the larger tubes.   After heating once to the high temper-
ature the hitherto dull surface of the small Pythagoras
tube acquired a greyish black glaze, due to the condensation
of molybdenum vapour on it.   It is thought that this might
be the reason for the better performance of the small size
tubes, for the larger tubes never acquired such a glaze.

The Heating Curves.

A selection of the heating curves is reproduced in
figs. (20) (21) (22) (23) (24) (25) (26).   It is to be
noted that whenever FeO occurs the points from the Fe-O
system (Part III. pp.33) occur and complicate matters.
It is proposed that the solid change involving the dissoc-
iation of $3FeO.Al_2O_3$ into $2FeO$ and $FeO.Al_2O_3$ should be
given the name of a peritectoid, for it is the analogue in
the solid state to a peritectic in the liquid-solid state,
much in the same way as a eutectoid is analogous to a
eutectic.

Fig.	Melt		Remarks.
	FeO/Al_2O_3	Arrest	
20	98/02	1227° C	Peritectoid.

Part V.

1270°C   Thermal $\overset{arrest}{\wedge}$ accompanying the completion

of the solution of FeO.Al$_2$O$_3$ in FeO.

1330°C   Solidus.

1365°C   Liquidus, probably including the 1370°C

peritectic of the Fe-O system.

1410°C $\gamma - \delta$ Fe change point.

1456°C   Completion of liquefaction due to the

crossing of the liquidus of the Fe-O

system.

----

21   95/D5   1180°C   Eutectic of FeO-Fe$_3$O$_4$ in the Fe-O system.

1229°C   Peritectoid.

1305°C   Eutectic of FeO solid solution and FeO.Al$_2$O$_5$.

1370°C   Peritectic of the Fe-O system.

1410°C   This is a small point, but it is probably too

large for the $\gamma - \delta$ Fe change, and is probably

the $\gamma - \delta$ Fe change together with the final

liquefaction point of the Fe-O system as

lowered by the small solution of Al$_2$O$_3$ in the

FeO.

----

21   95/05   A time inverse rate curve is reproduced. Due to

the smallness of the melt only a large arrest has

much influence on the times. The only point which

showed was the eutectic. The actual times are

plotted. The arrest was 1305°C.

----

21   95/05   A heating curve from a different batch of

FeO. Shows the variation in size in the

1170°C 1370°C and 1410°C points but the

1305°C point and the peritectoid are

unchanged. The former points are smaller.

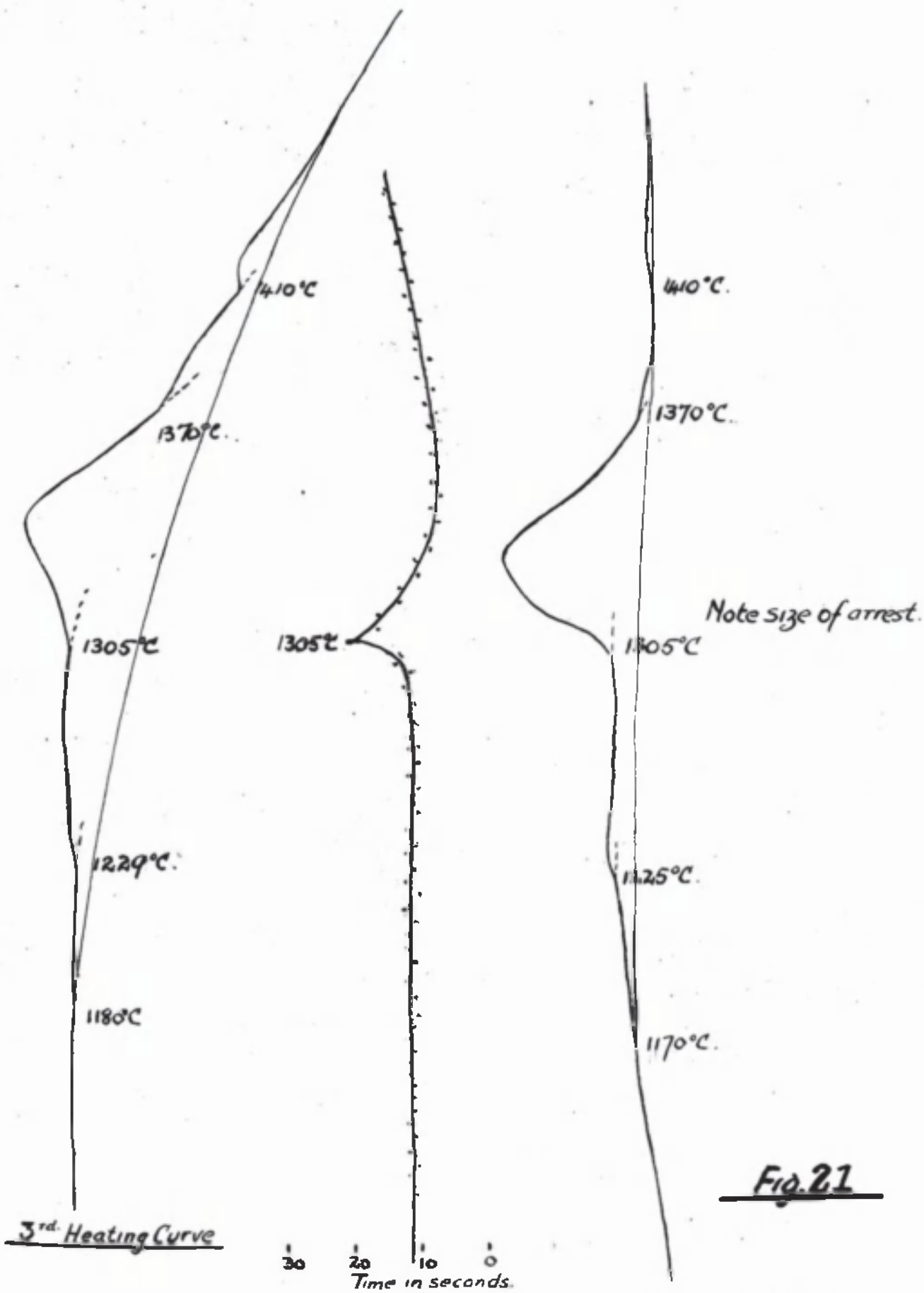These are dependent on the oxygen content

of the FeO.

98% FeO. 2% Al_2O_3.

1456°C.

1410°C.

1365°C.

1330°C.

1270°C.

1227°C.

1448°C.

1360°C.

1345°C.

1305°C.

1238°C.

1180°C.
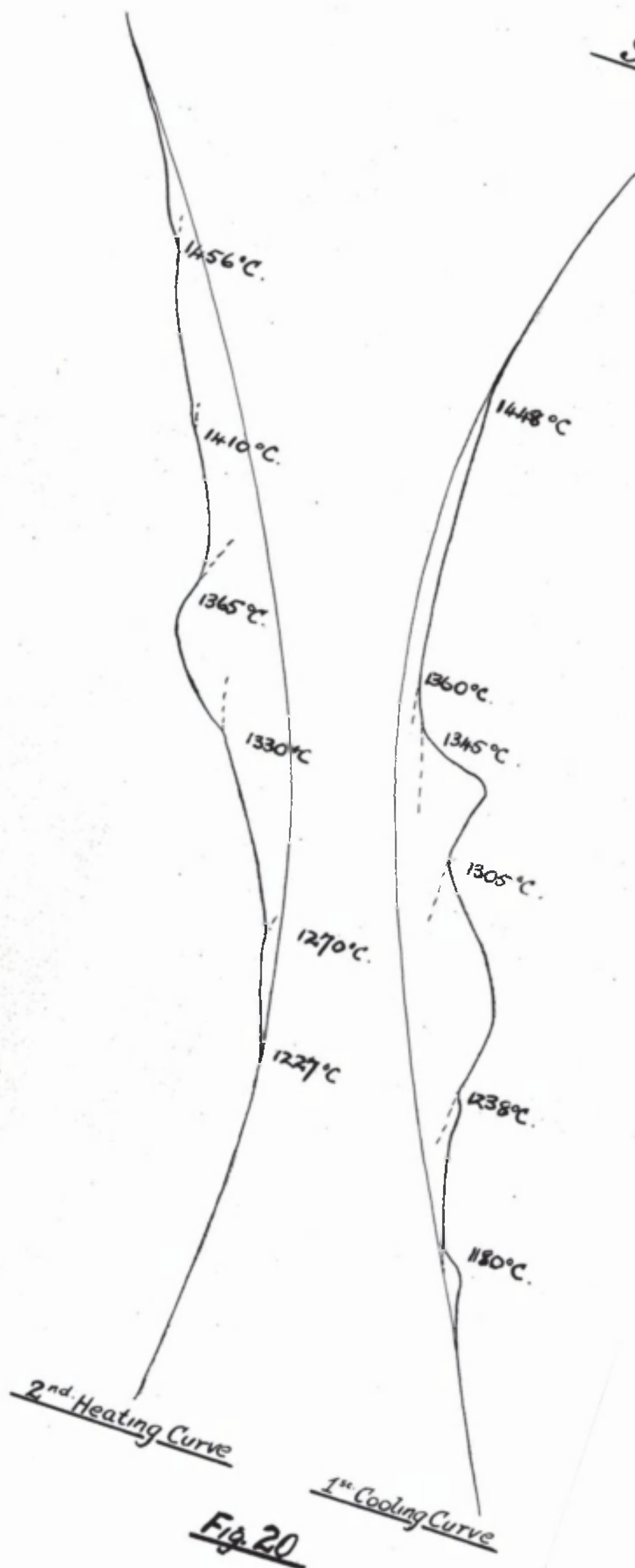
2nd. Heating Curve

1st. Cooling Curve

Fig. 20

95% FeO. 5% Al₂O₃.

410°C
1370°C
1305°C
1229°C
1180°C

410°C.
1370°C.
1305°C.
1229°C.
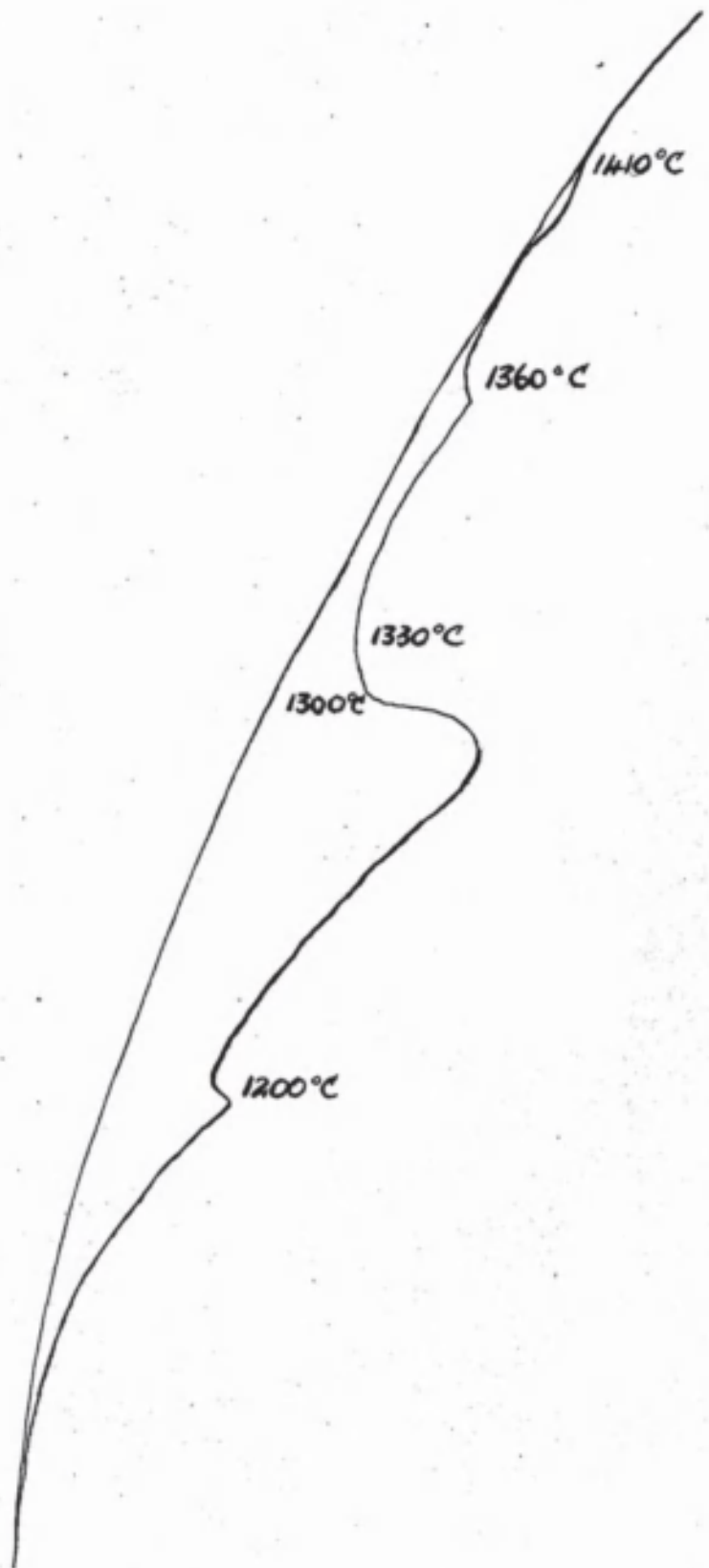
Note size of arrest.

410°C.
1370°C.
1305°C
1125°C.
1170°C.

3rd. Heating Curve

30   20   10   0
Time in seconds.

Fig. 21

Inverse Rate and Differential Curves
of same mixture using different
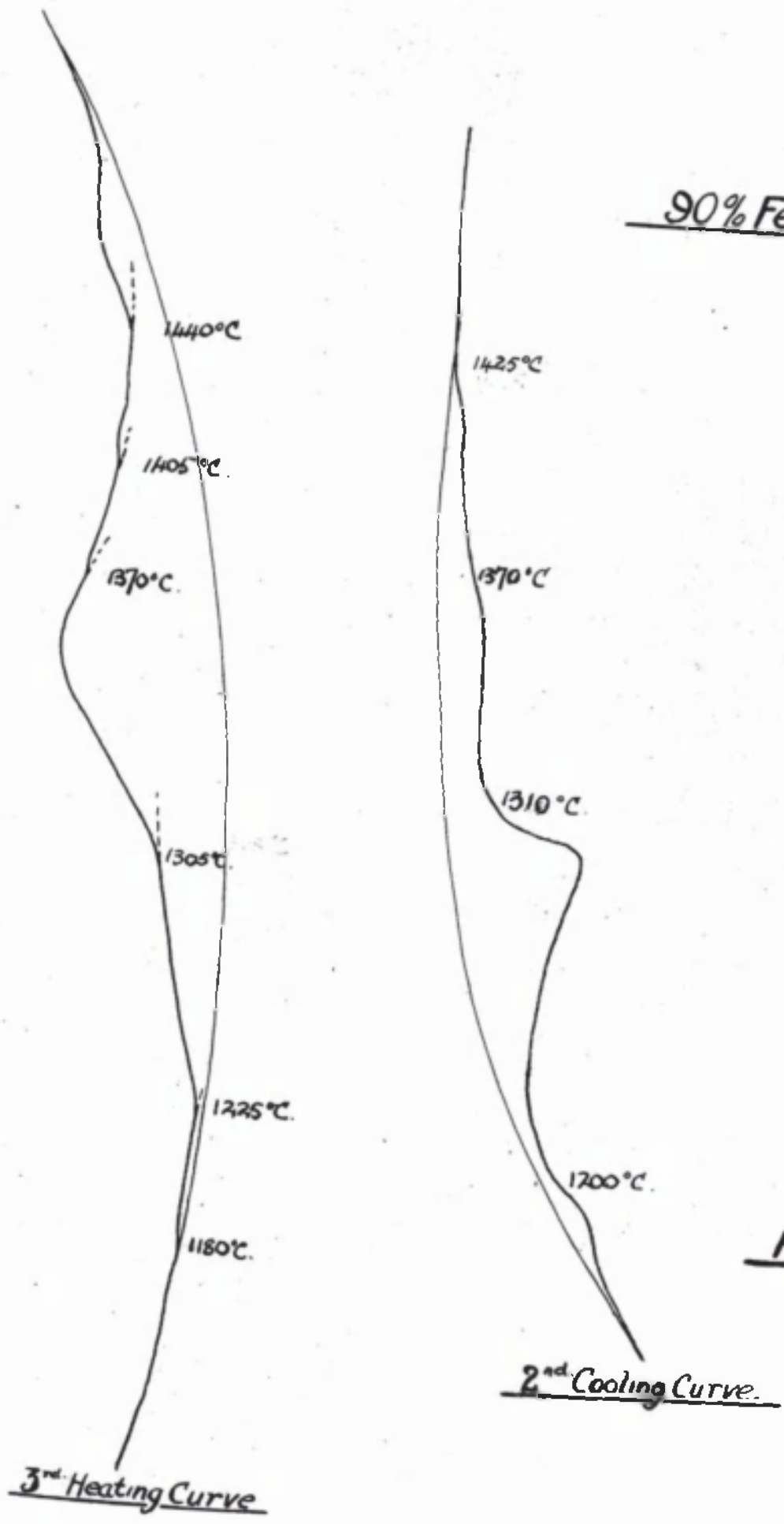batch of FeO.

1440°C

95% FeO. 5% Al₂O₃

1ˢᵗ· Cooling Curve

1360°C

1330°C

1300°C

1200°C

Fig. 22.

90% FeO. 10% Al₂O₃.

Fig. 23.

3rd Heating Curve

2nd Cooling Curve.

85% FeO. 15% Al₂O₃.

Heating Curves (left group):

Curve 2:
- 1470°C.
- 1440°C.
- 1400°C.
- 1370°C.
- 1305°C.
- 1225
- 1180.

Curve 3:
- 1470°C.
- 1440°C.
- 1410°C.
- 1370°C.
- 1305°C.
- 1225
- 1180.

Cooling Curves (right group):

Curve 1:
- 1440°C.
- 1430°C.
- 1370°C.
- 1305°C.
- 1270°C.

Curve 2:
- 1425°C.
- 1370°C.
- 1305°C.
- 1215°C.

Fig. 24

1500°C.

1490°C

1440°C.

1425°C.

1410°C.

1370°C.

1305°C

1305°C.

1225°C

1215°C.

1180°C

1st Cooling Curve

80% FeO. 20% Al₂O₃.

2nd. Heating Curve.

Fig. 25

75% FeO. 25% Al₂O₃

1540°C   1535°C

1440°C   1430°C

1370°C   1370°C

1305°C

1305°C   1305°C

1225°C

Cooling Curve

1180°C
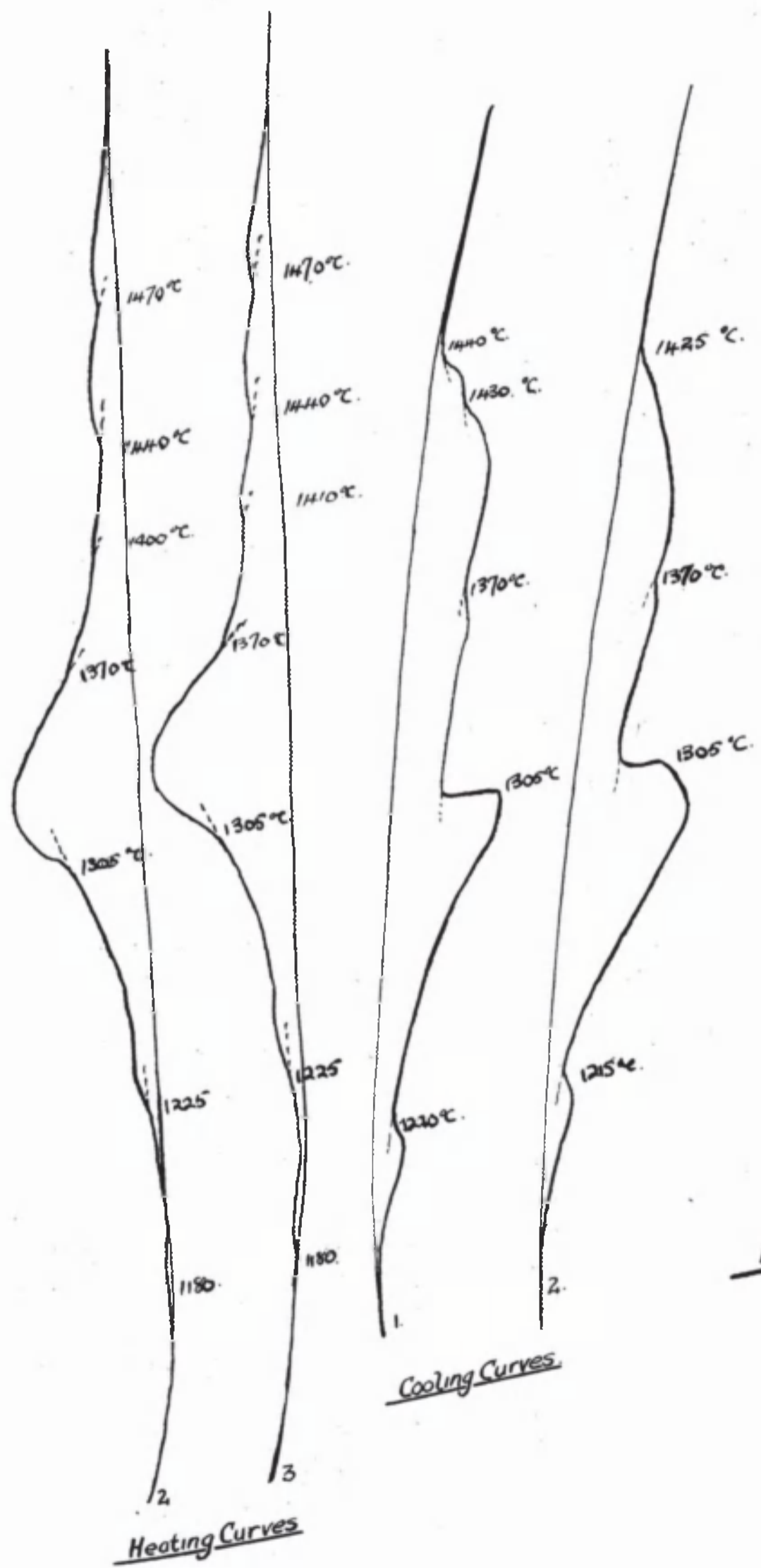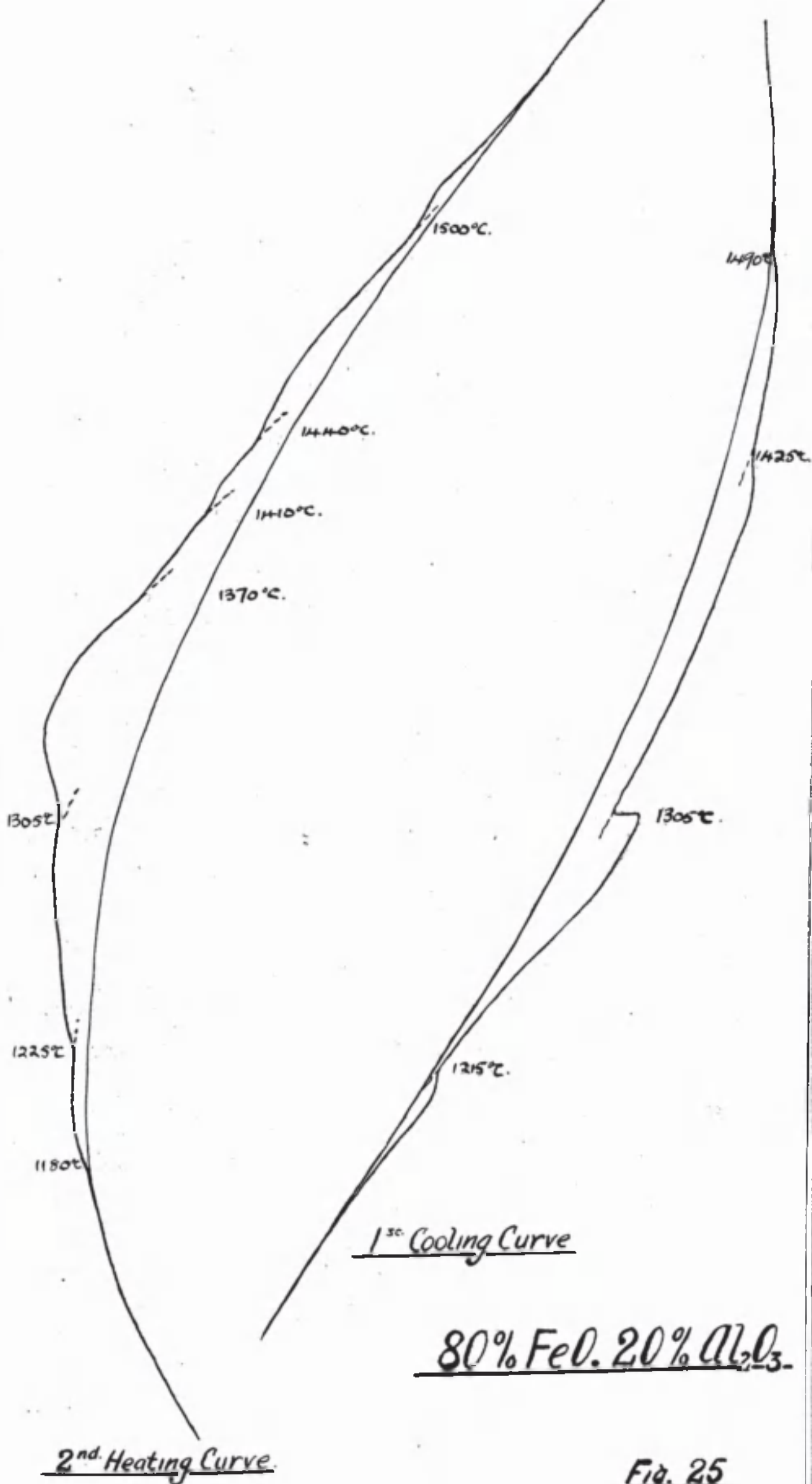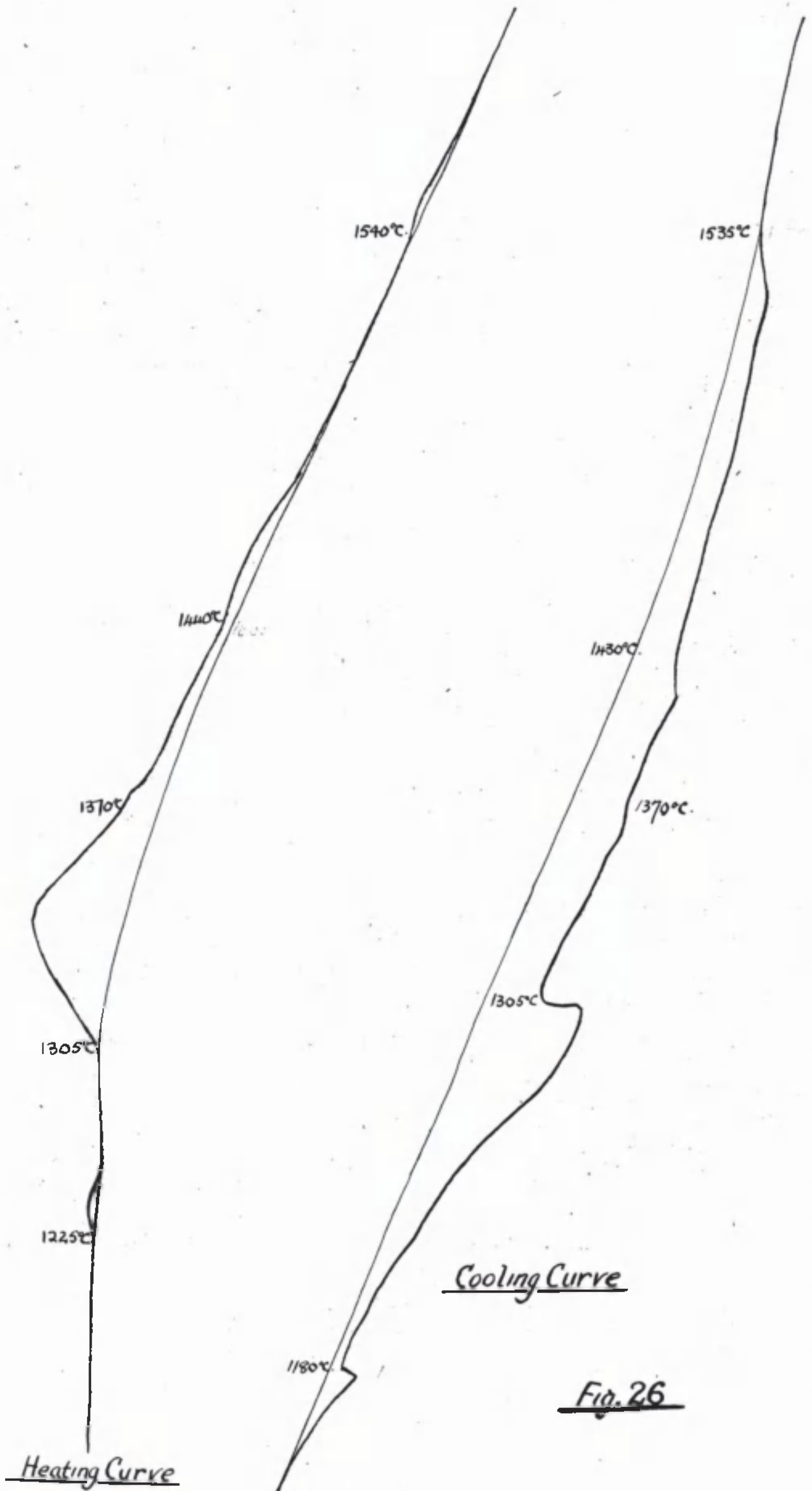
Fig. 26

Heating Curve

Part V.

1170°C   Eutectic of $FeO-Fe_3O_4$ in the system Fe-O.

1225°C   Peritectoid.

1305°C   Eutectic of FeO solid solution and

              $FeO.Al_2O3$.   Note its size, and also

              compare the sizes of the other points.

              This is 100% eutectic.

1370°C   The peritectic of the Fe-O system.

1410°C   Completion of liquefaction of the Fe-O

              system probably including the γ-δ Fe point.

----

23   90/10   1180°C $FeO-Fe_3O_4$ eutectic of the Fe-O system.

             1225°C   Peritectoid.

             1305°C   Eutectic of FeO solid solution and

                    $FeO.Al_2O_3$.

              1370   Peritectic of Fe-O system.

               1405 γ-δ Fe point.

            1440° C   Liquidus of the $FeO-Al_2O_3$ system, includ-

                    ing the final liquefaction of the Fe-O

                    system.

----

24   85/15   1180°C $FeO-Fe_3O_4$ eutectic of the Fe-O system.

             1225°C   Peritectoid.

              1305°C   Eutectic of FeO solid solution and

                     $FeO.Al_2O_3$.

             1370°C   Peritectic of the Fe-O system.

             1400°C γ-δ Fe point.

             1440°C   Peritectic dissociation of $FeO.Al_2O_3$.

             1470°C   Liquidus of the $FeO-Al_2O_3$ system.

----

24   85/15   Confirmatory heating is given, the points on

             which are the same as above.

----

25   80/20   1180°C $FeO-Fe_3O_4$ eutectic of the Fe-O system.

             1225°C   Peritectoid.

              1305°C   Eutectic of FeO solid solution and

                     $FeO.Al_2O_3$.

Part (V)

		1370°C	Peritectic of the Fe-O system.
		1410°C	γ-δ Fe change.
		1440°C	Peritectic dissociation of $FeO.Al_2O_3$.
		1500°C	Liquidus of the $FeO-Al_2O_3$ system.

26	75/25	1225°C	Peritectoid.
		1305°C	Eutectic of FeO solid solution and $FeO.Al2O_3$.
		1370°C	Slight indication of the peritectic of the Fe-O system.
		1440°C	Peritectic dissociation of $FeO.Al_2O_3$
		1540°C	Liquidus of the $FeO-Al_2O_3$ system.

| | 70/30 | | This was melted by heating to 1650°C, but did not give satisfactory curves. |

| | 60/40 | | This was not melted by heating to 1650°C. |

| | 43/57 | | This was the melt at which Herty reported the occurrence of a eutectic melting at 1480°C. This was heated to 1670°C, but no thermal arrests were found. The contents of the crucible were slightly sintered, and the melt came out of the crucible as a plug, which could be easily crumbled in the fingers. This would be expected from the present work, which shows that this mixture should form a very small amount of eutectic and have a melting range of nearly 500°C, with a liquidus temperature of nearly 1800°C. Thus we have conclusive evidence of the absence of a eutectic at this composition, at any rate with a melting point lower than 1670°C. |

The Cooling Curves.

| 20 | 98/02 | 1448°C | Liquidus of the system Fe-O. |

Part (V)

20 98/02 1448°C Liquidus of the system Fe-O.

‑‑‑‑‑‑ δ-γ Fe did not show on this curve.

1360°C Peritectic of the system Fe-O.

1345°C Liquidus of the system FeO-Al$_2$O$_3$.

1305°C Solidus.

1238°C First precipitation of FeO.Al$_2$O$_3$.

1180°C Peritectoid.

It will be noticed that hysteresis is not very pronounced.

---

22 95/05 1410°C Liquidus and δ-γ Fe point of the system Fe-O.

1360°C Peritectic of the system Fe-O.

1300°C Eutectic of FeO solid solution and FeO.Al$_2$O$_3$.

1200°C Peritectoid.

---

23 90/10 1425°C Liquidus of the system FeO-Al$_2$O$_3$.

1370°C Peritectic of the system Fe-O.

1310°C Eutectic of FeO solid solution and FeO.Al$_2$O$_3$.

1200°C Peritectoid.

---

24 85/15 (1) 1440°C Liquidus of the FeO-Al$_2$O$_3$ system, depressed somewhat.

1430°C Peritectic formation of FeO.Al$_2$O$_3$.

1370°C Peritectic of the system Fe-O.

1305°C Eutectic of FeO solid solution and FeO.Al$_2$O$_3$.

1210°C Peritectoid.

---

24 85/15 (2) 1425°C Liquidus and peritectic of the system FeO-Al$_2$O$_3$ appearing together due to the depression of the liquidus, below the peritectic temperature.

Part (V).

		1370° C	The peritectic of the system Fe-O.
		1305°C	Eutectic of the FeO solid solution and FeO.Al_2O_3.
		1215°C	Peritectoid.

25	80/20	1490°C	Liquidus of the system FeO-Al_2O_3.
		1425°C	Peritectic formation of FeO.Al_2O_3.
		1305°C	Eutectic of FeO solid solution and FeO.Al_2O_3.
		1215°C	Peritectoid.

26	75/25	1535°C	Liquidus of the FeO-Al_2O_3 system.
		1430°C	Peritectic formation of FeO.Al_2O_3.
		1305°C	Eutectic of FeO solid solution and FeO.Al_2O_3.
		1180°C	Peritectoid.

When the point at 1225°C was received with such constancy in the heating curves, it was thought that this might be the eutectic temperature. The constant point at 1305°C would then have been another peritectic reaction. An experimental melt of 97% FeO and 3% Al_2O_3 was melted. It was then crushed, placed in a molybdenum crucible, and heated to 1270°C, i.e. a temperature above the first constant point, but below the second. When cooled, the melt could easily be withdrawn from the crucible, and could be readily crushed between the fingers. There had been no melting at the 1225°C point, so that this point was definitely not an eutectic.

Photographs of the system.

Each of the melts was sectioned, and the surface prepared and photographed. The melts were exceedingly difficult to polish, and a technique had to be developed before this could be done satisfactorily. This has been

Part (V)

described in Part (II), page 28 .   It must be remembered
that the eutectic lies very close to the FeO end of the
diagram and for that reason it is very unlikely that well
developed eutectic structures will be obtained.   Also
the spinel seems to be very prone to surfusion.   In
addition to this the formation of the eutectic is follow-
ed by the peritectoid reaction involving the reaction of
the two partners of the eutectic.   This causes a change
in the form of the eutectic and in some cases almost
destroys the eutectic structure altogether.

Plate. No.	Melt.	Remarks.
17	FeO/Al_2O_3	
	98/02	$FeO.Al_2O_3$ separating from FeO. The spinel has such a strong crystalline habit that the separated material has almost formed the plates which are so characteristic of the spinels. The very light material is the $FeO.Al2O_3$ and the half tone material is the FeO. The FeO is soft and scratched. The black patches are holes, but there are dark grey places where there is evidence of the reaction of FeO and the $FeO.Al_2O_3$ to form $3 FeO.Al_2O_3$. These reaction zones appear as fringes or rims to the light spinel, between it and the FeO. x 94. Etched by $1''$ HCl in water.
18	98/02	Light $FeO.Al_2O_3$, and half tone FeO. Reaction rims. Remarks as in plate 17. x 94. Etched by $1''$ HCl in water.
19	98/02	FeO, half tone and scratched. $FeO.Al_2O_3$. Dark reaction zones show quite clearly. Other remarks as in plate 17. x 94. Etched by $1''$ HCl in water.

PLATE 17

Etched 1% HCl   x 94

98 % FeO / 02 % Al₂O₃
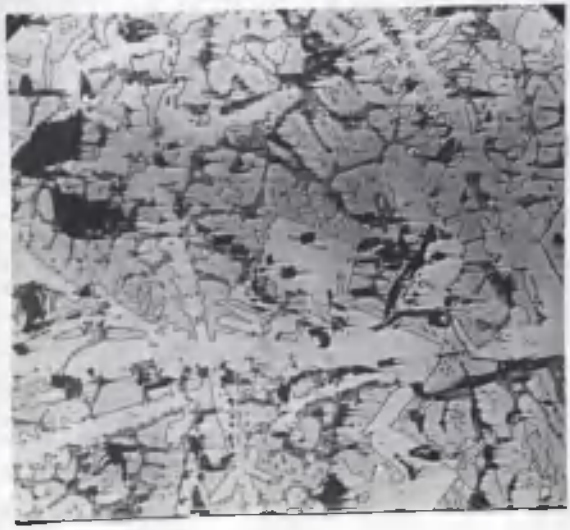
PLATE 18

Etched 1% HCl   x94

98 % FeO / 02 % Al₂O₃
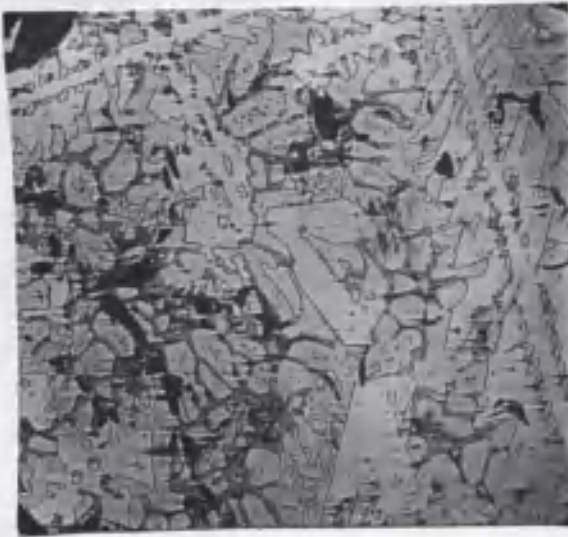
PLATE 19

Etched 1% HCl   x 94

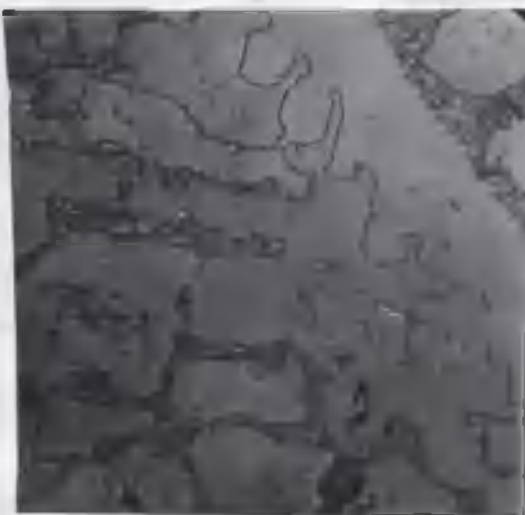98 % FeO / 02 % Al₂O₃

PLATE 20

Etched 1% HCl   x 370

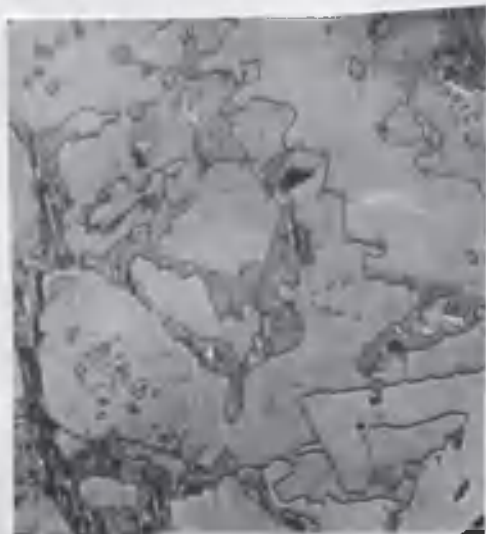98 % FeO / 02 % Al₂O₃

PLATE 21

Etched 1% HCl   x 370

98 % FeO / 02 % Al₂O₃

Part (V)

20. 98/02   The above melt at a magnification of 370.
Shows FeO half tone and scratched, and
spinel light and not scratched. In the
left hand top corner there is visible a
scratch running through the FeO, hardly
touching the spinel, and reappearing in the
FeO. This field shows the reaction zones
where the peritectoid is taking place with
the interaction of FeO and FeO.Al_2O_3 to
form $3FeO.Al_2O_3$, which is dark in colour.
In the top right hand corner the reaction
has been completed at spots and the dark
spinel $3FeO.Al_2O_3$ can be seen quite clearly.
x 370. Etched by 1% HCl in water.

---

21. 98/02   Remarks as in plate 20.
x 370. Etched by 1% HCl in water.

---

22. 95/05   According to the diagram constructed from
the work being described, this melt should
be 100% eutectic when just solid. Note
how the strong crystalline habit of the
spinel, has caused it to form a plate, leav-
ing the FeO. Some of the eutectic of the
FeO, and the FeO.Al_2O_3 can be seen in the
bottom left hand corner. Reaction zones
are in evidence in this plate also. The
light material is FeO.Al_2O_3 and the half
tone scratched material is FeO. Note that
it is the light spinel which is present.
x 370. Etched by 1% HCl in water.

---

23. 95/05   Practically complete divorcing of the
eutectic partners. Note the small islands
of FeO entrapped in the spinel. Light

PLATE 22

Etched 1% HCl   x 370

95 % FeO / 5 % Al$_2$O$_3$

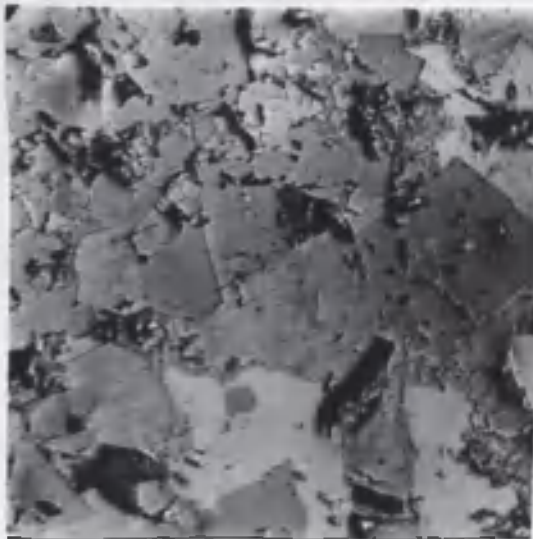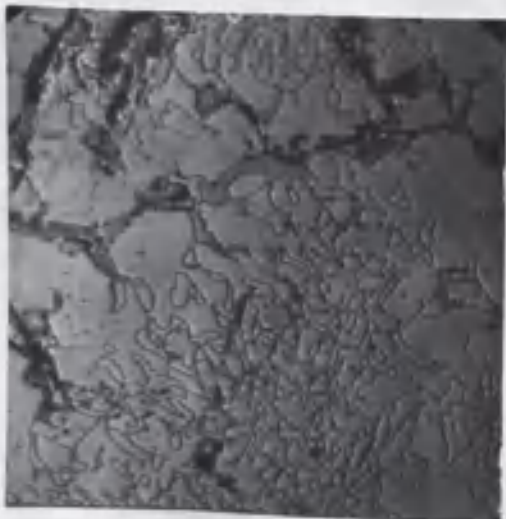
PLATE 23

Etched 1% HCl   x 370

95 % FeO / 5 % Al$_2$O$_3$

PLATE 24

Etched 1% HCl   x 370

90 % FeO / 10 % Al$_2$O$_3$
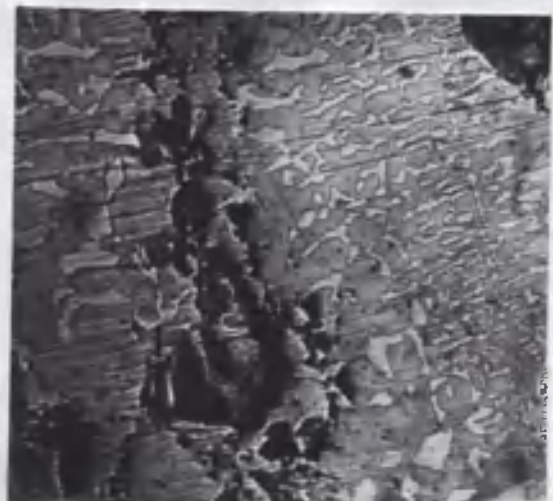

PLATE 25

Etched 1% HCl   x 370

90 % FeO / 10 % Al2O$_3$

PLATE 26

Etched 1% HCl   x 370

90% FeO/ 10% Al$_2$O$_3$ (Deeply Etched)

Part (V)

$FeO.Al_2O_3$ spinel and half tone FeO which
is scratched.   Note the reaction rims
between the spinel and the FeO.
x 380. Etched by 1% HCl in water.

----

24   90/10   This micrograph, showing three phases in a
binary system, necessarily, from the phase
rule, depicts a metastable state.   In this
part of the melt no eutectic structure can
be seen, there has probably been surfusion
of the spinel.   The three phases are:
1.   Half tone FeO scratched.
2.   Light spinel $FeO.Al_2O_3$.
3.   Dark spinel $3FeO.Al_2O_3$.
Note the dark reaction rims between the FeO
and the light spinel.   These ultimately
become the dark spinel $3\ FeO.Al_2O_3$.   Note
the occurrence of two "embryo" dark spinels,
one, where a small island of FeO, has
existed in the light spinel, and the other
where, right in the centre of the field, a
small crystal of the light spinel has exist-
ed in the FeO.   Other than these the dark
spinel is always in closest proximity to the
FeO.
x370. Etched by 1% HCl in water.

----

25   90/10   This micrograph shows a field of eutectic.
Note the greater amount of FeO in the
eutectic as would be required by the com-
position of the latter.   Reaction zones
showing where the dark spinel $3FeO.Al_2O_3$ is
being produced.   The eutectic is of
FeO (solid solution) and the light spinel

Part (V)

25   90/10 $FeO.Al_2O_3$.

x 370.   Etched by 1% HCl in water.

----

26   90/10   Another field of eutectic, but this time
                 more deeply etched.   It will be seen that
                 FeO is more readily etched than the spinel.
                 Note that the scratches appear very deeply
                 in the FeO and hardly at all in the spinel.
                 Also note the greater amount of FeO than
                 the spinel, together with the fact that the
                 spinel tends to be angular, thus showing
                 that its crystalline habit is very strong.
                 x 370.   Etched deeply with 1% HCl in water.

----

27   90/10   Part of a field of eutectic to show the
                 production of dark spinel from the light
                 spinel by absorption of FeO.   Note the
                 massive nature of the FeO, which is the
                 scratched material.
                 x 370.   Etched with 1% HCl in water.

----

28   85/15   With the existence of primary spinel,
                 surfusion seems to occur to such an extent
                 that there is no eutectic structure.   The
                 spinel which appears is not however the
                 primary spinel, but the dark spinel, and
                 with the latter's appearance there is
                 practically no differentiation in the
                 tones of the FeO and the light spinel;
                 they can be differentiated nevertheless by
                 their resistance to abrasion.   In this
                 particular field the peritectoid has gone
                 almost to completion, leaving practically
                 none of the light spinel, although there is
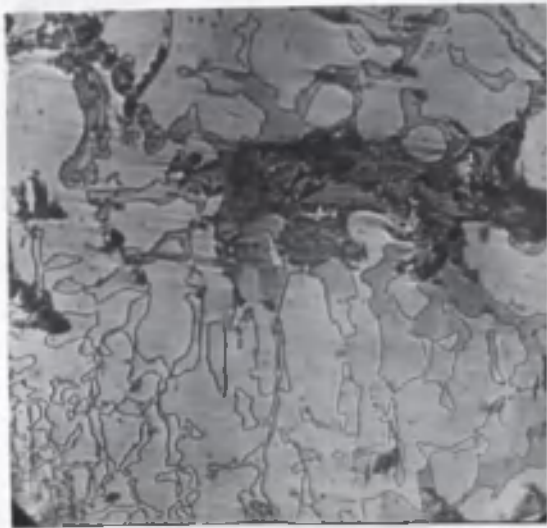   a little in the top left hand corner.

PLATE 27

Etched 1% HCl   x 370

90 % FeO / 10 % Al$_2$O$_3$

PLATE 28

Etched 1% HCl   x 370

85 % FeO / 15 % Al$_2$O$_3$

PLATE 29

Etched 1% HCl   x 370

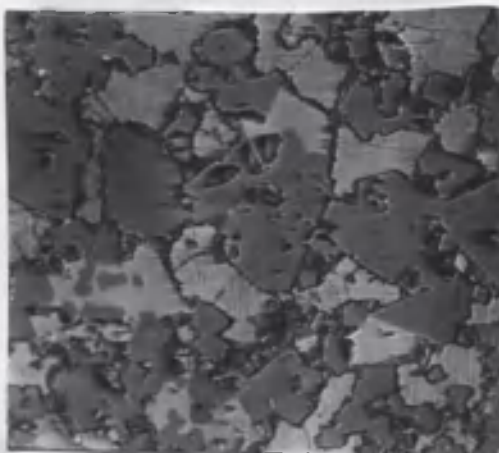85 % FeO / 15 % Al$_2$O$_3$

PLATE 30

Etched 1% HCl   x370

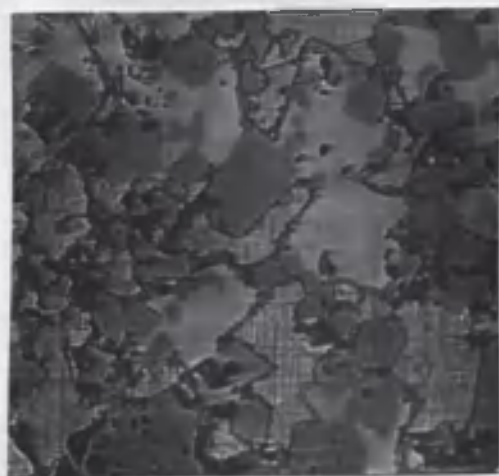80 % FeO / 20 % Al$_2$O$_3$

PLATE 31

Etched 1% HCl   x370

80 % FeO / 20 % Al$_2$O$_3$

Part (V)

28 85/15

Note that in this field where there is almost completion of the reaction, there is almost 50% of FeO and 50% of the dark spinel, if anything there being more of the FeO. This was part of the evidence for the placing of the composition of the dark spinel at $3FeO.Al_2O_3$.

x 370. Etched by 1% HCl in water.

---

29 85/15

Again in this field there is no eutectic structure, the micrograph showing a metastable state of three phases, which are the dark spinel, the light spinel and FeO. Note that the only difference between the two latter is the existence of scratches in the FeO. Note the reaction rim between the light $FeO.Al_2O_3$ and the scratched FeO, also where an island of FeO in the light spinel has given rise to a crystallite of the dark $3FeO.Al_2O_3$.

x 370. Etched by 1% HCl in water.

---

30 80/20

Micrograph shows three phases viz. FeO which is the scratched, cross-hatched material, the dark spinel and the light spinel. The reaction is well on the way to completion. Note that the melt would have about two thirds of the dark spinel and one third of the FeO when the reaction is complete. This is additional evidence for the placing of the composition of the dark spinel at $3FeO.Al_2O_3$. Reaction rims are still in evidence.

x 370. Etched by 1% HCl in water.

PLATE 32

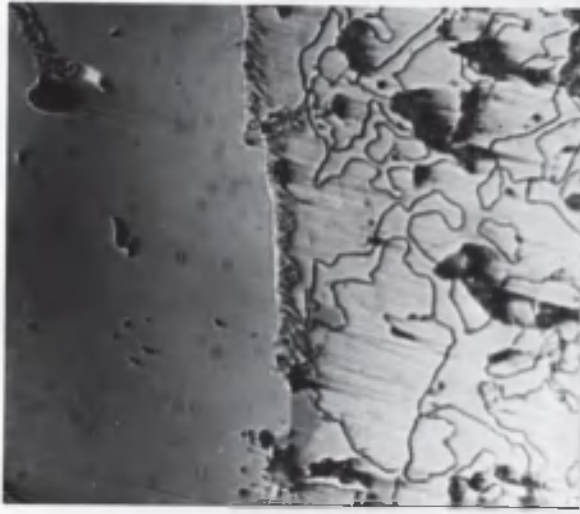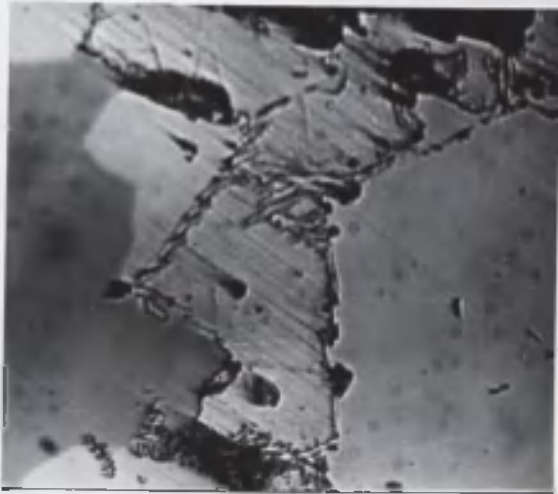Etched 1% HCl   x 435

85 % FeO / 15 % Al$_2$O$_3$

PLATE 33

Etched 1 % HCl   x 435

85 % FeO / 15 % Al$_2$O$_3$

PLATE 34

Etched 1% HCl   x 435

85 % FeO / 15 % Al$_2$O$_3$

Annealed for five days at 1150°C

Part (V)

31　80/20　　The same remarks as in plate 30.　In
these plates there is no eutectic
structure, the spinel seems to surfuse
markedly.

x 370.　Etched by 1% HCl in water.

32　85/15　　In order to verify the existence of a
reaction between the FeO and the light
spinel four grams of this mixture were
made up and melted.　One half was section
-ed, on cooling, and the other half was
annealed at a temperature below $1225^{\circ}C$
the peritectoid temperature.　It was
annealed for five days at $1150^{\circ}C$.
Plate 32 shows the melt before annealing
giving primary light spinel, fringed with
a reaction rim, and a field of the
eutectic of the FeO solid solution and
$FeO.Al_2O_3$.　Note where the dark spinel
has been produced at the reaction rim.

x 435.　Etched by 1% HCl in water.

33　85/15　　Another field of the same melt before
annealing.　Shows a characteristic
crystal of the light primary spinel.　Note
the reaction rim round it.　FeO is also
present and it will be noticed in the left
of the photograph the dark spinel has been
produced.

x 435.　Etched by 1% HCl in water.

34　85/15　　After annealing for five days at $1150^{\circ}C$.
Note the increase in the amount of the
dark spinel.　The reaction is one which

Part (V)

34 85/15 is governed by the diffusion of the
reactants and is therefore necessarily
sluggish, requiring a long time for its
completion. The melt was very brittle
after annealing and was difficult to polish.

Observations made on the Melts after Solidification.

Colour. On the FeO side of the eutectic the melts were jet
black with a bluish irridescence. On the Al_2O_3 side of the
eutectic the melts changed progressively to a slate grey.

Fluidity. The melts with a high FeO content were very
fluid, but the fluidity decreased rapidly as the Al_2O_3
content increased beyond 5%. The fluidity could only be
judged very qualitatively by observation on the depth of the
concavity of the meniscus. The maximum temperature to which
all of the melts were heated was approximately the same.
In some cases when a cracked crucible was used one could
observe to what extent the melt had exuded through the crack.
Surface. Each of the melts tested had a low surface
tension and gave a concave meniscus, the liquid climbing up
the walls of the crucible.

Hardness. FeO is soft and friable, but the addition of so
small a quantity as 2% Al_2O_3 made it so hard that it could
not be cut with a saw and could only be filed with great
difficulty. The melts could be used as glass cutters.
Their hardness was slightly greater than 9 on Moh's Scale
of Hardnesses.

Brittleness. All melts containing Al_2O_3 were exceedingly
brittle, this seeming to be due to the easy cleavage of the
spinel crystals. The technique of polishing these has
already been described.

Crystal Habit and Crystal Size. Melts with a high FeO
content were coarsely crystalline whilst those with a high

Part (V)

Al_2O_3 content had a much finer crystalline appearance. This is probably due to the higher melting point of the latter. The pronounced crystalline habit of the spinels is obvious from the micrographs in plates 17-34. Whenever a "pipe" appeared in the melts this contained beautiful bluish black triangular or hexagonal plates, piled up on each other in a manner reminiscent of the "key pattern" of cast bismuth. The prolonged annealing of the 85/15 melt resulted in a very coarsely crystalline structure.

Part (V)

PART (VI)

THE TERNARY SYSTEM FeO-MnO-Al$_2$O$_3$.

Previous Work.

An extensive search of the literature showed that
no work had been published on this system.

THE Binary Systems Involved.

The binary systems MnO-Al$_2$O$_3$ FeO-Al$_2$O$_3$ have been
described in Parts (IV) and (V) of this thesis.   The diagram
used for the system FeO-MnO is that described by Hay, White,
and Howat in the Journ. West of Scot. Iron and Steel Inst.
1933-34 Vol. 41, and briefly it is as follows.   FeO is
soluble in MnO to an extent of 42% at a temperature of
1430°C.   At that temperature a peritectic reaction with the
liquid containing 89% FeO, produces from this limiting solid
solution of FeO in MnO a conjugate solid solution of MnO in
FeO containing 30% MnO.   Below 1430°C and between 70-100%
FeO the two constituents are wholly soluble.   The conjugate
solutions of 30% MnO and 42% FeO show decreasing solubility
with falling temperature.

Experimental Work.

The technique of the experimental work has been
described in Part (II).   Due to the easily oxidisable and
reducible nature of FeO the work was done in oxygen-free
nitrogen in a "Pythagoras" tube.   In Part (V), the procedure
of a run has been described in detail, and the same procedure
has been employed for the ternary.   The compositions of the
melts for the thermal work were fixed by keeping the FeO
constant, first at 10%, and then varying the MnO and Al$_2$O$_3$
from the high MnO end to the high Al$_2$O$_3$ end until the melts
were infusible within the limits of the Pythagoras tube.   The
FeO was then increased by 10% and the other two constituents
varied again.   In this way the whole of the fusible field of
the system was covered.   Where necessary melts of intermediate
compositions were made.   As was the general practice three

heating /

heating and two cooling curves were taken in a day's run,
and the run was repeated until the curves were satisfactory.
These melts were more difficult to render homogeneous than
the binary melts, because FeO, being comparatively low
melting with respect to MnO and Al_2O_3, tended to melt first
and run away from them.   In such cases the MnO sat up like
a ball and was streaked with undissolved Al_2O_3.   Wherever
possible this was taken from the crucible and turned upside
down, more of the particular mixture added and the curves
attempted again.   As has been stated above, the curves were
an indication of whether the mixture had been completely
molten or not.   Invariably, a "wriggly" curve meant that
the melting had been incomplete.   Micro-examination of each
melt was carried out immediately upon completion of the
thermal work and confirmation of any doubtful point obtained
before proceeding to the next mixture.

A selection of the curves is reproduced, in figs.
27-43.   The same effects of rates of heating and cooling as
described in Part (II), have been noticed.   First heats
have not been reproduced, the curves which are given are
curves which have been taken on melts which have already been
molten.   In general the first heats showed a high liquidus
due as explained in part (II) to the liquation of the
eutectic.   The melts were all soaked at the high temperature,
on the first heat.   This was to make them as homogeneous
as possible.

The curves have been subdivided according to the
number of arrests which they show.

In what follows, E = Eutectic Trough; P = Peritectic;
L = Liquidus.

(1).   Curves on the Al_2O_3 side of the eutectic trough,
which show three points.
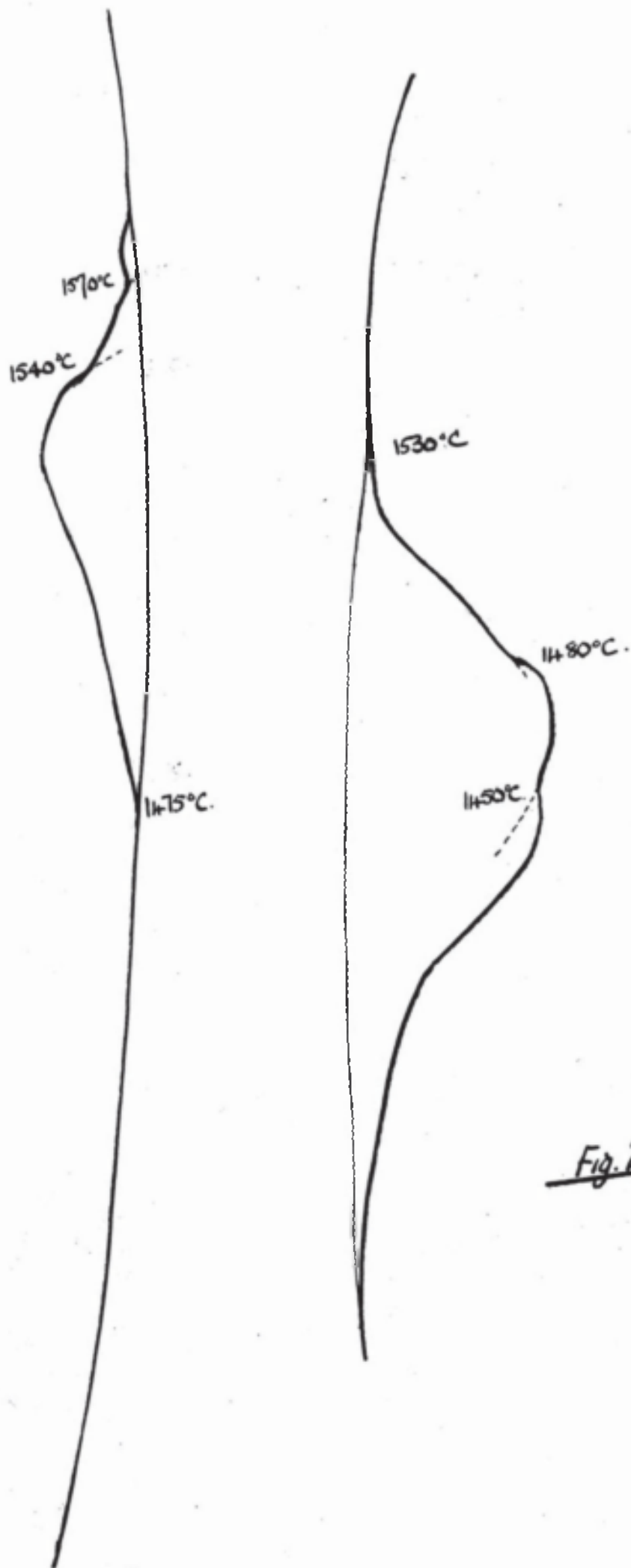
MnO 60%. FeO 10%. Al₂O₃ 30%.

1570°C
1540°C
1530°C
1480°C.
1475°C.
1450°C

Fig. 27.

MnO 50%. FeO 20%. Al₂O₃ 30%.
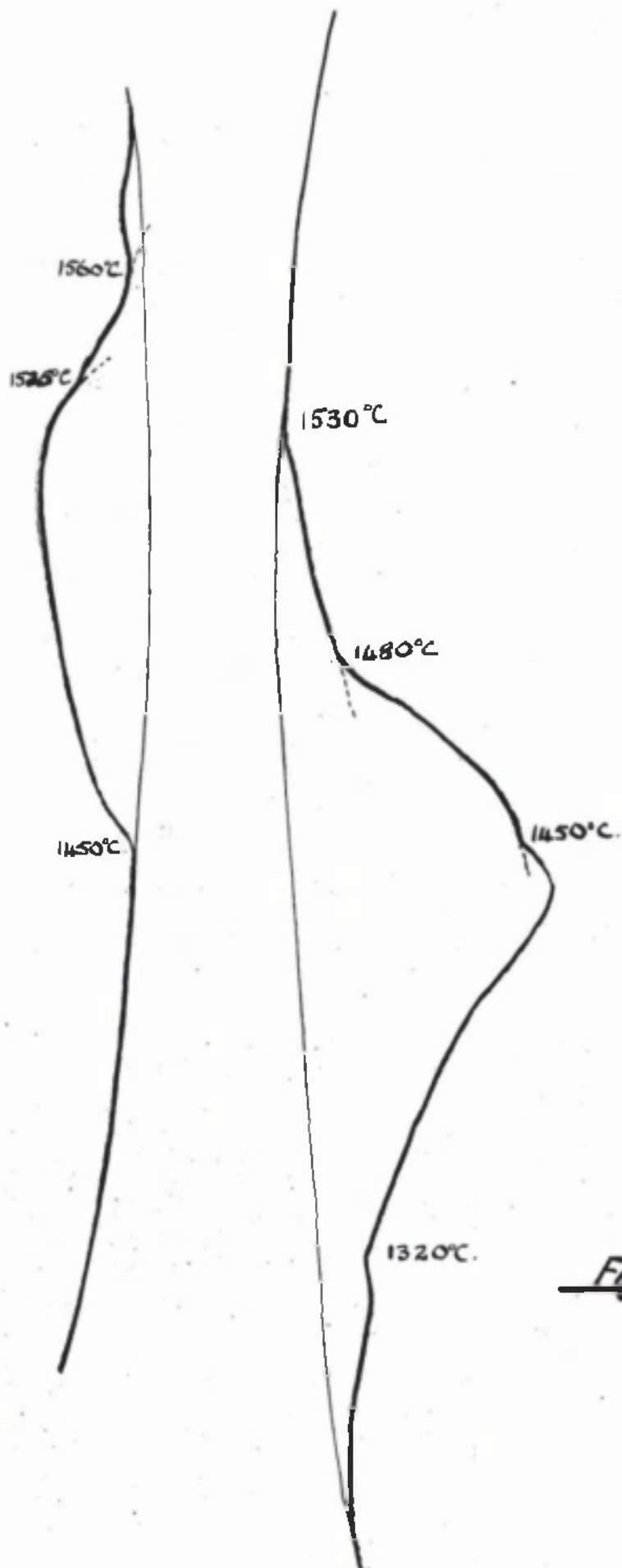
Fig 28.

MnO 40%. FeO 30%. Al₂O₃ 30%.

1570°C.

1510°C.

1500°C.

1470°C.

1440°C.

1440°C.

Fig. 29

MnO 30%. FeO 40%. Al₂O₃ 30%

$MnO\ 30\%.\ FeO\ 40\%.\ Al_2O_3\ 30\%$

1575°C.

1480°C.

1495

1445°C.

1380°C.

1380℃

1270°C
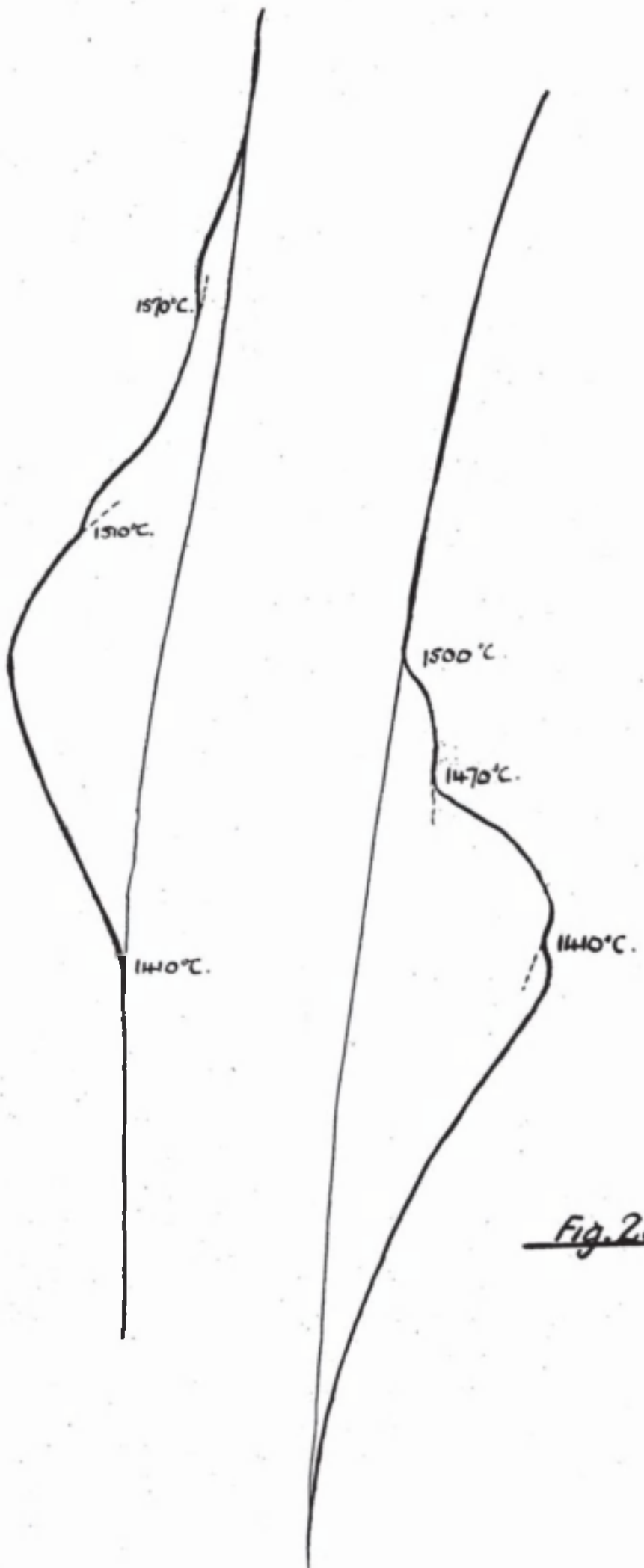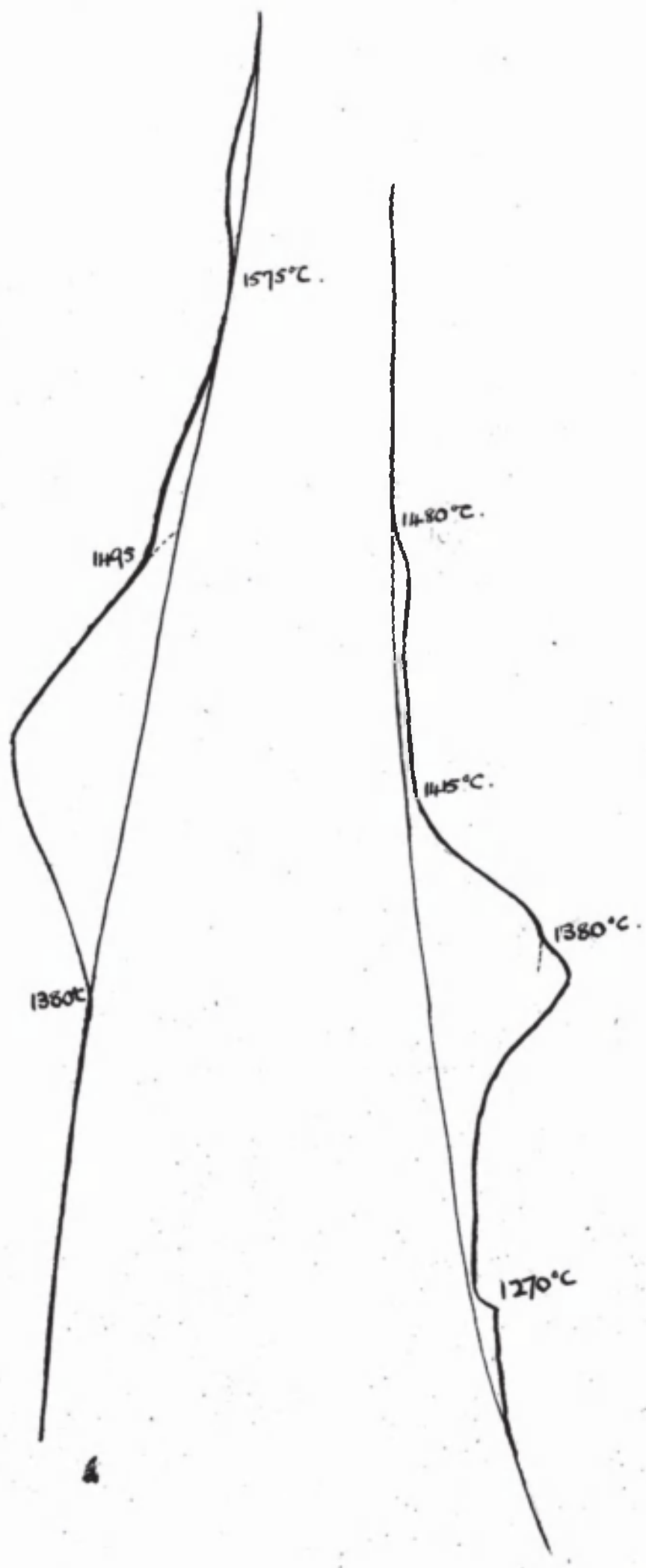
Fig. 30

MnO 20%. FeO 50%. Al$_2$O$_3$ 30%

1570°C.

1480°C

1475°C

1445°C

1360°C

1360°C

Fig.31

1220°C.
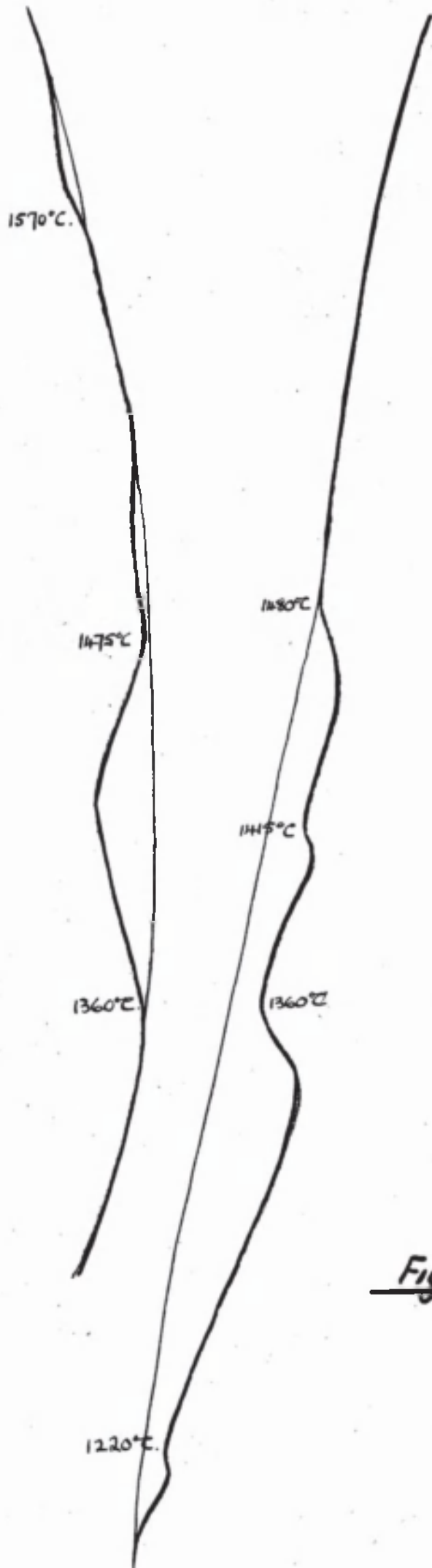
MnO 20%. FeO 60% Al₂O₃ 20%.
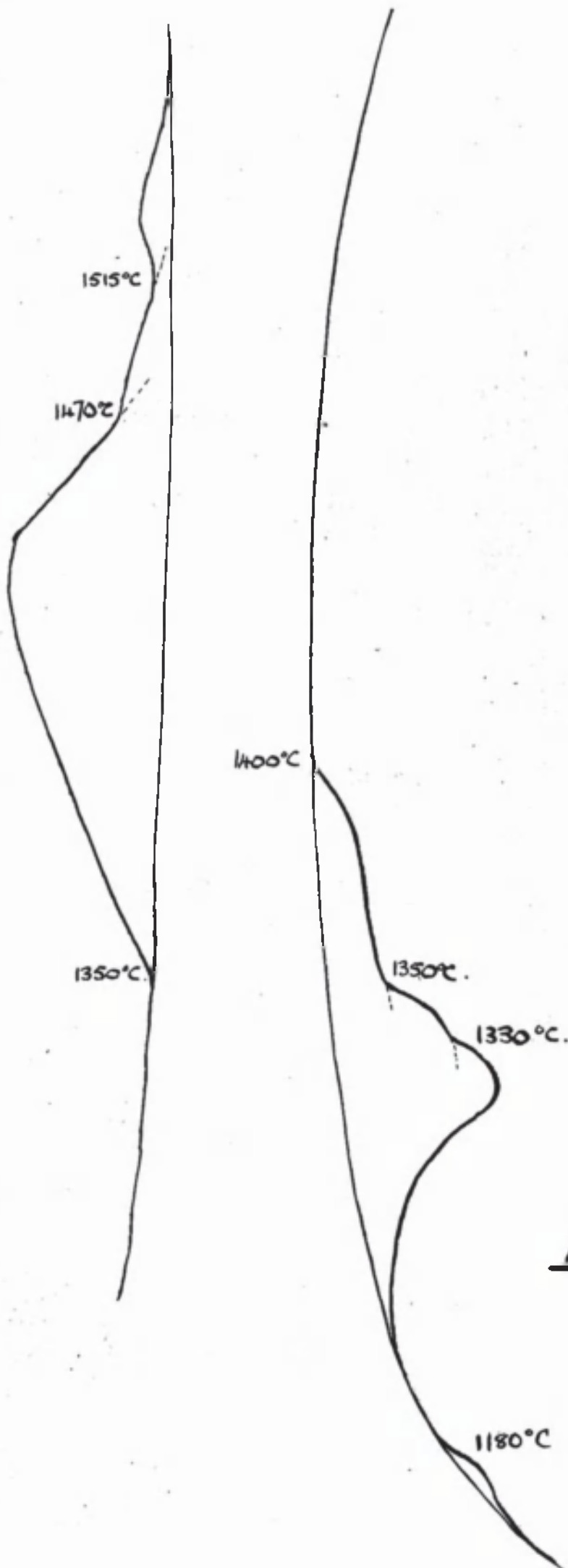
Fig. 32

MnO 30%. FeO 50%. Al₂O₃ 20%.

1495℃.

1400℃.

1380℃.

1378℃.

1280℃.
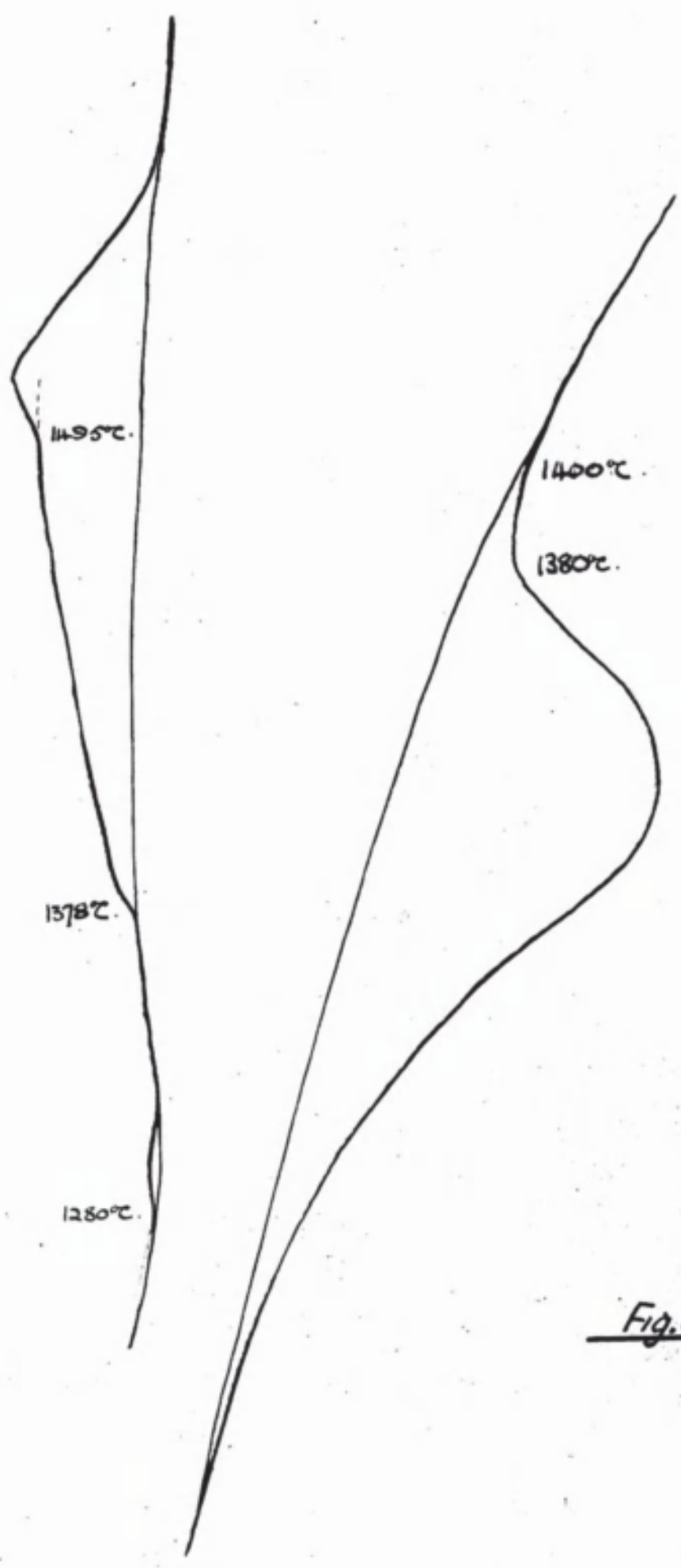
Fig. 33.

MnO 70%. FeO 20%. Al₂O₃ 10%.

Fig. 34.

Part (VI)

				Heating.		Cooling.	Remarks.
Fig. 27.	MnO	60	E	1475°C	E	1450°C	Slight
	FeO	10	P	1540°C	P	1480°C	super
	Al$_2$O$_3$	30	L	1570°C	L	1530°C	cooling.

28.	MnO	50	E	1450°C	E	1450°C	Super-cooling of
	FeO	20	P	1560°C	P	1480°C	Peritectic
	Al$_2$O$_3$	30	L	1560°C	L	1530°C	and Liquidus arrests.

29.	MnO	40	E	1410°C	E	1410°C	
	FeO	30	P	1510°C	P	1470°C	
	Al$_2$O$_3$	30	L	1570°C	L	1500°C	

30.	MnO	30	E	1380°C	E	1380°C	Super cooling in
	FeO	40	P	1495°C	P	1415°C	Liquidus and
	Al$_2$O$_3$	30	L	1575°C	L	1480°C	peritectic.

31.	MnO	20	E	1360°C	E	1360°C	
	FeO	50	P	1475°C	P	1415°C	
	Al$_2$O$_3$	30	L	1570°C	L	1480°C	

32.	MnO	20	E	1350°C	E	1330°C	
	FeO	60	P	1470°C	P	1350°C	
	Al$_2$O$_3$	20	L	1515°C	L	1400°C	

33. (11). Melts showing two points on the Al$_2$O$_3$ side of the eutectic trough.

MnO	30	E	1378°C	E	1380°C	Note the size of the
FeO	50	L	1495°C	L	1400°C	eutectic arrest.
Al$_2$O$_3$	20					

34. (111). Melts which show two points on the FeO-MnO side of the eutectic trough.

MnO	70	E	1450°C	E and L together 1430°C.	Super cooling has
FeO	20	L	1650°C		depressed the liquidus so far that it appears along with the eutectic
Al$_2$O$_3$	10				

MnO 60%. FeO 30%. Al₂O₃ 10%

Fig. 35

1600°C

1490°C

1428°C

1410°C

1360°C

1320°C

MnO 50%. FeO. 40%. Al₂O₃ 10%.

1590℃

1450℃

1400℃

1370℃

1360℃

Fig. 36

1250℃

MnO 40%. FeO 50%. Al₂O₃ 10%.

$MnO\ 40\%.\ FeO\ 50\%.\ Al_2O_3\ 10\%.$

1550°C.

1470°C.

1400°C.

1390°C.

1350°C.

1260°C.
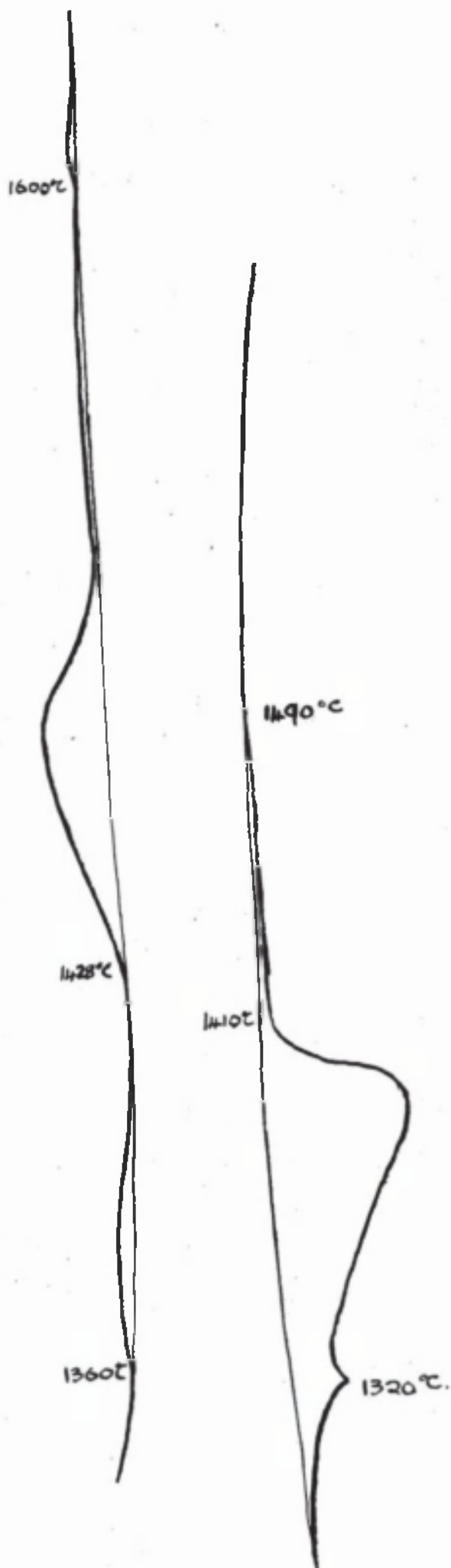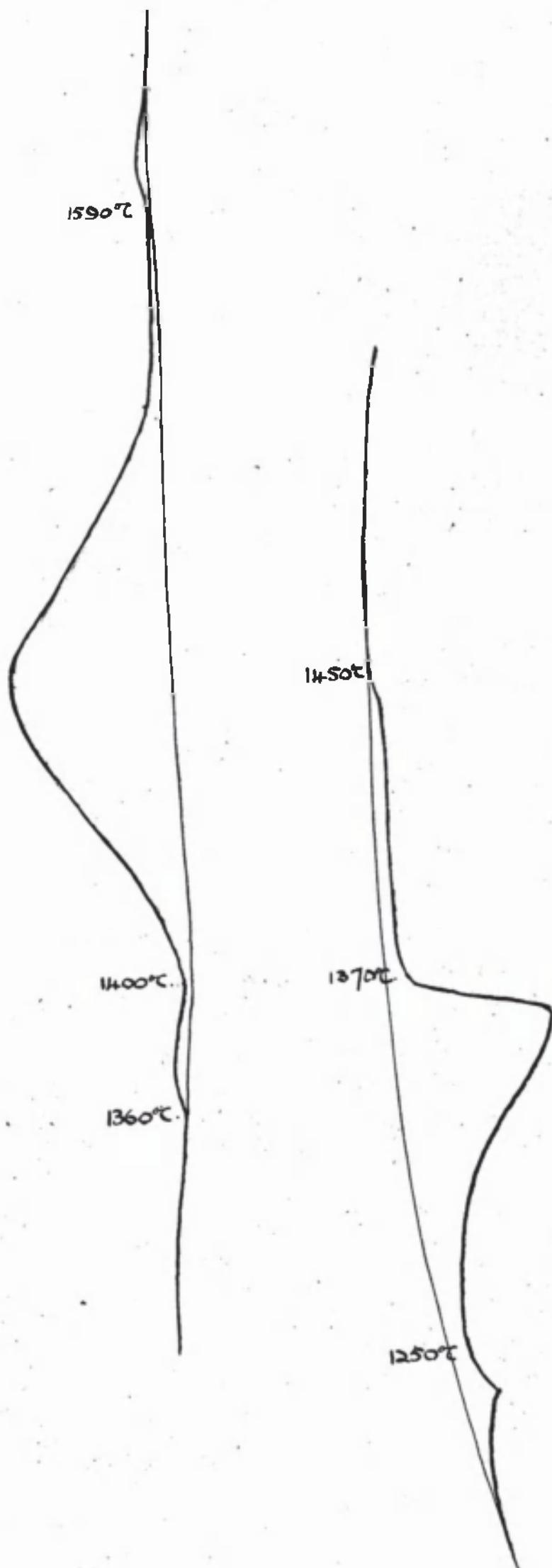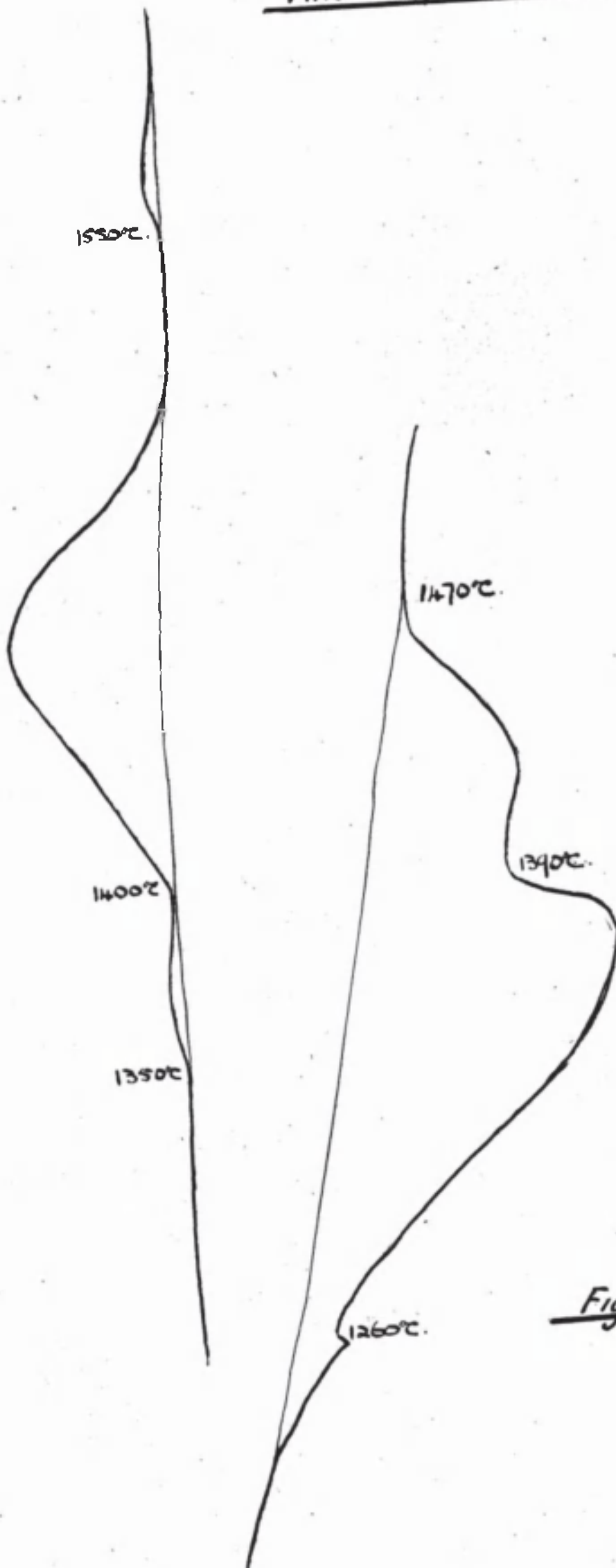
Fig. 37.

MnO 30%. FeO 60%. Al₂O₃ 10%.

1500°C

1470°C

1370°C

1360°C

1260°C
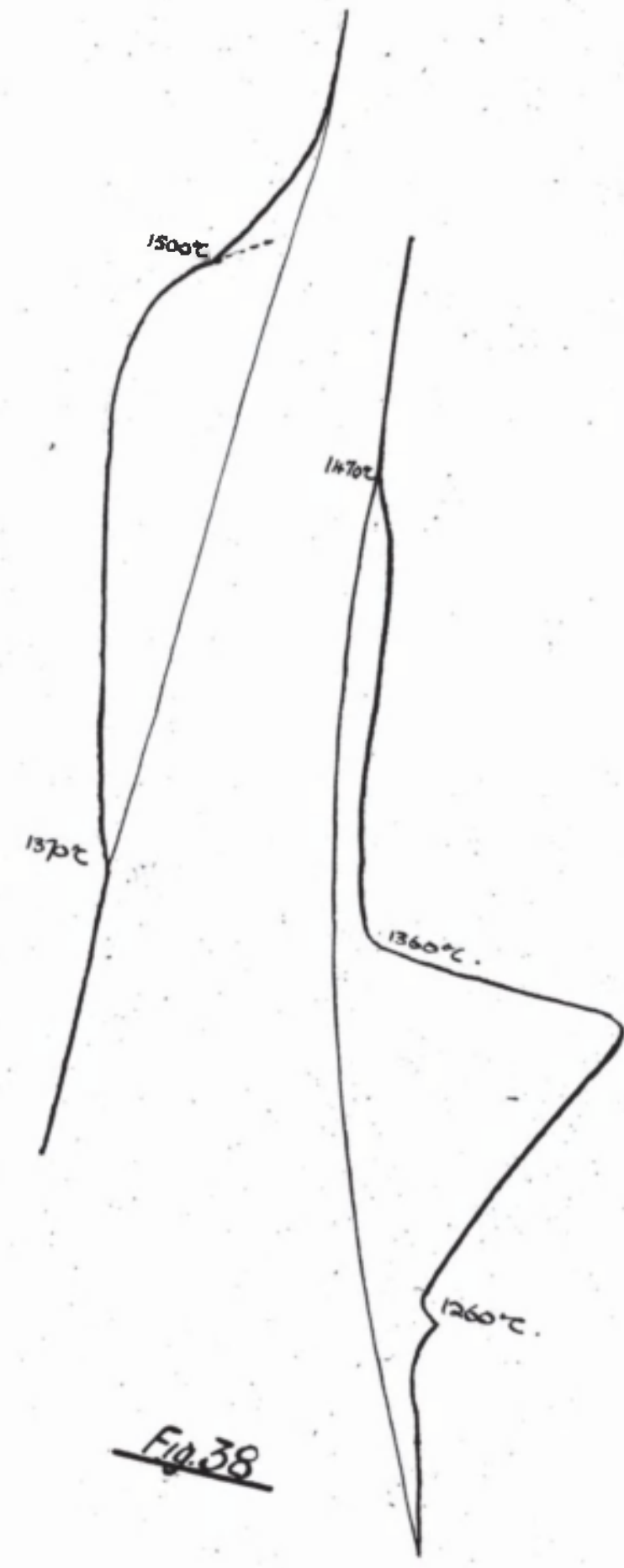
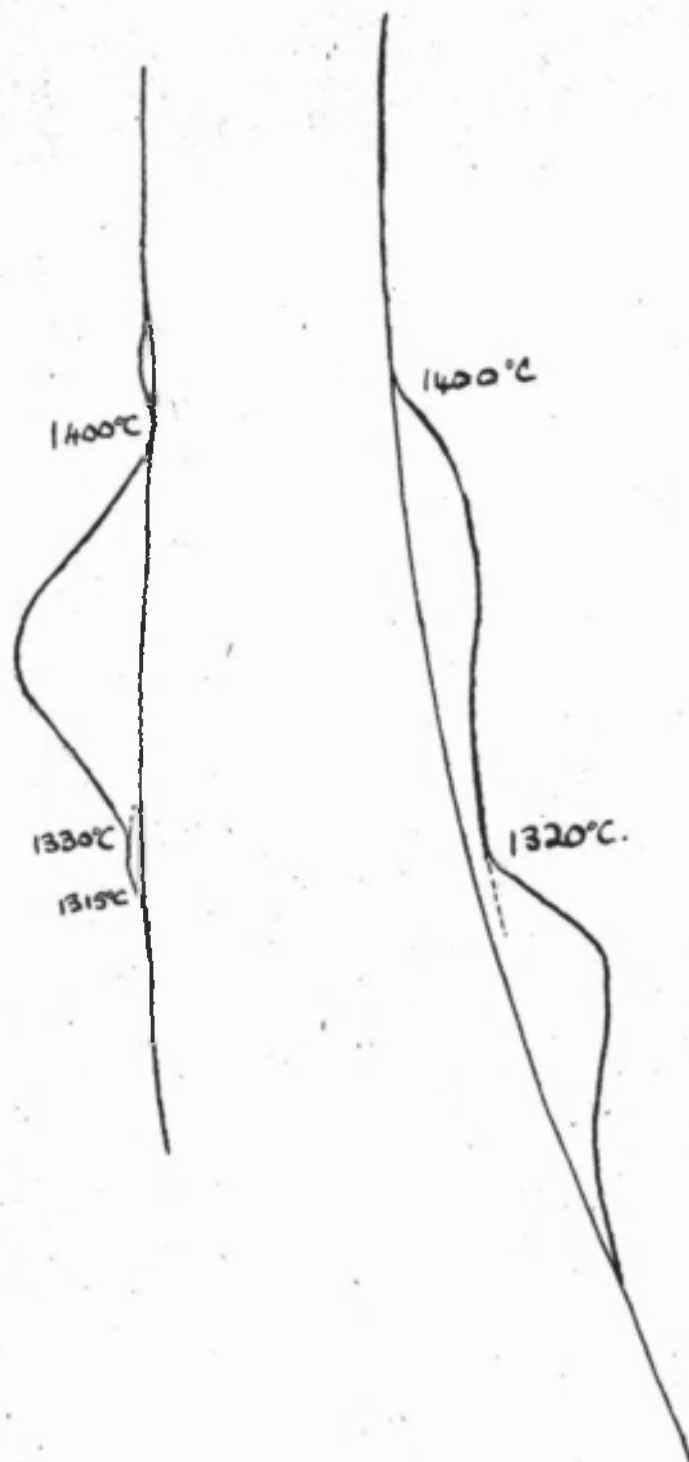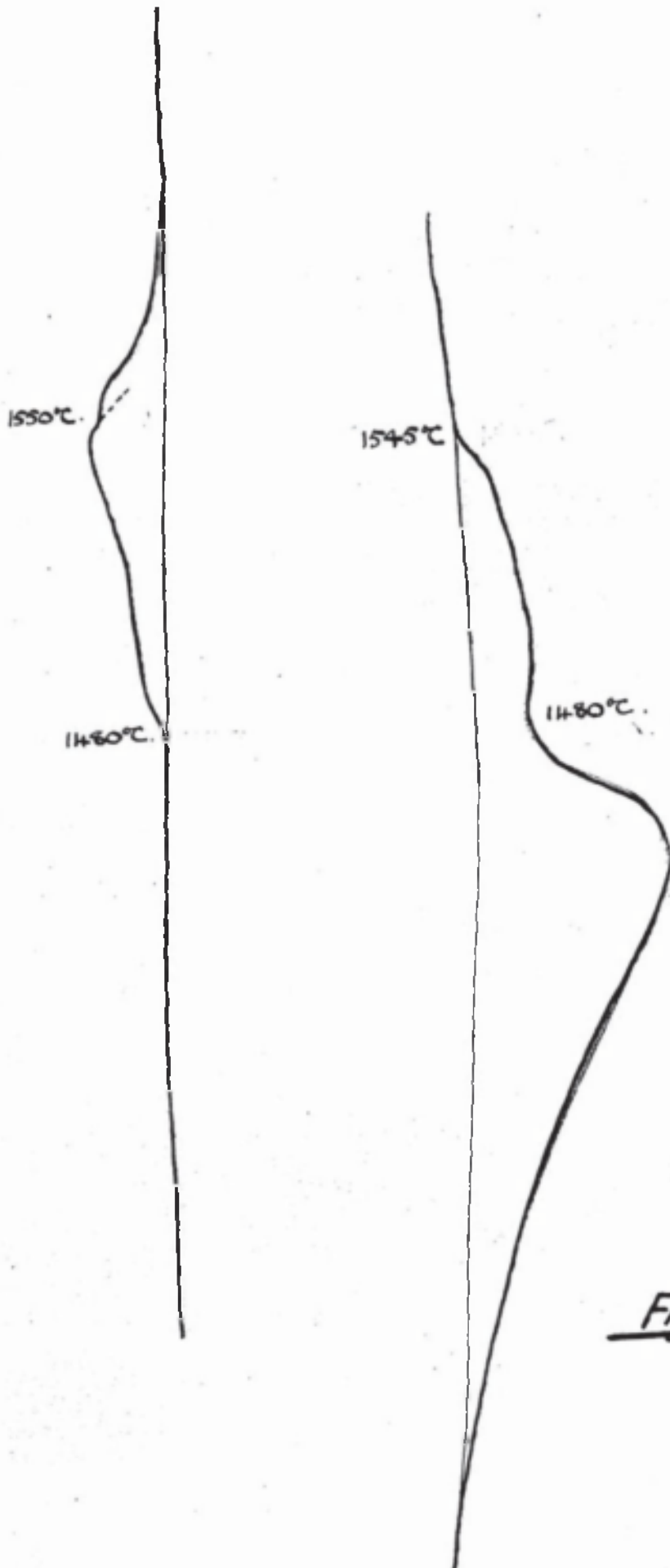Fig. 38

MnO 10%. FeO 80%. Al₂O₃ 10%.

Fig.39

MnO 70% FeO 10% Al₂O₃ 20%.

Fig. 40

MnO 60%. FeO 20%. Al₂O₃ 20%
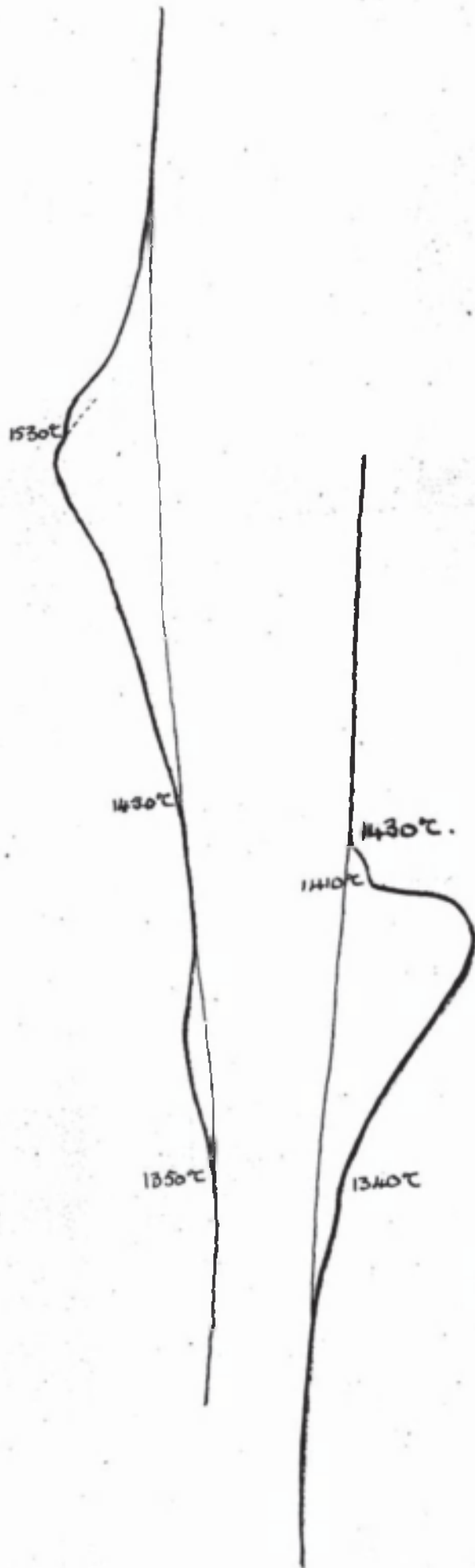
Fig. 41

MnO 50%. FeO 30%. Al₂O₃ 20%.

1418°C.

1418°C.

1280°C.

100% Eutectic.

Fig. 42

Mn0 40%. Fe0 40% Al₂O₃ 20%.

1400°C.

1400°C.

1260°C.
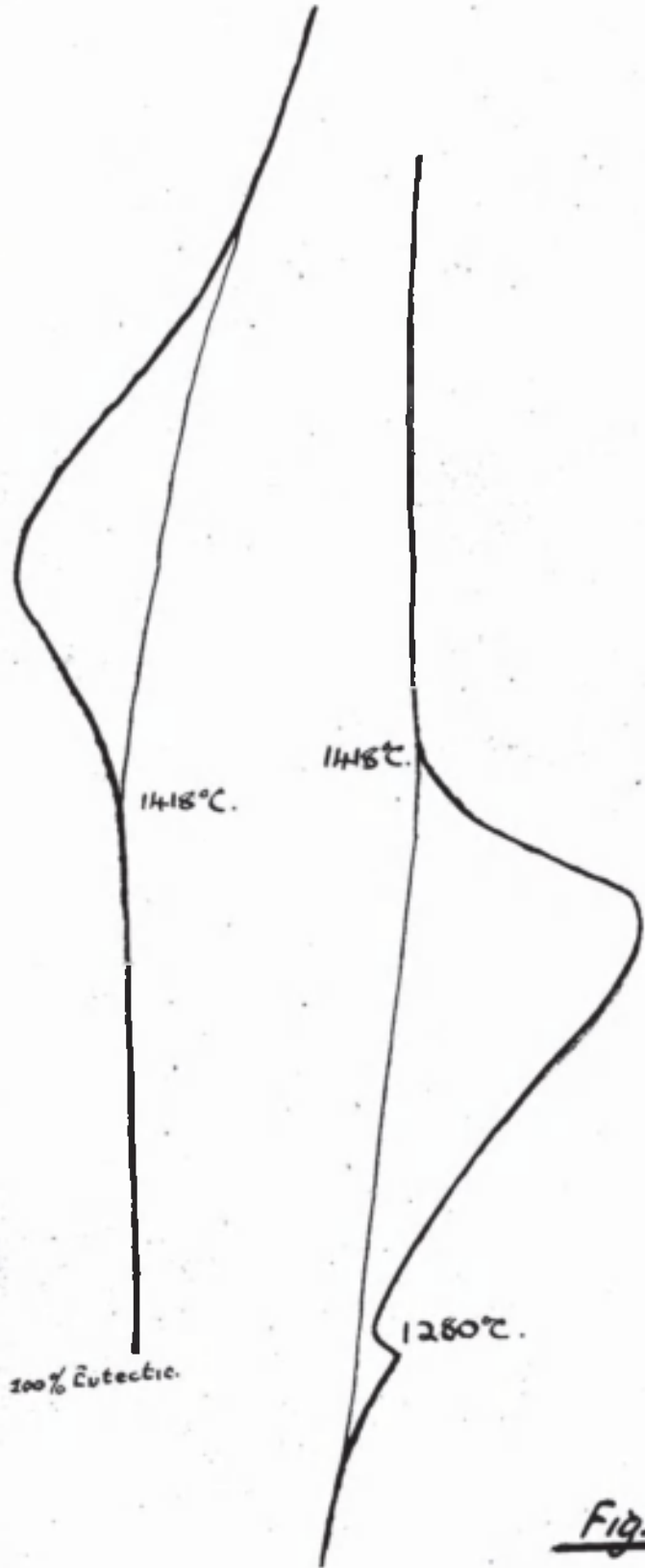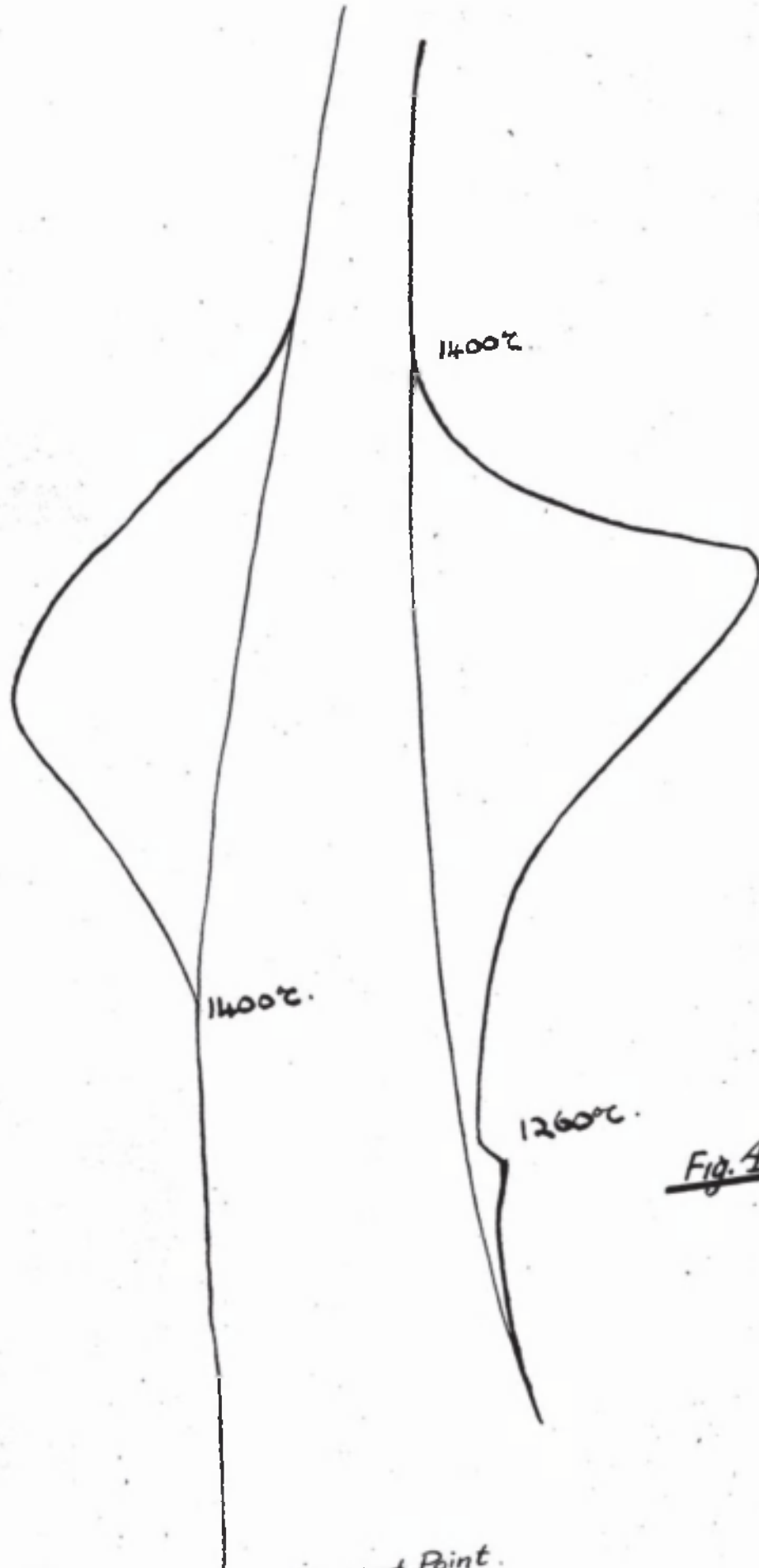
Fig. 43.

Invariant Point.

100% Eutectic

				Heating.		Cooling.	Remarks.
35.	MnO	60	E	1428°C	E	1410°C	Super cooling of Liquidus and eutectic.
	FeO	30	L	1600°C	L	1490°C	
	Al$_2$O$_3$	10					
36.	MnO	50	E	1400°C	E	1370°C	Super cooling of Liquidus and eutectic.
	FeO	40	L	1590°C	L	1450°C	
	Al$_2$O$_3$	10					
37.	MnO	40	E	1400°C	E	1390°C	Super cooling of Liquidus and eutectic.
	FeO	50	L	1550°C	L	1470°C	
	Al$_2$O$_3$	10					
38.	MnO	30	E	1370°C	E	1360°C	Super cooling of Liquidus and eutectic.
	FeO	60	L	1500°C	L	1470°C	
	Al$_2$O$_3$	10					
39.	MnO	10	E	1330°C	E	1320°C	Super cooling of eutectic only.
	FeO	80	L	1400°C	L	1400°C	
	Al$_2$O$_3$	10					
40.	MnO	70	E	1480°C	E	1480°C	Super cooling of Liquidus but not eutectic.
	FeO	10	L	1550°C	L	1545°C	
	Al$_2$O$_3$	20					
41.	MnO	60	E	1450°C	E	1410°C	Super cooling of Liquidus and eutectic.
	FeO	20	L	1530°C	L	1430°C	
	Al$_2$O$_3$	20					
42.	(IV). Melts showing one point i.e. 100% eutectic.						
	MnO	50	E	1418°C	E	1418°C	
	FeO	30					
	Al$_2$O$_3$	20					
43.	MnO	40	E	1400°C	E	1400°C	This is the invariant point.
	FeO	40					
	Al$_2$O$_3$	20					

The melts were prepared for micro-examination in the same manner as those of the FeO - Al₂O₃ system, except that, since they were not so brittle, the crucible, after its sides had been sawn, could be eased away from the melt, without the latter's fracturing. The melts were about 0.3 ins. in diameter and were ground down to about 0.2 ins. on a steel plate covered with wet carborundum powder. The melt was then finished off, as has been described in Part (11).

A selection of the micrographs is reproduced in Plates 35 - 52.

Plate No.	Composition.	Remarks.
35.	70% MnO 10% FeO 20% Al_2O_3	✗ Primary MnO (with some Al_2O_3 in solution), and eutectic of MnO and the solid solution of the spinels. Note that the eutectic is of the extremely finely divided nature which was characteristic of the MnO - Al_2O_3 system. In some parts the separation of the primary MnO has caused impoverishment of the liquid and to restore equilibrium there has been a greater precipitation of spinel. x 214. Etched with 1% HCI in water

✗ In what follows when MnO or FeO is mentioned it should be understood that this has some Al_2O_3 in solid solution.

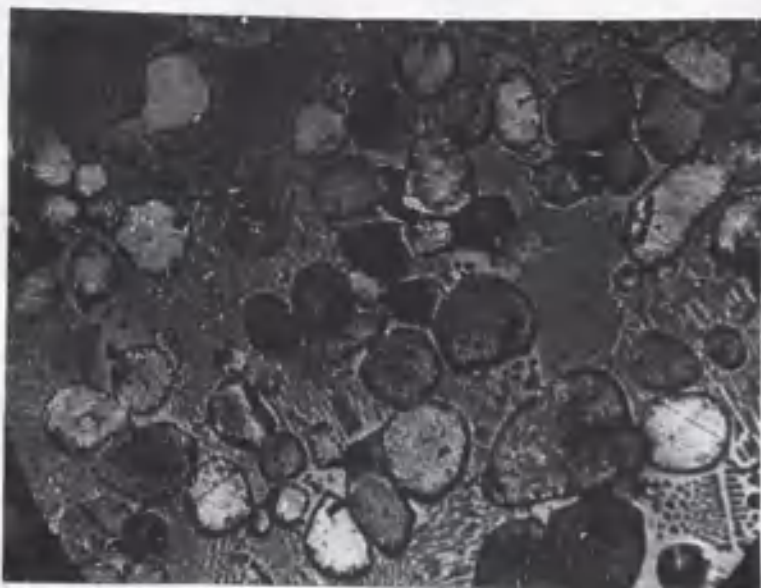| 36. | 70% MnO 10% FeO 20% Al_2O_3 | Same remarks as 35. Note how in a manner reminiscent of MnO-Al_2O_3 the eutectic is being forced to assume the spinel habit, even although it is not the primary. x 214. Etched with 1% HCI in water |

PLATE 35   70% MnO. 10% FeO. 20% Al$_2$O$_3$

Etched 1% HCl   x 214
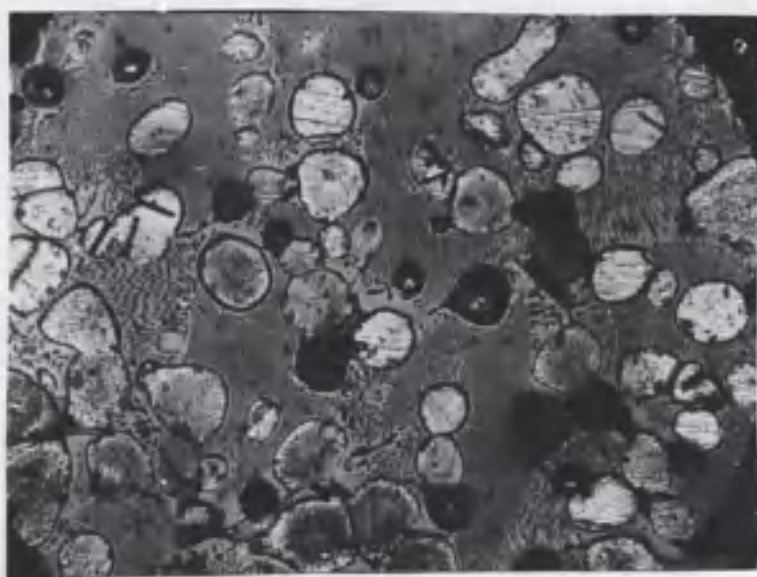

PLATE 36   70% MnO. 10% FeO. 20% Al$_2$O$_3$

Etched 1% HCl   x 214

PLATE 37   60% MnO. 30% FeO. 10% Al$_2$O$_3$

Etched 1% HCl   x 214

Plate No.	Composition.	Remarks.
37.	60% MnO 30% FeO 10% Al$_2$O$_3$	Dendrites of MnO in a background of eutectic of MnO and spinel solid solution. Note the extremely finely divided nature of the eutectic, and also that it tends to crystallize in the spinel habit. The dendritic nature of the MnO may be taken as evidence of a solubility of one or both of the other constituents in it. x 214. Etched with 1% HCI in water.
38.	60% MnO 30% FeO 10% Al$_2$O$_3$	Same remarks as in 37. The actual extent of the solid solubility has not been found. x 214. Etched with 1% HCI in water.
39.	50% MnO 30% FeO 20% Al$_2$O$_3$	This melt is practically 100% eutectic. There is a dendrite of MnO in this field, but this was due to the slight difference in homogeneity noted in the text. In other fields there were occasional spinels. Note the finely divided nature of the eutectic, which is of MnO and the spinel solid solution. It again shows the characteristic spinel habit. The eutectic was so finely divided that it appeared to act somewhat like a diffraction grating in the same manner as pearlite in steel. In the micograph as shown these fields appear very dark. x 104. Etched with 1% HCI in water.

PLATE 38   60% MnO. 30% FeO. 10% Al_2O_3
Etched 1% HCl.   x 214

PLATE 39   50% MnO. 30% FeO. 20% Al_2O_3
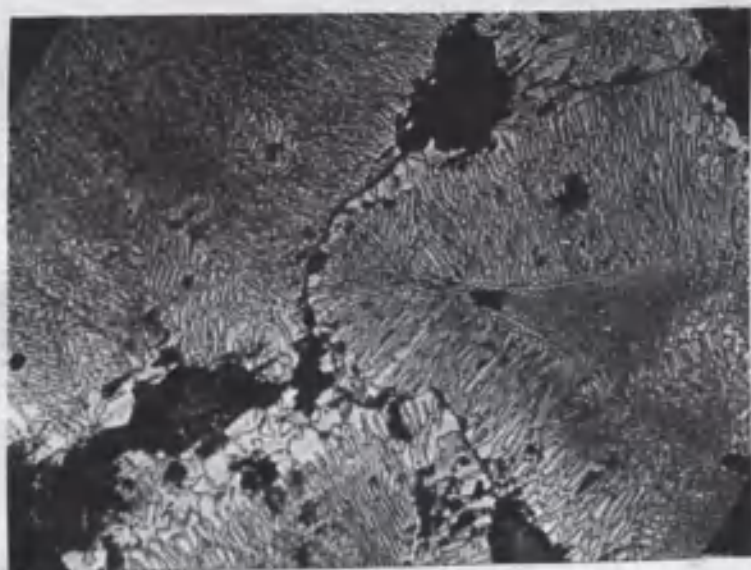Etched 1% HCl   x 104

PLATE 40   50% MnO. 30% FeO. 20% Al_2O_3
Etched 1% HCl   x 214

Plate No.	Composition.	Remarks.
40.	50% MnO 30% FeO 20% Al_2O_3	100% eutectic of MnO and spinel solid solution. x 214. Etched with 1% HCI in water.
41.	50% MnO 30% FeO 20% Al_2O_3	Practically 100% eutectic. This is a field of the same melt as 39 and shows a spinel crystal, where it (39) showed a dendrite of MnO. x 214. Etched with 1% HCI in water.
42.	40% MnO 30% FeO 30% Al_2O_3	Primary spinel and eutectic of MnO and spinel solid solution. The characteristic spinel shape of the eutectic is again in evidence. Note how finely divided the eutectic is. It again acted in the manner that gave pearlite its name. In this melt the spinel appeared at the top of the melt and this has been taken as evidence of the less specific gravity of the spinel solid solution than the eutectic The characteristics of the spinel are still those of the MnO. Al_2O_3 type. x 214. Etched with 1% HCI in water.
43.	50% MnO 40% FeO 10% Al_2O_3	Dendrites of MnO with eutectic of MnO and spinel solid solution. x 214. Etched with 1% HCI in water.
44.	50% MnO 40% FeO 10% Al_2O_3	Dendrites of MnO is a background of eutectic of MnO and spinel solid solution. x 214. Etched with 1% HCI in water.

PLATE 41   50% MnO. 30% FeO. 20% Al_2O_3

Etched 1% HCl   x 214

Top of Melt

PLATE 42   40% MnO. 30% FeO. 30% Al_2O_3

Etched 1% HCl   x 214
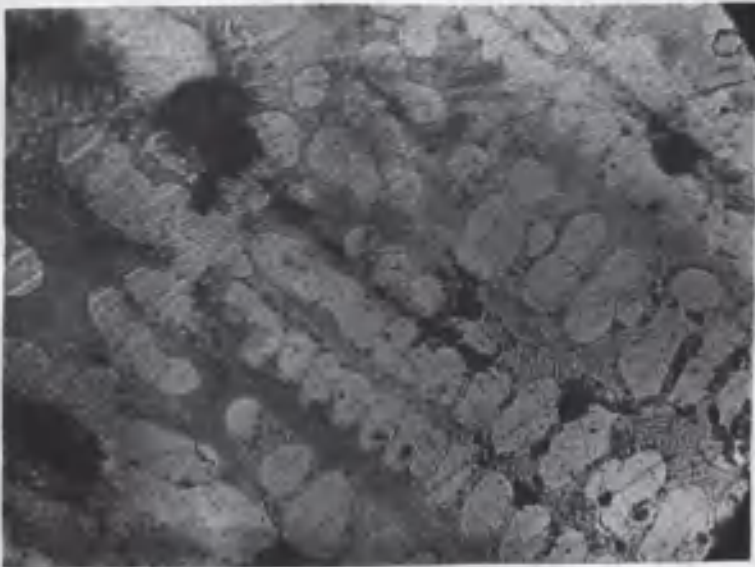

PLATE 43   50% MnO. 40% FeO. 10% Al_2O_3

Etched 1% HCl   x 214
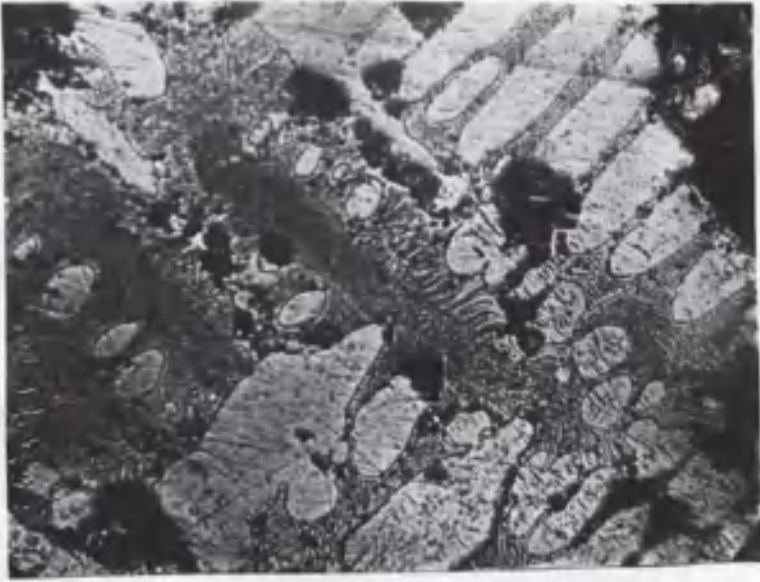
PLATE 44   50% MnO. 40% FeO. 10% Al_2O_3

Etched 1% HCl   x 214

PLATE 45   40% MnO. 40% FeO. 20% Al_2O_3

Etched 1% HCl   x 214

PLATE 46   40% MnO. 40% FeO. 20% Al_2O_3

Etched 1% HCl   x 214

Plate No.	Composition.	Remarks.
45	40% MnO 40% FeO 20% Al_2O_3	This is the composition of the invariant point and the melt shows 100% eutectic. x 214. Etched with 1% HCl in water.
46.	40% MnO 40% FeO 20% Al_2O_3	Remarks as in 45. x 214. Etched with 1% HCl in water.
47.	40% MnO 50% FeO 10% Al_2O_3	This is a melt in the FeO-MnO peritectic region. The first material to separate is MnO. The peritectic reaction will give some FeO and so in this region it may be that both MnO and FeO can occur in the same melt as primaries. The eutectic is not so finely divided as before, and is more of the type formed by the $FeO-Al_2O_3$ series, although it still seems to be influenced by the strong spinel crystalline habit, which is a property more characteristic of the $MnO-Al_2O_3$. x 214. Etched with 1% HCl in water.
48.	40% MnO 50% FeO 10% Al_2O_3	Same remarks as in 47. The eutectic has not reproduced well in this micrograph. x 214. Etched with 1% HCl in water.

PLATE 47   40% MnO. 50% FeO. 10% Al$_2$O$_3$
Etched 1% HCl   x 214

PLATE 48   40% MnO. 50% FeO. 10% Al$_2$O$_3$
Etched 1% HCl   x 214

PLATE 49   30% MnO. 60% FeO. 10% Al$_2$O$_3$
Etched 1% HCl   x 214

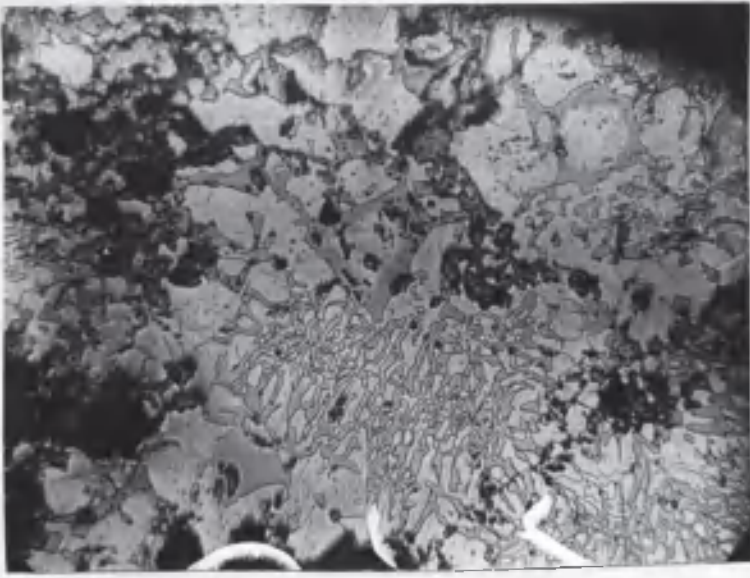| Plate No.	Composition.	Remarks.
49.	30% MnO 60% FeO 10% Al_2O_3	Almost 100% eutectic of FeO and spinel solid solution. The FeO is the soft and scratched half tone material. Note that now that FeO is one of the eutectic partners the spinel solid solution shows evidence of the peritectoid reaction of the $FeO-Al_2O_3$ system, and in consequence of this reaction the spinel is at times the dark $3FeO.Al_2O_3$ type and at others the light $FeO.Al_2O_3$ type, the latter being really the eutectic partner in solution with $MnO.Al_2O_3$, while the dark spinel is this after reaction with FeO. On close inspection some reaction zones can be seen. x 214. Etched with 1% HCl in water
50.	30% MnO 60% FeO 10% Al_2O_3	Same remarks as in 49. The light spinel has been practically all transformed to the dark spinel. Note the reaction rims, and also how the spinel is coalescing to form the characteristic spinel plates. x 214. Etched with 1% HCl in water.
51.	20% MnO 60% FeO 20% Al_2O_3	Primary spinel of the $FeO.Al_2O_3$ Type and eutectic of FeO and spinel solid solution. The FeO is the soft, scratched half tone material. x 214. Etched with 1% HCl in water.

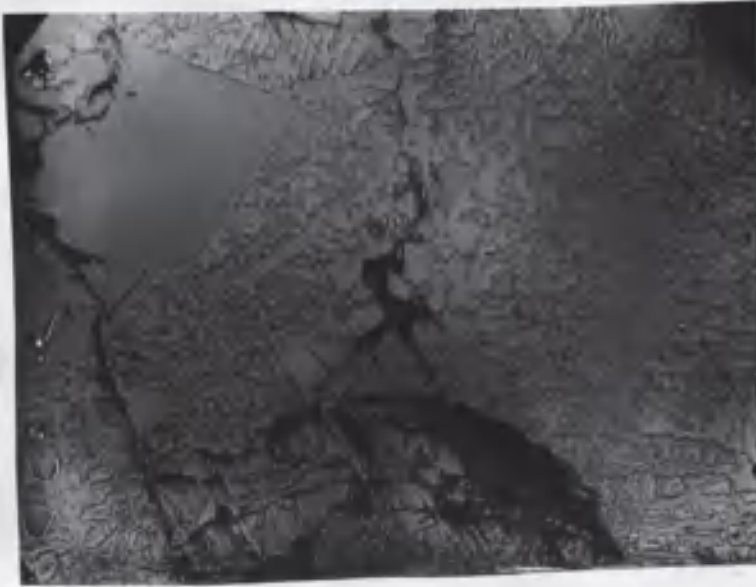PLATE 50   30% MnO. 60% FeO. 10% Al_2O_3

Etched 1% HCl   x 214

PLATE 51   20% MnO. 60% FeO. 20% Al_2O_3
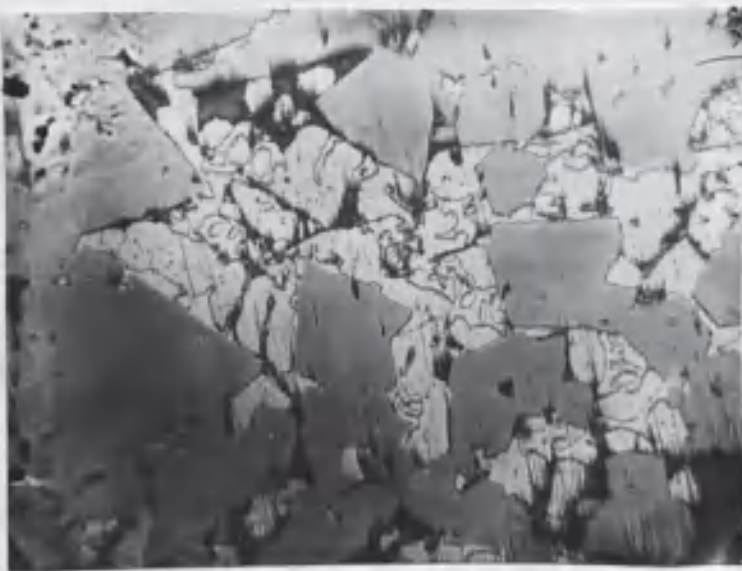
Etched 1% HCl   x 214

PLATE 52   20% MnO. 60% FeO. 20% Al_2O_3

Etched 1% HCl   x 214

Plate No.	Composition.	Remarks.
52.	20% MnO 60% FeO 20% Al_2O_3	It was noted in the FeO-Al_2O_3 system that the spinel tended to surfuse to a very pronounced extent, and this has happened here. Note how some of the light spinel is still among the FeO, but that otherwise the light spinel has been transformed to the dark spinel. The FeO is the soft, scratched half tone material. x 214. Etched with 1% HCl in water.

The ternary model has been constructed from the thermal curves, with confirmation from the photomicrographs.

Fig.(44) shows the solid model of the system FeO-MnO-Al_2O_3.   It will be seen that there is no ternary eutectic but that there is an invariant point, at 40% MnO, 40% FeO, 20% Al_2O_3.   This is where the section which the FeO-MnO peritectic plane makes with the liquidus runs into the eutectic trough.   At this point FeO, MnO, spinel, and liquid are in equilibrium, and hence there are no degrees of freedom here.   A continuous binary eutectic trough runs from the MnO-Al_2O_3 side to the FeO-Al_2O_3.   FeO.Al_2O_3 forms a wedge of solid solutions with MnO. Al_2O_3 solid solution.   The spinel peritectic surface is continuous from the 100% Al_2O_3 axis to its section with the liquidus surface.   The eutectic surface is also continuous and joins the FeO-MnO peritectic surface in two straight lines.   The limits of the peritectic region in the ternary must only be considered as tentative.   For its complete elucidation, much more experimental work would have to be done at very small intervals of composition in the region.   As far as the usefulness of the system to the steelmaker is concerned this region is one of little moment, the liquidus surface and eutectic trough being of far greater importance. The range of the peritectoid reaction of the FeO-Al_2O_3 system has /

THE TERNARY SYSTEM

FeO - MnO - Al$_2$O$_3$

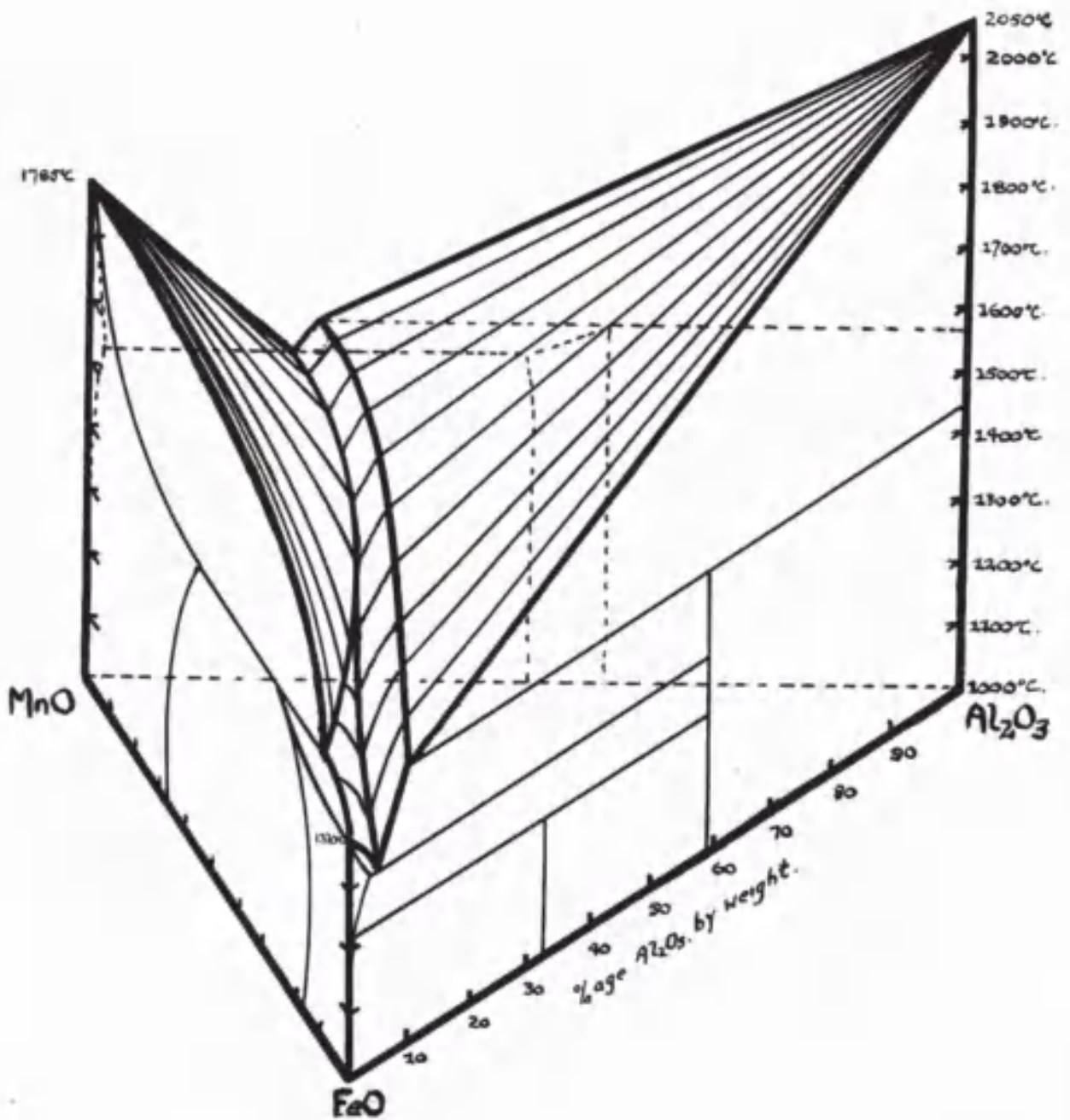Fig. 44

has not been established but its effect can be seen in both
the micrographic and the thermal work, more so when the melt
is on the FeO-Al$_2$O$_3$ side of the invariant point.

From the thermal curves the figs. (45), (46) and (47)
have been constructed.

Fig. (45) shows the isotherms of the liquidus surface.
On the Al$_2$O$_3$ side these have not been drawn beyond 1600°C.
This is because all of the melts containing 40% of Al$_2$O$_3$ or
more were infusible within the limits of the "Pythagoras"
tube, on the first heats.   It is thought probable that these
will be smooth and almost parallel to the 1500°C and 1600°C
isotherms right up to 2050°C at 100% Al$_2$O$_3$.   Note that the
1400°C isotherm has its apex on the eutectic trough at the
invariant point.   The temperatures along the side are the
temperatures of the liquidus points of the binaries.

Fig. (46) shows the isotherms of the spinel peritectic
surface.   It will be noticed that the isotherms all cut the
100% Al$_2$O$_3$ axis, so that the axis lies vertically in the
surface between 1440°C and 1560°C.   The surface is a twisted
one.   The end isotherms are the peritectics of the MnO-
Al$_2$O$_3$ and the FeO-Al$_2$O$_3$ systems.   The end of the surface is
where the liquidus surface cuts it, the line of section being
almost parallel to the eutectic trough.

Fig. (47) shows the isotherms of the eutectic surface.
This is another twisted surface.   The ends of the isotherms
show the compositions of the eutectic partners which are
spinel solid solution and MnO solid solution, or spinel solid
solution and FeO solid solution, dependent on which side of
the invariant point the melt lies.

Fig. (48) constructed from the micrographs shows the
principal phases which occur, at room temperature, in the
melts, and fig. (49) gives a key to the micrographs of the
system which are reproduced.

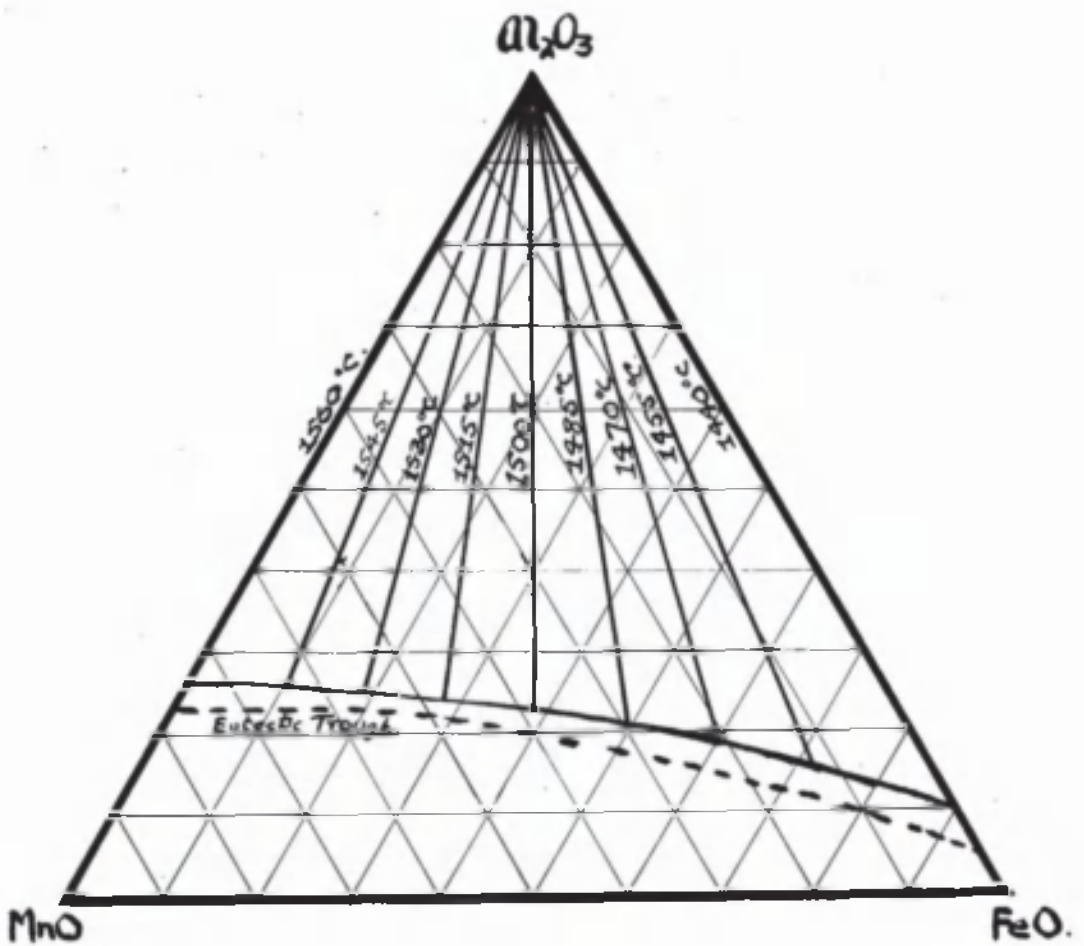The following observations were made during the
work. /

THE TERNARY SYSTEM
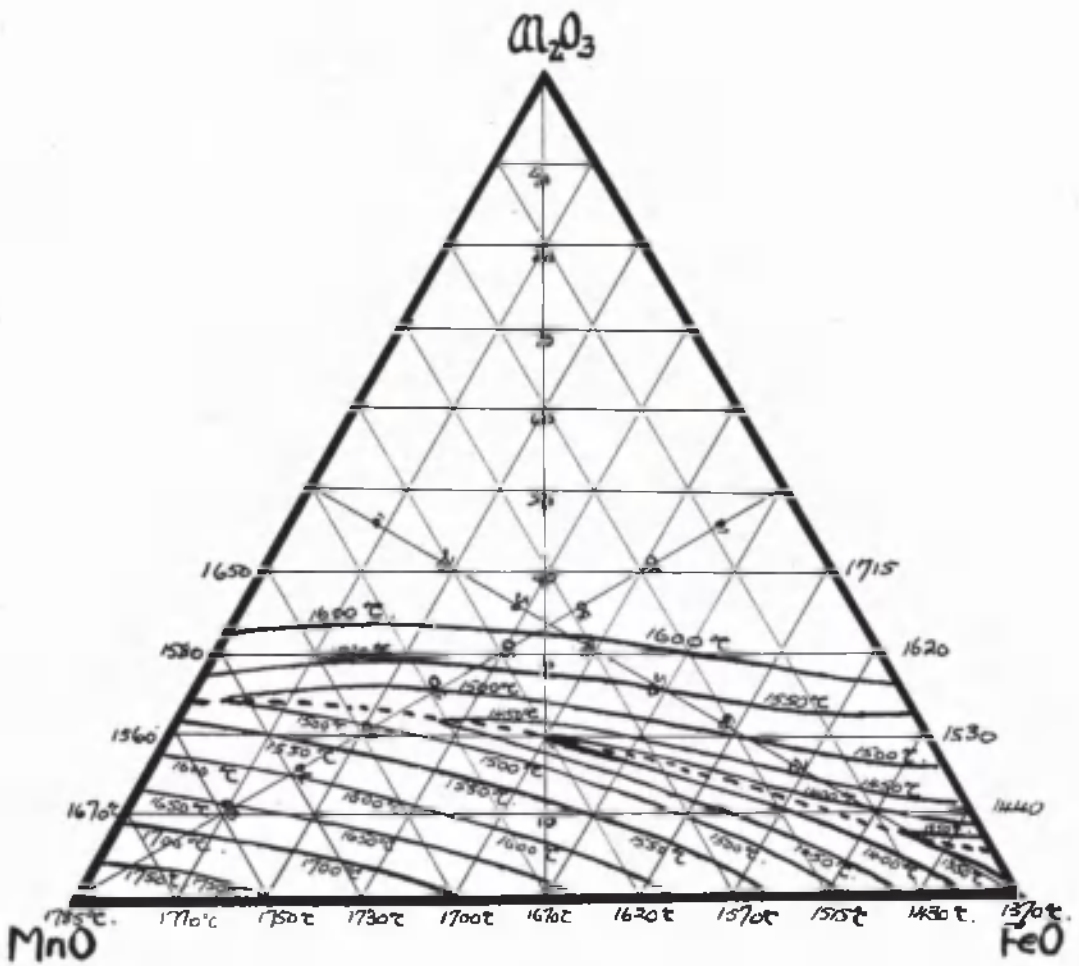
$FeO - MnO - Al_2O_3$

ISOTHERMS OF LIQUIDUS SURFACE

Fig 45.

THE TERNARY SYSTEM

FeO − MnO − Al₂O₃

Fig. 46

ISOTHERMS of SPINEL PERITECTIC SURFACE

THE TERNARY SYSTEM

FeO – MnO – Al₂O₃

Isotherms of eutectic surface diagram with vertices Al₂O₃ (top), MnO (bottom left), FeO (bottom right), labeled "Eutectic Trough"
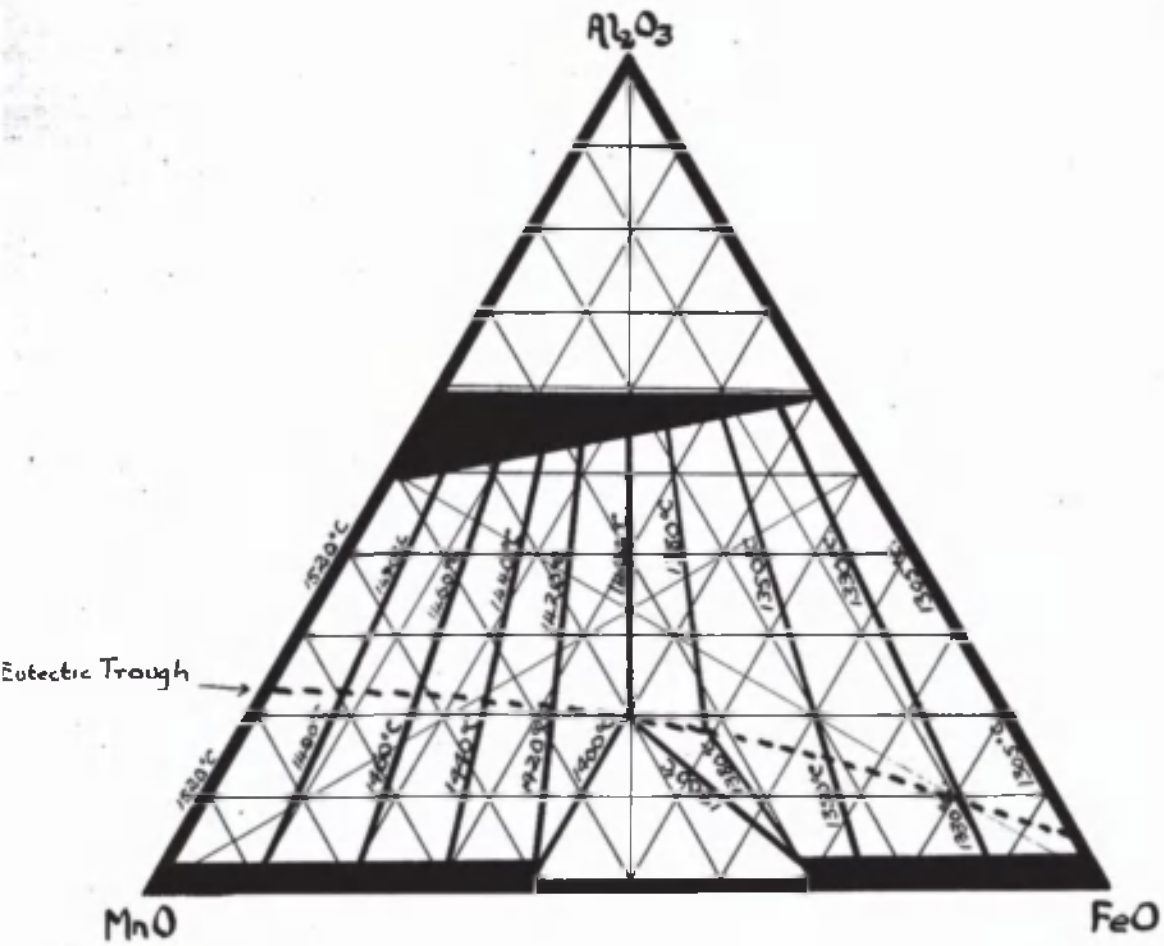
ISOTHERMS of EUTECTIC SURFACE
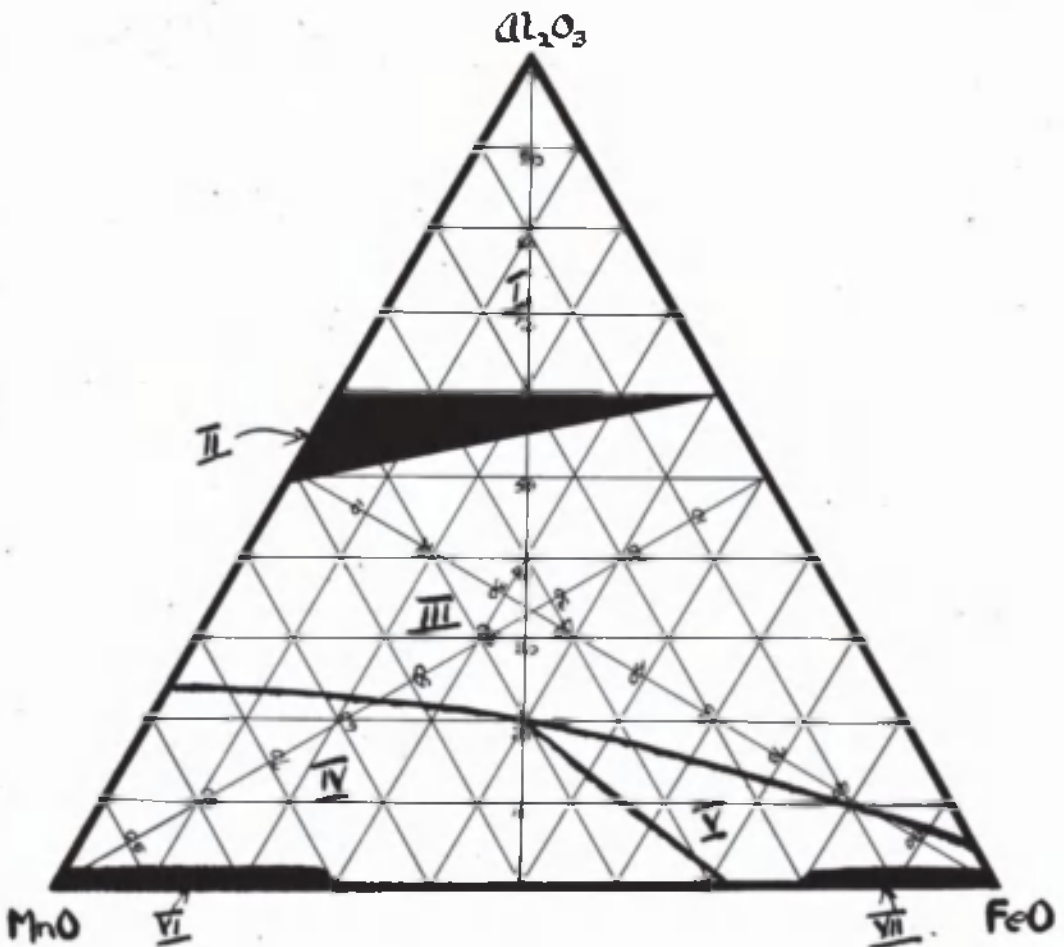
Fig. 47.

THE TERNARY SYSTEM

$FeO - MnO - Al_2O_3$

Principal Phases Occurring at Room Temperature.

I Al_2O_3 + SPINEL SOLID SOLUTION.
II SPINEL SOLID SOLUTION.
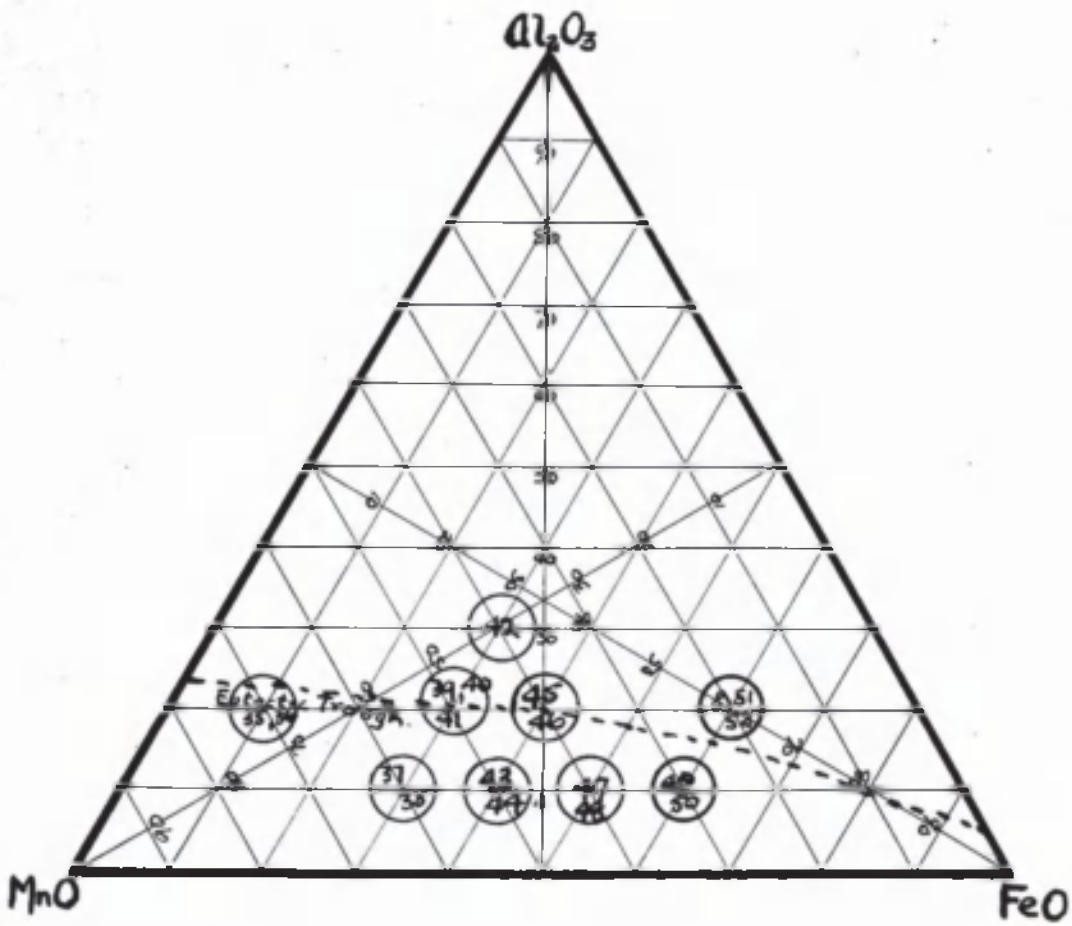III SPINEL + EUTECTIC
IV MnO + EUTECTIC
V FeO + EUTECTIC
VI. MnO SOLID SOLUTION.
VII. FeO SOLID SOLUTION.

Fig. 48

THE TERNARY SYSTEM

$FeO - MnO - Al_2O_3$

Key To The Micrographs Of The System.

Fig. 49

Colour.

The melts were all black.   It was not found possible
to find any relationship with respect to the effect of
additions of the constituents of the colour.   Some were jet
black, with a lustre, others had no lustre.   Others were
greenish black or greyish black, while the melts high in FeO
showed a bluish iridescence.

Fluidity.

The melts had all been fluid at the maximum temperature
of about 1650°C, as judged qualitatively by the extent to
which the melt had sunk in the crucible.   With low Al_2O_3 the
high MnO melts did not sink as much as the high FeO melts while
increase of Al_2O_3 to 20-30% lessened the concavity of the
meniscus.   The melt 40MnO. 30FeO. 30Al_2O_3 had however penetrated
a crack in the crucible, showing that the fluidity had been
quite high.

Surface Tension.

All of the melts showed a low surface tension in that
they climbed the walls of the crucibles.

Hardness.

The melts were all intensely hard.   They could easily
cut glass.   They resisted a high speed tool steel drill, and
could not be sawn.   The hardness was between 9 and 10 on Moh's
Scale of Hardness.

Brittleness.

The melts were not so brittle as either the $MnO-Al_2O_3$
or the $FeO-Al_2O_3$ melts.   When the crucibles were sectioned by
sawing and easing apart the sides of the crucibles the melts
remained intact, whereas the binary melts invariably split
when treated in this manner.

Crystal Habit.

In the micrographs the spinels have shown a pronounced
crystal habit.   In the binary melts, plates of the spinel were
visible to the unaided eye whenever the melt showed a "pipe"
or contraction cavity.   These were not seen in the ternary
melts/

melts although it is almost certain that had the melts been
fractured, in the method of section used in the binaries,
these plates caused by the cleavage of the spinel crystals
would have been visible.

Liquation.

         The melts which were rich in spinel showed great
tendency for the eutectic to liquate away from the spinel.
This may be taken as indication of the less specific gravity
of the spinel than the eutectic.   This was especially evident
in the melt containing 40%MnO. 30%FeO. 30%Al_2O_3.

Comparative Crystal Size as Judged by Visual Examination of
the Surface of the Solidified Melts.

         The melts high in FeO looked coarsely crystalline.
Those high in MnO were much less coarsely crystalline, while
those high in Al_2O_3 were microcrystalline.

PART (VII)

EXPERIMENTAL WORK ON THE DEVELOPMENT OF AN APPARATUS TO
MEASURE THE SPECIFIC HEATS AT HIGH TEMPERATURES OF THE
CONSTITUENTS OF NON-METALLIC INCLUSIONS IN STEEL.

Introduction.

The experimental methods used in determining specific
heat and heat content data at high temperatures fall into
three general classes:-

(1) The Method of Mixtures.

(2) Methods depending on heating or cooling rates.

(3) Methods for obtaining true specific heats directly.

The Method of Mixtures.

The method of mixtures is the one which has been
used most, and consists in dropping samples of the substance
under study, from various known temperatures, into a prev-
iously calibrated calorimeter and measuring the rise of
temperature of the latter.   The calorimeter may be of the
liquid type, water being the usual calorimetric substance,
or the calorimeter may be a block of some metal having a
high thermal conductivity, such as copper, aluminium, etc.

Various corrections are necessary, because heat will
be lost by convection, conduction, and radiation.   A suit-
able *correction* is probably obtained from Newton's Law of Cooling.
Losses can be prevented, however, by making the method an
adiabatic one, by enclosing the calorimeter in a bath whose
temperature is continuously adjusted to that of the calori-
meter.

This type of work has received thorough attention
from White[1] in America, and from Jaeger[2] and his co-workers in
Amsterdam.

The technique of this type of work is relatively
easy, when the temperatures are not far removed from room
temperatures, but when the temperature, from which the
material is quenched, is raised the technique becomes much

PART(VII.)

more difficult.   A furnace is required which can be
precision-controlled, which will be free from temperature
gradients, and from which the calorimeter must be pro-
tected.   In addition there must be a suitable method of
dropping the specimen into the calorimeter.   White in
his work has used two main methods, (a) by fusing a
supporting wire by the passage of a heavy electric
current (b) by a mechanical arrangement resembling a cam.
The latter method was more difficult to perform with
certainty.   Jaeger in his work has used method (a).
For the high temperatures both of these workers have
used a platinum wound furnace, the atmosphere, inside
the furnace, being air.   The substances used by White
were supported on a platinum loop inside the furnace,
and were not oxidisable substances.   Jaeger and his
co-workers used a platinum crucible which could be
evacuated and thus could work with oxidisable substances.
Eastman, Williams, and Young[3] in their work on the specific
heats of Mg, Ca, Zn, Al, Ag at high temperatures used the
same technique as White but sealed a block of the metal
inside a platinum can in vacuo.   Practically all of the
workers have used a Platinum-Platinum 10% Rhodium thermo-
couple for the measurement of high temperatures.   The low
temperature measurements of Jaeger were made with thirty-
six Copper-Constantan couples arranged in four series of
nine each, with an elaborate arrangement of the cold
junctions in a copper ring immersed in paraffin wax.
An accuracy of $0.0001^{\circ}C$ is claimed in the measurements of
temperature differences.   White did not take such pre-
cautions as Jaeger and measured his low temperatures at
first with a Beckmann thermometer, and then with a copper-
constantan couple.   One of his publications deals
exclusively with the calibration of the copper-constantan
couple, for which he claims an accuracy of $0.0001^{\circ}C$ with
his method of calibration.   In their work on the specific

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heats of tungsten, molybdenum, and copper, Bronson, Chisholm, and Dockerty[4] have used a Beckmann thermometer in their earlier work, and then for greater accuracy substituted a Platinum Resistance thermometer, and claimed an accuracy of $0.0005^{\circ}C$. They measured slight differences in temperatures between the calorimeter, and its surrounding jacket with a six-junction copper-constantan differential thermocouple giving a deflection of about 5mm. for a temperature difference of $0.001^{\circ}C$. White has also used the platinum resistance thermometer. Jaeger water cooled the outside of his high temperature furnace and also used elaborate water cooling devices to prevent heat-transfer between the furnace and the calori-meter. He enclosed his calorimeter in a Dewar flask kept in position by a zinc cylinder, surrounded by another zinc cylinder with a wide copper mantle having an ebonite base on which rested the cold junctions. The outer zinc cylinder had holes in its base to allow water to circulate between the two cylinders. The whole was enclosed in a much larger zinc cylinder. Water, kept at a temperature of $20^{\circ}C \pm 0.001^{\circ}C$ by electric heating spirals of nickel wire, one of which was attached to a thermo-regulator, circulated through the whole apparatus outside the inner zinc cylinder. Jaeger and his co-workers have taken very great care to eliminate all sources of error, using the method up to $1600^{\circ}C$ and claiming an accuracy of 0.1° for their results.

Weiss, Piccard, and Carrard[5] have used White's method with slight modifications while Awbery and Ezer Griffiths[6] have used the method of mixtures to find the specific heats of solids and molten metals and salts, as well as their latent heats of fusion. They took special precautions to prevent loss of the calorimetric liquid by evaporation.

Part (VII)

Bibliography of White's Work.

White, W.P. Calorimetry in Furnaces.   Jour. Phys. Chem.
1930, p.1121.

Silicate Specific Heats.   Am. Jour. Sci.
vol.47 1919, p.1.

Specific Heats at High Temperatures.
Phys. Rev. vol. 28 1909, p.461.

Specific Heats of Silicates and Platinum.
Am. Jour. Sci. vol.28. 1909, p.334.

The Latent Heats of Fusion of Nickel and
Monel Metal.   Chem. Met. Eng., vol.25,
1921, p. 17.

The Modern Calorimeter.   Chem. Catalogue
Co., New York, 1928.

The Specific Heat of Platinum at High
Temperatures.   Phys. Rev. vol. 12, 1918,
p. 436.

O ther papers appear in the Journ. Am. Chem.
Soc. 1914, 1918 in which he treats the whole
method from a theoretical standpoint.

Bibliography of the Work of Jaeger and Co-workers.

Pro. Acad. Sci. Amsterdam.

Vol.	Year	Page	Subject.
35	1932	352	The exact determination of the specific heats of solid substances between 0° and 1625°C. (Also Rec. trav. chim., vol.52, 1933 89)
34	1931	808	The exact measurement of the specific heats of Iridium and Ruthenium between 0° and 1604°C.
34	1931	85	The exact measurement of the specific heats of osmium and rhodium between 0° and 1625°C.
33	1930	457	The exact measurement of the specific heats of solid substances at high temperatures --- Palladium and tungsten.
36	1933	291	The exact measurement of the specific heats at higher temperatures ---- Fused and solidified silver under different circumstances.

These are the principal publications of this school and
are in English.   There are numerous publications in
other continental scientific journals but the themes are
covered by the above.   The results have been applied to
the Law of Neumann-Joule-Kopp-Regnault concerning the
Molecular Heat of Chemical Compounds in Function of the

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Atomic Heats, and have also been applied to the Periodic
System of the Elements.

Other References To Work On The Method of Mixtures.

3. Eastman, Williams, and Young. The specific heats of
    magnesium, calcium, zinc, aluminium, and silver at
    high temperatures. Journ. Am. Chem. Soc. 46, 1924,
    1178.

4. Bronson, Chisholm and Dockerty. On the specific
    heats of tungsten, molybdenum, and copper. Can.
    Jour. Research, vol.8, 1933, p. 282.

5. Weiss, Piccard, and Carrard. Arch. de Geneve (4), 43,
    22, 1917.

6. Awbery, and Ezer Griffiths. Proc. Phys. Soc. (London)
    vol. 38, 1926, 378.   The specific heat was obtained
    by differentiation of the temperature - total heat
    curves.

Bradshaw and Emery (Gas Journ. 1920 cl. 579, Journ. of the
Society of Glass Technology, 1921, v. 25-26) found the
mean specific heats of refractory materials at high
temperatures by dropping a heated weighed cylindrical
test piece into a calorimeter containing water, measuring
the temperature with a Beckmann thermometer and found mean
specific heats between $25-1000^{o}C$, $25-1200^{o}C$, and $25-1400^{o}C$.

Objections to the Method of Mixtures.

1. The chief theoretical objection to the Method of
Mixtures is that in quenching from a high temperature the
resulting physical state of the material, may not always be
the same, especially if in the course of cooling the
substance undergoes a change in state.   It is probable
that there will only be an appreciable error when the
structure of the material depends upon the thermal treat-
ment.

2. We know from other work in metallurgy, of the great
effects brought about by variation in the rate of cooling
even though this is varied only by change in the initial
temperature to which the material is heated.   With all

other variables constant except the initial temperature,
measurements of mean specific heats are thus done with
variation in cooling rate, which may have an effect on
the resulting state of the material.

3. This method is not satisfactory for measuring the
instantaneous specific heats of liquids at high temper-
atures.   One of the most important thermal constants of
a non-metallic inclusion is its specific heat in the
liquid condition, and a method is required which is
capable of determining the true specific heats of the
substances not only in the solid but also in the liquid
condition.   A quenching method can measure total heat
content, but there is a question to be answered, before
results could be taken as trustworthy by this method,
"Has supercooling any effect on the amount of latent heat
evolved on solidification, for in a quenching method there
is bound to be a certain amount of supercooling?"   Thermo-
dynamically if the resulting states were always the same,
the heat evolved in the course of the transition must
always be the same.   But as we know the resulting state
is not always the same.   For example, quenching a liquid
slag would probably give a glass.   If the resulting state
were always the same, the method of mixtures could be
adapted to give the true specific heats at high temper-
atures as well as the latent heats of solidification.

Due to this, the method is unsuitable for measur-
ing small heat effects which accompany transitions in
solids, e.g. the deposition of a solute from a solid
solution, euteotoid transformations, etc.

4. Assuming that the method can give mean specific heats over
certain periods of temperature, this does not give the
true specific heats unless some mathematical expansion,
say a MacLaurin's Series, is assumed to show the relation-
ship between mean specific heat and temperature.   Differ-

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entiation of the area under this curve should then give true specific heat at any temperature.   Kelley (U.S. Depart. of Commerce, Bureau of Mines, Bull. No.371, "Contributions to the Data on Theoretical Metallurgy", has pointed out that this may lead to erroneous conclusions, because on deriving a power series of the form

$$C_p = a + bT + cT^2 \quad \text{------}$$

to conform to experimental data, the coefficient c may be negative.   This would indicate that C_p would have a maximum at some value of T, a conclusion which has no physical significance, but which is merely due to the form of the derived equation.

The author, realising the limitations of the "power series" method of representation of specific heat values questions the validity of true specific heat values found by the differentiation of some algebraic equation, such as is shown above.

II.   Methods Depending on Heating and Cooling Rates.

Experimental methods involving heating and cooling rates have been employed extensively in the determinations of specific heats.   The rate of heating or cooling of a given material is compared with the corresponding rate under identical circumstances, of a substance whose specific heat is known.   Dulong and Petit perfected this method but it is unsuitable for solids due to the variations in temperature within the latter, although the method is of use when dealing with liquids.   Marley, (Proc. Roy. Soc. Lond. 45, 591, 1933) has applied the method to the measurement of the specific heats of poor conductors.

The method has given but few reliable data, due to differences in conductivity between the substances studied, and that used as standard, and due to the difficulty of reproducing heating and cooling rate conditions.   The latter difficulties are especially important at high temperatures

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where even the smallest displacement of the sample in the furnace may greatly affect the rate at which radiant energy is received. Further the method depends on the knowledge of the specific heat of a standard material at the high temperatures and this is a great disadvantage to the method. The difficulties would be supernumerable and for this reason no further attention was paid to it.

III. Methods for obtaining the true specific heats directly.

These methods depend on the measurement of the heat necessary to raise the temperature of the sample by a relatively small amount, ranging from a fraction of a degree to several degrees, depending on the method used. The great difficulty at high temperatures is to keep account of all the losses especially those due to radiation which may be very large.

The method depends on generating heat by the passage of a current through a conductor. If c is the current passed through a conductor of resistance R and E the potential difference across its ends, the energy spent in t seconds is Ect ergs, provided that E and c are in electromagnetic units. If this energy raises the temperature of m grams of a substance through dT then if C_p is the specific heat of the substance

$$\frac{Ect}{J} = MC_p dT$$

where J is the mechanical equivalent of heat. If E is in volts, and c in amperes, the energy spent is in Joules. The method depends on the measurement of E, c, t, and R and dT.

The measurement of R during the heating period is difficult, and it is preferable to measure the other quantities.

The method presents few difficulties at low temperatures and has been used by Griffiths (Phil. Trans. A (1893), Proc. Roy. Soc. 55, 1894), Jaegar and Steinwehr

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(Ann. d. Physik. 64, 305, 1921), and others to obtain the specific heat of water and the mechanical equivalent of heat.

Callendar and Barnes (Phil. Trans. A. 199, 55) have developed a steady flow calorimeter to find the specific heats of liquids in which the liquid was heated by a central conductor of platinum wire.

Applied to solids, Gaede (Phys. Zeit. 4, 805, 1902) was probably the first to use the electrical method. E.H. and E. Griffiths (Phil. Trans. A. 213, 1913. Proc. Roy. Soc. A 89, 561, 1914) determined the specific heats of metals from -160 to +100°C. The substance was in the form of a calorimeter which was cooled below the desired temperature, and then was heated by electrical energy, the temperature being measured by a resistance thermometer. The calorimeter was kept in a constant temperature bath.

Specific heats at very low temperatures have been measured by the Nerst Vacuum Calorimeter (Book by Nernst - "The New Heat Theorem" - Methuen & Co., London 1926 Pp. 29, 37, 48). Euken, Schwers and Günther (see Nernst's book) modified the temperature measurement so that a thermocouple was used independent of the heating coil.

Dearden (Carnegie Memoirs, Iron and Steel Institute, 1928, Vol.XVII) has applied the Nernst Method to the measurement of the specific heat of iron below 400°C, but his results differ from those found by Griffiths and Griffiths where the ranges coincided. However no allowance was made for the heat absorbed by the disc of the heater, and no allowance was made for any losses at all and these must have been considerable.

Enunciation of the Problem which was the Object of the Research being described.

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The measurement of the true specific heats of the constituents of non-metallic inclusions in iron and steel in both the solid and liquid condition.

For reasons stated above, a quenching method could not be used to find the true specific of the liquid materials.

First Experimental Method Used.

The first method was based on the Nernst Vacuum Calorimeter. The essential theory is that if we have a small heating element of resistance R ohms, and a current C amperes is passed through it then the heat produced in time t seconds is $\dfrac{C^2Rt}{J}$ calories. If this heat is absorbed by a body of specific heat C_p and mass m grams, giving a rise of temperature dT then

$$\frac{C^2Rt}{J} = mC_p dT.$$

The unit is shown in fig. (50) in section. It was made of low carbon steel (about 0.1% carbon) and was in two parts. The inside part was the container or crucible which was to hold the slag. The other part was in the form of a cover for the container and fitted closely over the thickened bottom of the crucible having a simple slotting arrangement which kept it firmly in position. WW' were holes to allow the leads of the heating element to be led out. TT' were holes through which the thermocouple leads were taken out.

The heating element was of platinum of diameter 0.008 inches. The wire was wound on a very thin - walled former, made of baked alundum cement which was almost half an inch in internal diameter and was a close fit over the narrow crucible. The resistance of the element at room temperature was 1.75 ohms. This had a

W   T   T'

W₁
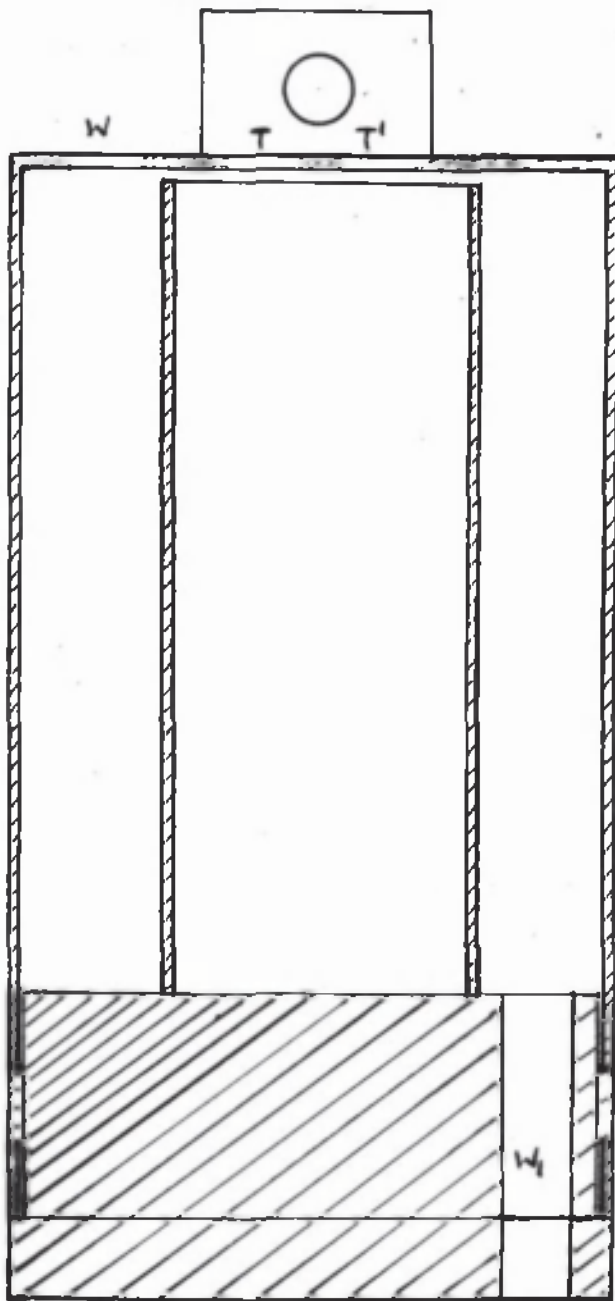
Crucible and Cover For Nernst Method Unit.

Pt. Winding is not shown.

Scale :- X 4

Fig. 50.

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very thin sheath of baked alundum cement, which fitted
very closely over it and prevented the platinum short-
ing on to the steel of the crucible cover.   It was
known that these alundum parts would cause losses, but
in the method which was to be used it was hoped that
this would not be important.   The upper surface of the
crucible cover had a small projection with a hole in it
for suspending the unit.   The platinum was at first
joined to Kanthal leads, for no particular reason other
than they were at hand at the time.   The point which
was being investigated at this stage was the maximum
temperature to which the small unit would rise.   The
leads had a total resistance equal to that of the unit.
No attempt was made at this stage to make precision
measurements.

For the first few experiments the unit with the
winding in position and the thermocouple in place was
suspended inside the largest Thermos flask obtainable
commercially, this being about three and a half inches
in diameter.   Great care had to be exercised in fit-
ting these flasks with bungs, because of their great
fragility.

The external electrical circuit is shown in
fig. (51).   Ten nickel-iron storage cells were charged
continuously from the mains, by placing a thirty two
candle power carbon filament lamp in series with them.
The batteries were used as a source of a low voltage
and being constantly on charge, smoothed out any fluc-
tuations in the mains, and delivered a steady voltage.
A Vernier resistance was placed in parallel with these
batteries and so, acting like a potential divider,
could be arranged to give any or all of the twelve volts
of the batteries, this being the e.m.f. applied to the
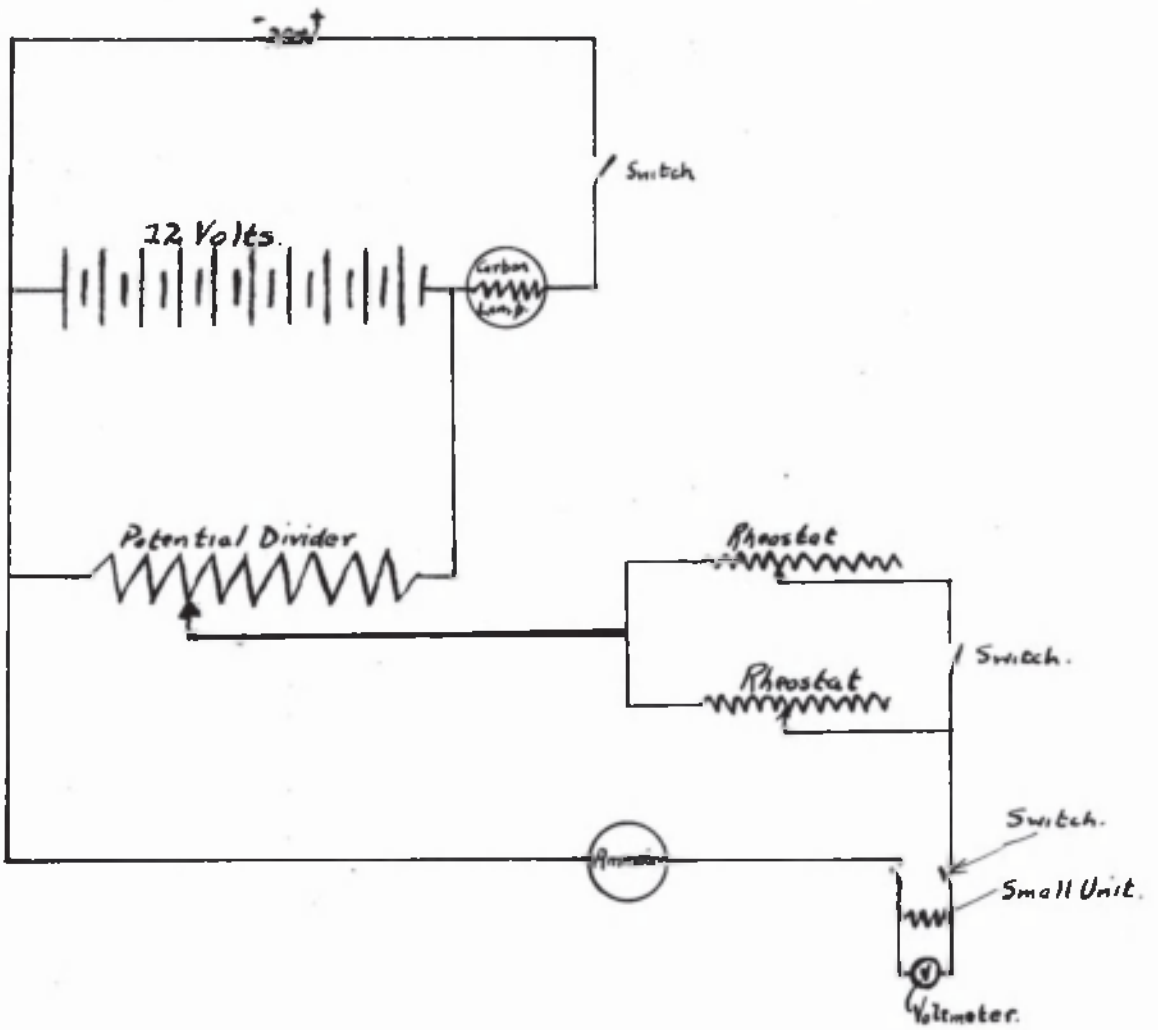
External Electrical Circuit Used in
Specific Heat Experiments.

Fig.51.

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small heating coil.   Two other resistances in parallel
were placed in series with the small heating element and
so was an ammeter.   A voltmeter was connected across the
the leads coming from the small coil.

Time was, at first, measured by a stop watch,
which was calibrated against Greenwich time.

The first few runs were taken with no slag in the
crucible.   The Thermos flask was evacuated by an Edward's
Cenco Hyvac pump, and when the bung was sealed with the
solution of celluloid in amyl acetate, the mercury in the
manometer showed no fall overnight.

A current of 1.75 amperes was passed through the
coil and readings of current, temperature, voltage, and
time were taken as nearly as possible simultaneously.
The temperature, as measured by the thermocouple in the
crucible, reached about $350-400^{\circ}C$ in an hour.   The outer
casing of the Thermos flask became quite warm.   A ther-
mometer bulb was placed against it and the mercury
showed a reading of $28^{\circ}C$.   Room temperature was $17^{\circ}C$.

An energy-temperature curve and a time temper-
ature curve were plotted and are shown in fig. (52).
From the shape of the curve it will be seen that no
matter how energy was put in to the coil the temperature
would never increase much more than $350-400^{\circ}C$.   This
could have been due to (1) the inability of the coil to
give a higher temperature and (2) the losses of heat
being very large.

That these losses were taking place was, of
course, realised, but with the method which was in the
author's mind at the time, it was hoped that the
specific heats would be obtainable, provided that these
losses were the same in two consecutive runs between the
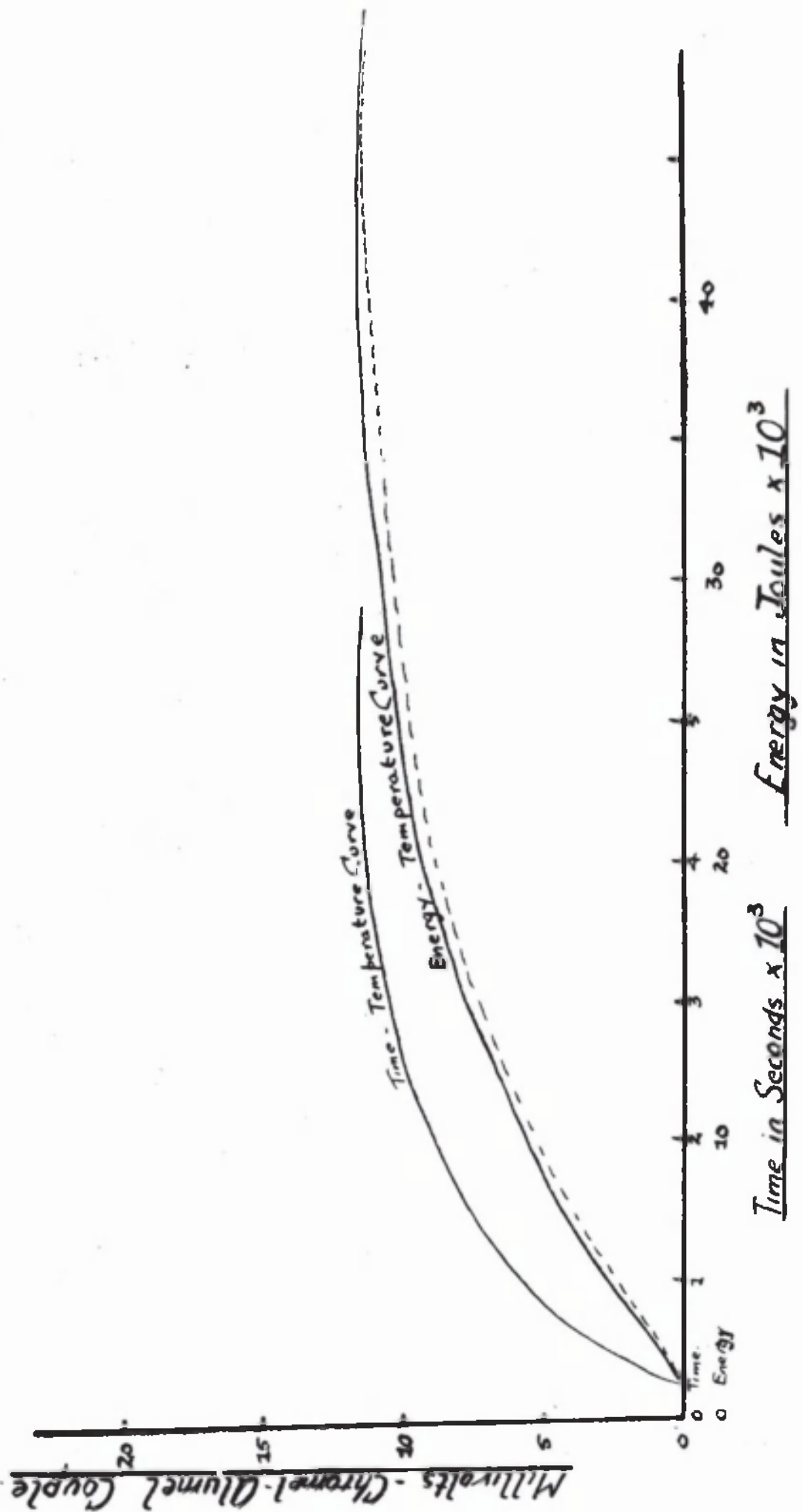same limits of temperature.

Time - Temperature Curve

Time - Temperature Curve

Energy - Temperature Curve

Time.

Energy

Millivolts - Chromel-Alumel Couple

Time in Seconds x 10³

Energy in Joules x 10³

Fig. 52.

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This was as follows. An energy temperature curve of the form shown in fig. (52), could be represented by E=f(t), and this function could be derived from the experimental values as a power series. Now, if some heat absorbing material, the sample, were placed in the crucible, more energy should be required to reach the same temperature, the difference being that necessary to raise the temperature of the sample, i.e. the theoretical curve in the curve in the second would be as shown dotted in fig. (52). This could be represented by E = f'(t). and this function could again be derived from the experimental data.

The specific heat of the sample would then be given by the expression,

$$\frac{1}{J} \int_{T_1}^{T_2} \left\{ f'(t) - f(t) \right\} dt \quad = \quad mC_p(T_2 - T_1)$$

As stated above, this makes the assumption that the losses are constant in the two consecutive runs. If that were the case, a constant would appear in both f(t) and f'(t), and so would cancel out and not affect the difference of energy as found by the above integration.

To test out this projected method, some iron filings were placed in the crucible, and the run repeated with everything the same as in the blank run. This was repeated several times, and in each case it was found that the energy temperature curve was coincident with that found in the blank determination.

If we look on the heat absorbed by the sample as an additional heat loss then the interpretation of this result was that the losses existing during the blank run were already so large that the small additional loss due the sample was negligible in comparison.

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The mass of the iron filings was in each case five grams.

These experiments thus gave the following information:

(1) The small platinum winding was incapable of giving anything like the temperatures that would be required.

(2) The losses of heat were exceedingly large, probably so large as to preclude any measurement of specific heat by the method, as described above.

These two points suggested the next step. The small winding was capable of giving a temperature rise of about 350-400°C from room temperatures. If the small unit were surrounded by a larger unit, which could produce a steady temperature then, the passage of a small current through the small unit would produce a small temperature rise. At the same time the losses other than those due to the leads of the small unit would be satisfied by energy coming from the outside unit, and since no measurements would be made on the outside unit they would not affect the small unit. When a steady state of affairs was reached there would be practically no temperature difference between the outside and inside units. The radiation losses from the small unit would be to the larger unit and as there would only be a very small temperature difference, these would not be very great. It was intended that the theory described above could be applied for the determination of the specific heats.

A Nichrome furnace was made of sufficient size to comfortably take the small unit, with ample room for the leads. It was suspended concentrically with the small unit in the Thermos flask and the flask was evacuated. Unfortunately, when the temperature reached about 450°C in the inside of the small unit the

flask cracked and the bung melted. The flask had cracked
due to the heat of the outer unit, and as this was the
largest obtainable, commercially, it was decided to attempt
the making of an arrangement which would in essence, be a
large vacuum flask.

Two bells jars were silvered by reducing silver
nitrate and precipitating the silver on to the surfaces of
the jars.

Fig. (53) shows the arrangement of the two bell jars.
S'S' was a stand on which the outer bell jar ABC was support-
ed SS was a tripod stand inside the outer bell jar on which
was supported the inner bell jar DEF. A sheet of plate
glass, sealed the outer bell jar, but there was a space
between the top of the inner bell jar DEF and the plate glass
cover. This was to allow the whole to be evacuated at the
same time. Six holes were drilled in the plate glass, and
through these the various leads were passed ZK, YI, were the
leads to the outer furnace, or unit HIJK, QO, XM, were the
leads to the inner small unit LMNO, and the thermocouple leads
were led through the central hole as shown. The holes were
all fitted with closely fitting bungs with glass tubing and
rubber tubing with screw clips, so that they could be made
vacuum tight. The sixth hole was used, as shown, for the
evacuating pump connection. Soft rubber was tried for the
sealing of the outer bell jar, but the sealing was not
successful until the seal was first made with vaseline and
then covered on the outside with plasticene. As a precaution
against the danger of the bell jar's failing under the evac-
uation, the whole was enclosed in a steel cylinder, from an
old furnace, The internal diameter of the inner bell jar
was eight inches, while that of the outer one was ten inches,
there being about an inch of annular space between them.

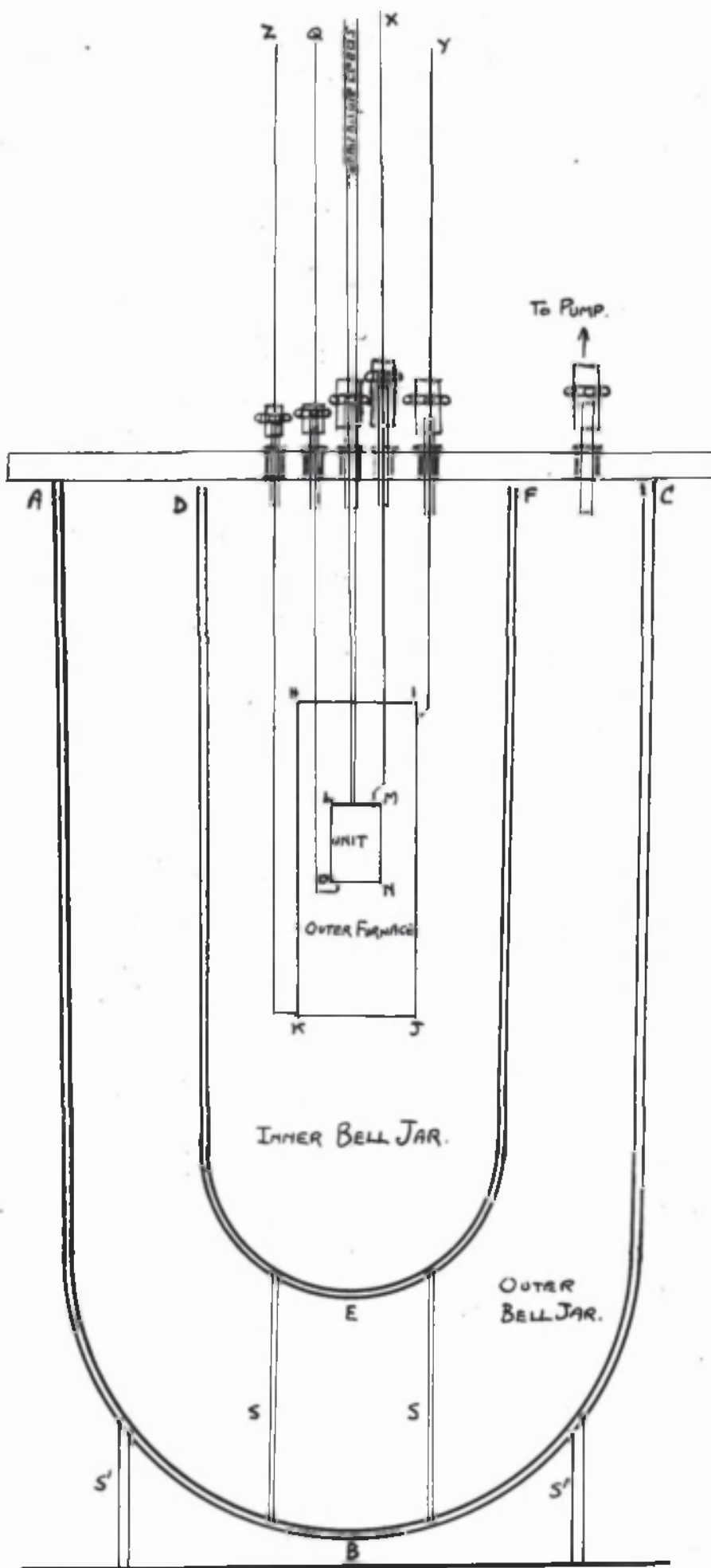The first point which was to be found out, was to

Z   Q   X   Y

To Pump.

A   D   F   C

H   I

L   M

UNIT

O   N

OUTER FURNACE

K   J

INNER BELL JAR.

E

OUTER
BELL JAR.

S   S

S'   S'

B

Fig. 53.

what temperature would bhe temperature of the thermocouple

be raised by the outer furnace alone and would the outer

bell jar get hot?   Two amperes were passed through the

outer furnace and nothing through the inner one and time

temperature readings were taken.   Gradually the current was

increased in the outer furnace, time temperature readings

still being taken, until the current was five amperes and

the temperature was $600^{\circ}C$.   It was then noticed that the

mercury in the manometer gauge was falling, and when the

seal of the outer jar was examined it was found that there

were bubbles coming from the vaseline.   The outside of the

outer bell jar was uncomfortably warm to the touch while the

plate glass top was too hot to be touched at all.   Obviously,

the heat losses to the outer bell jar were very large, so

large that if this method were to be used at higher temper-

atures, some method of cooling would have to be adopted

otherwise glass could not be used.   In addition, an efficient

method of sealing the top would have to be found, one which

would withstand the temperatures involved.   However, at this

time there was published in the Institute of Metals a paper

on "Methods for the Examination of the Thermal Effects due to

Order-Disorder Transformations" by C.Sykes and F.W.Jones,

(Monthly Journal of the Institute of Metals, September, 1936).

The writer saw that this method might be adapted to the

present problem, for Sykes and Jones claimed to measure the

instantaneous specific heats of β brass and copper-gold

alloys at the temperatures where these order-disorder trans-

formations took place.   It was appreciated that measuring

true specific heats of solids at temperatures up to about

$450^{\circ}C$ was a very different and much easier problem than

measuring the true specific heats of liquid slags at temper-

atures of about $1100^{\circ}C - 1600^{\circ}C$.

Principle of Sykes' Method.

Sykes' method was developed for the express purpose

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of the "Examination of Thermal Effects Due to Order-Disorder Transformations", and so was designed to allow of the measurements of heat while the temperature was continuously varied.   From the standpoint of the work in hand this was also essential.

The specimen S was mounted in a closed copper cylinder B fig. (54), and thermally insulated from it. The specimen was independently heated by a nichrome coil C. The outside copper cylinder was heated by the outside furnace at a uniform rate according to the line C_{T_B} . fig.(55). By suitable manipulation of the power input to the coil the temperature of the specimen could be made to follow the line C_{T_S} . fig.(55).   At the points of intersection of these two curves $T_S = T_B$ where T_S and T_B are the temperatures of the specimen and copper cylinder respectively and no external heat is being received by the specimen. Consequently the following equation could be applied:

$$Q = MC_p \left(\frac{dT}{dt} S\right)_{T_S = T_B} \qquad \text{----------- (1)}$$

where Q is the power supplied to the coil; M is the mass of the specimen and C_p is the instantaneous specific heat of the specimen at the temperature T_S.

If this were capable of application at high temperatures then the problem in hand could, in all probability, be solved.   One great difference, however, in the two problems was that where Sykes was using a single metal the author wanted the specific heats of slags, which would require to be contained in some kind of container.   It would then be necessary to apply Sykes' method to the metal of the container and find the specific heats of this over the temperature range required at the high temperature. Having found this, equation (1) would have to be modified as follows i.e. in the case where slag was present

$$Q = (MC_p + mC_s) \left(\frac{dT}{dt} S\right)_{T_S = T_B}$$

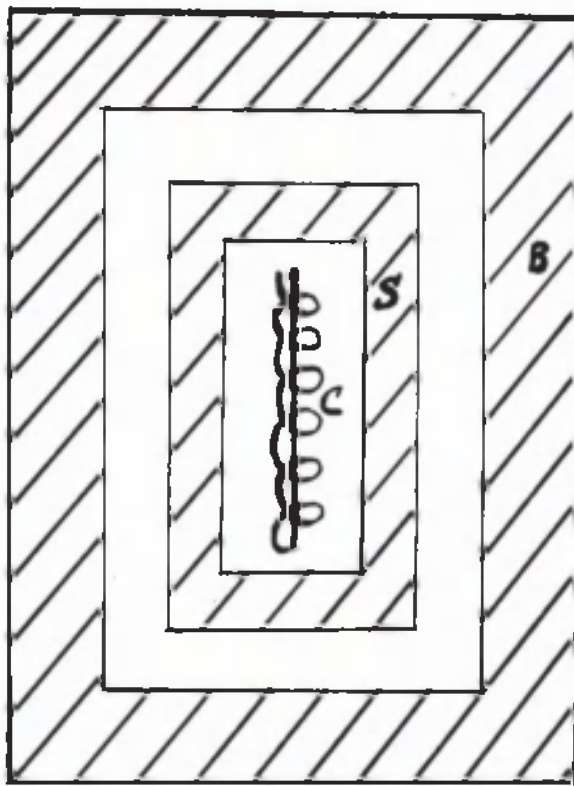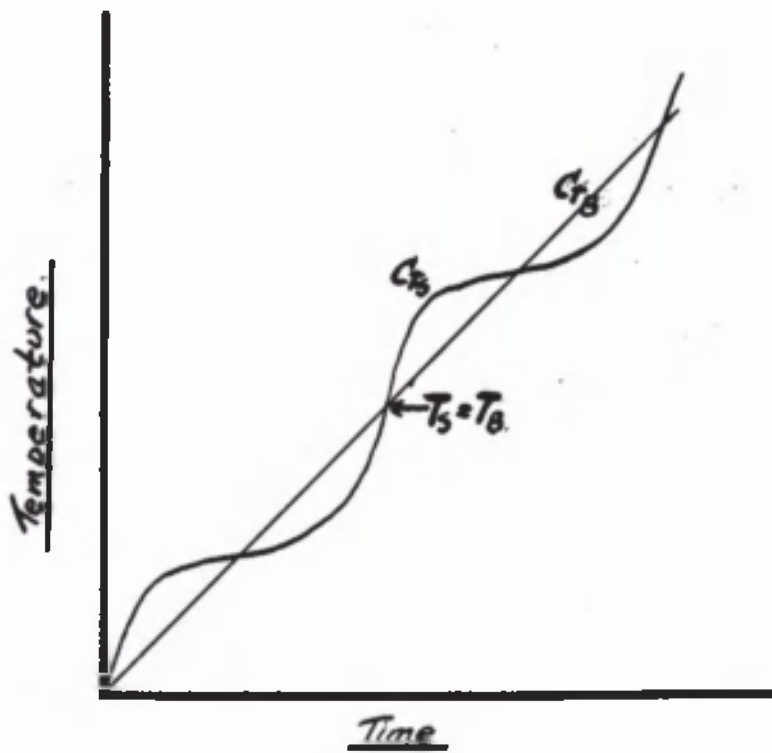where m is the mass of the slag and C_s the instantaneous

Fig. 54

Fig. 55

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specific heat of the slag.

Before any work was commenced on slags or even on
the metal of which it was proposed to make the container, it
was decided to try out the method at low temperatures with a
specimen of α/β 60/40 brass, with the object of finding what
were the difficulties that were to be expected and how many
of these could be surmounted in the first design of an
apparatus.

As Sykes has pointed out, the measurement of C_p
depends on the measurement of $\frac{dT_S}{dt}$ and Q.   He also states
that the measurement of $\frac{dT_S}{dt}$ is difficult because it is
governed primarily by the heat input of the coil, and it may
be necessary to change the power input at frequent intervals.
For that reason he expands $\frac{dT_S}{dt}$ as the sum of two terms thus:-

$$\frac{dT_S}{dt} = \frac{dT_B}{dt} + \frac{d(T_S - T_B)}{dt} \text{----------- (3)}$$

The reasons are as follows:-   The block, or cylinder,
receives its heat almost entirely from its external surround-
ings and in vacuo the thermal lag between the furnace and the
block is very high, so that minor fluctuations in winding
temperature are smoothed out considerably before they reach
the copper block.   Consequently the temperature- time curve
of the block may be taken to be a smooth curve, and inaccuracy
in experimental observation can be legitimately reduced by a
system of averaging.

In addition,

$$\frac{dT_B}{dt} = \left(\frac{dT_B}{dV_B}\right) \times \frac{dV_B}{dt} \text{--------------------- (4)}$$

where V_B is the e.m.f. of the thermocouple in the outer
block.   Sykes does not make it very clear how he measured
$\frac{dV_B}{dt}$.   However since the heating curve of the block is a
smooth one it was considered that it would be easy enough to
derive the gradient at any point.

In part (II) of this thesis a discussion was given on
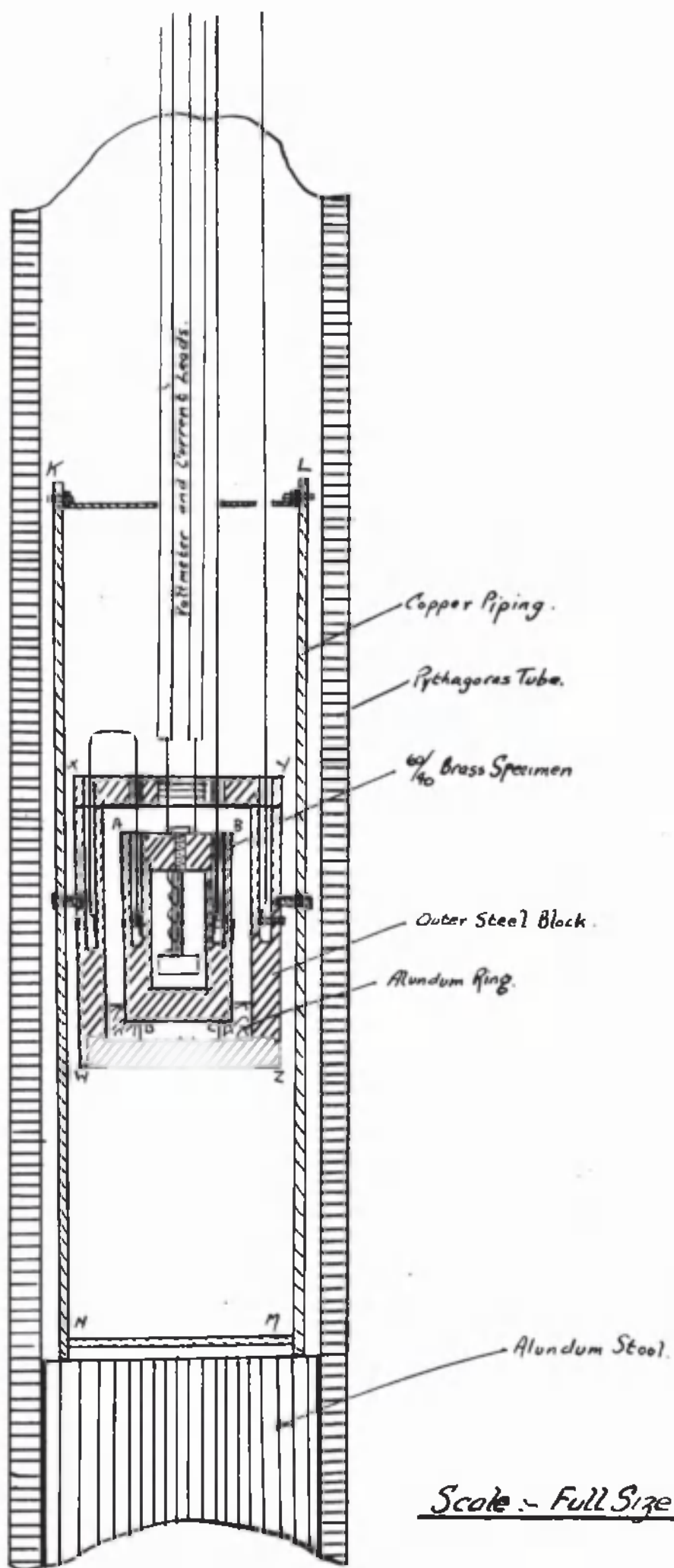differential thermocouples and it was shown that a drift was

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to be expected in the differential galvanometer.   There was
also the difficulty of calibrating a galvanometer so that a
deflection obtained at, say, 1200°C, would represent a known
temperature difference between the junctions of the differ-
ential thermocouple, at that temperature.   For that reason,
it was decided to use two straight thermocouples one to the
inside specimen and one to the outer block, and to take time-
temperature, curves of these two and attempt to obtain the gradient
of the time temperature curve of the inner specimen, i.e.
equation (3) was not to be used.

Apparatus for the initial work at low temperatures.

A section through the apparatus is shown in fig.(56),
which is full size.

The Specimen.   ABCD is the specimen which was made of 60/40
brass.   The specimen was not of interest as a specimen of
brass, but merely that this was the most convenient material
of which to make a specimen for the examination of the
variables of the method.   The lid of the specimen was made
in two pieces, to facilitate the insertion of the heater.
The specimen was supported on a ring of St.Daniel and was
surrounded by a block of mild steel, XYZW.   At the temper-
ature of working there would be no changes in the steel block
except the change in solubility of cementite in α Ferrite.
The lid of the block was made in two pieces to ease the
general assembly of the apparatus.   The block was supported
inside a six inch length of copper piping, which was closed
at the bottom and provided with a lid through which the leads
and thermocouples could be led.   The supporting was done by
grub screws.   This latter piece of piping served to smooth
out any temperature gradients before they could affect the
block.   The whole assembly was thus movable as one unit and
was supported on an alundum stool, enclosed in a "Pythagoras"
tube.   A Nichrome wound furnace was used as the external
heating source.

Voltmeter and Current Leads.

Copper Piping.

Pythagoras Tube.

60/40 Brass Specimen

Outer Steel Block.

Alundum Ring.

Alundum Stool.

Scale :- Full Size

Fig. 56.

Brass Screw.

Brass Washer.

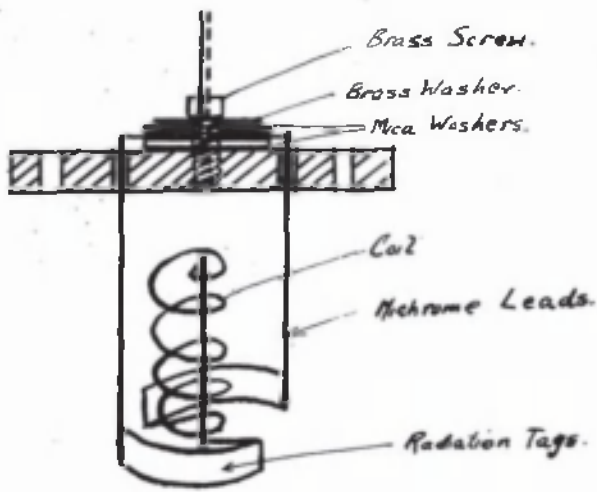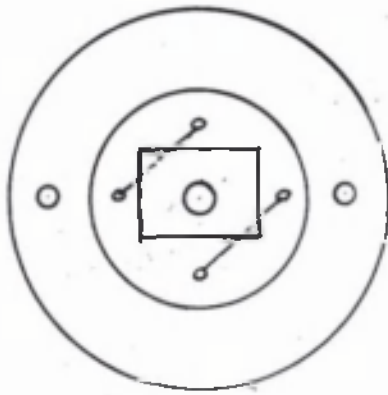Mica Washers.

Coil

Nichrome Leads.

Radiation Tags.

Fig. 57.

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The Heating Coil. The heating coil is shown in position in
fig.(56), and a more detailed drawing is given in fig.(57).
The coil was designed practically on the lines suggested by
Sykes (loc. cit.).

It had a developed length of fifteen centimetres and
a wire diameter of 0.25 millimetres. The ends of the coil
were hard soldered to two pieces of copper foil, which formed
radiation tags, to prevent heat from being conducted away
along the leads. The other ends of these tags were hard
soldered to two stout Nichrome wires which led through the
lid and were insulated from the lid by silica sheathing.
On the outside of the specimen these Nichrome leads were
flattened out and bent over, so that they could be rigidly
clamped between mica washers and held fast by a brass screw.
Ammeter and voltmeter connections.

The stout Nichrome leads of the heating coil, on
emerging from the outer steel block were each hard soldered
to two copper leads, 18 S.W.G. these being a voltmeter and
ammeter lead respectively. These copper leads were led
through the lid of the outer steel piping and through the
bung of the "Pythagoras" tube, and were sheathed with silica
sheathing for insulation purposes.

The Electrical Circuit. This has already been explained in
connection with the Nernst Method which was tried. When a
higher voltage was required, some more cells were added to
the circuit.

The Thermocouples. The thermocouple system shown in fig.(58)
is a differential one and was that used in the later work.
As stated above, two straight thermocouples were used and
these were passed through the bungs of the "Pythagoras" tube,
through the lid of the outer copper piping, through holes
left for them in the outer steel block, and down into small
holes in the specimen. For the length of wire clear of the
steel block, they were sheathed with silica sheathing but
inside the unit proper they were sheathed with silica quill,

D_2 D_1 D_1 T_1 D_2 T_1
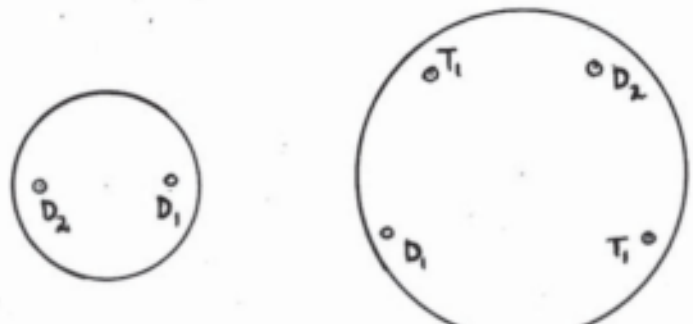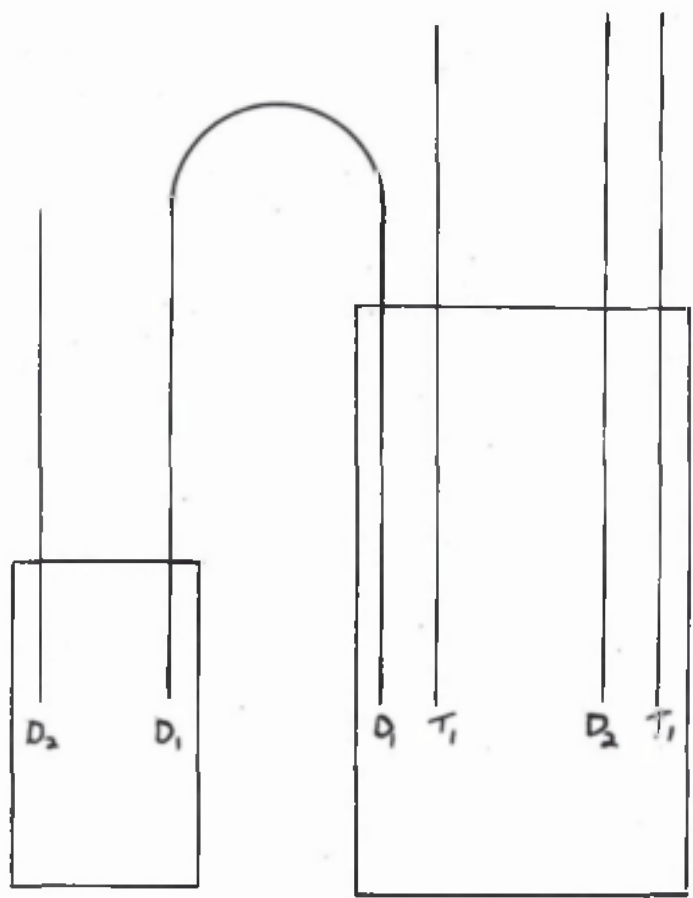
$D_1 D_1 \, D_2 D_2 =$ Differential Thermocouple.
T, T_1 = Temperature Thermocouple.

Differential Couple System.

Fig. 58.

except at the contact which was made by a grub screw passing
through a hole in the wall of the specimen and gripping the
end of the thermocouple wire.   There was only one thermo-
couple element in each hole, the junction of the thermo-
couple really being the specimen itself.

The Measurement of the Temperature.

There were two thermocouples.   A Tinsley Vernier
Potentiometer can accommodate two thermocouples, and, with
care, the selector switch could be manoeuvred so that a
block temperature could be read, then a specimen temperature,
and so by taking alternate readings the heating curves of
both the block and the specimen could be obtained.   When the
coil was being energised it was necessary to obtain readings
of the time for every 0.01 millivolt increase for the specimen
as is explained later.   For that reason the readings of the
block had to be sacrificed.   An occasional reading of the
block could be obtained, but the main thing was to note when
the specimen had passed it in temperature.   At least three
readings of the specimen had to be taken after this point,
for this was necessary for the determination of the gradient
of the heating curve.   After these had been taken a few more
points on the curve of the block were taken, as a verificat-
ion of the course of the block curve as determined by the
readings before the temperature of the specimen rose rapidly
due to the energising.

The experimental work.

The first few determinations were done with a volt-
meter and ammeter which were later found to have a large
percentage error due to there being no zero adjustment, but
useful information was obtained from these experiments.

It was unfortunate that the coil was mounted in the
specimen before the latter had been weighed, and rather than
disturb the coil, the quantity MC_p was measured instead of
C_p.   The fact that this was some fifty times greater than

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C_p magnified the errors, as will be seen from the results reported below. The specimen was weighed immediately upon dismantling the apparatus and the values of C_p then found.

It was soon found that if the heating rate of the outer block, determined by the heating rate of the external Nichrome wound furnace, was too great, then before the coil was energised there was an increasing temperature difference between it and the specimen. This meant that the power input to the coil had to be relatively large in order to enable the heating curve of the specimen to cut sharply that of the block. The results obtained showed no agreement, and it was thought that due to the large power input to the coil there were temperature gradients being produced in the specimen. In these experiments, the temperature difference existing between the specimen and the block just before the coil was energised was of the order of 25°C. By reducing the heating rate of the outer block this was reduced to 0.75 - 2°C. This was dependent on the fineness of the rheostat controlling the outer furnace, and to obtain finer adjustment another rheostat was connected in parallel with the first one. The following was the procedure finally adopted. The temperature was brought to a constant value, and then the current was increased so that the furnace just began to heat. It was then found that the power required in the coil was greatly reduced and that sharp intersections could be easily obtained without temperature gradients in the specimen. The results were in closer agreement.

Even with the voltmeter and ammeter with their large errors, another point was soon evident. The voltage and current were not constant throughout. At first, the initial readings were taken, then the final readings were taken, and latterly the voltmeter and ammeter were read at equal small intervals of time and the average voltage and amperes found.

The voltmeter and ammeter were replaced by new instruments.

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The Voltmeter. The new instrument gave a full scale
deflection of 100 divisions for five, ten, or twenty volts
depending on the terminals used. Working on the "ten"
terminals, the smallest marked division was 0.1 volt, so
that 0.01 volt could be estimated. With the "five"
terminals the accuracy was double this and with the twenty
scale, which was not used at all, the accuracy would have
been half of this.

The Ammeter. The new instrument had a full scale deflect-
ion of 120 divisions, tenths of which could be estimated.
There were shunts to give the following values:

       (1)   0.02 amperes / division.
       (2)   0.10 amperes / division.
       (3)   0.20 amperes / division.

The determinations were carried out in vacuo at first, then
experiments were done to find the effect of the presence
of a gas on the technique and the results, for if the
method were capable of extension to high temperatures
determinations done in a "Pythagoras" tube at temperatures
above $1400^{o}C$ would require to be done in an inert gas to
prevent the collapse of the tube.

     Some of the curves are reproduced in figs. (59)
(60) (61) (62) (63) (64). It will be seen how difficult
is the measurement of the gradient of the heating curve
of the specimen at the point of intersection, especially
when there is a convergence of the curves after the inter-
section. By the application of Taylor's Theorem, a
method was derived for measuring the gradient of a curve
at a point. If, on a curve $y=f(x)$ the gradient is
required at a point $x_0 y_0$, and $x_1 y_1$, $x_2 y_2$, $x_3 y_3$ are points
equally spaced along the abscissa above $x_0 y_0$ by a small
amount h from each other and similarly are $x_{-1} y_{-1}$, $x_{-2} y_{-2}$,
$x_{-3} y_{-3}$, equally spaced below $x_0 y_0$ then the gradient at
$x_0 y_0$ is

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$$\frac{dy}{dx} = \frac{3}{4}h \left\{ (y_1 - y_{-1}) - \frac{1}{5}(y_2 - y_{-2}) + \frac{1}{45}(y_3 - y_{-3}) \right\}$$

(Practical Mathematics - Toft and McKay - Pitman - Page 160). The formula depends on the choice of equally spaced readings at very small intervals above and below the point of intersection of the curves. Since the readings of the specimen thermocouple were made at every 0.01 millivolt it was decided not to measure $\frac{dy}{dt}$ but its reciprocal $\frac{dt}{dv}$ i.e. to use the thermocouple readings as abscissa.

The following is a specimen calculation:

Run No.11.

Curves intersected at 8.99mv.

Average current   0.141 Amperes
Average Voltage   0.94 Volts.

$$\frac{EC}{J} = MC_p \frac{d(temperature)}{d(time)}$$

$$= MC_p \frac{d(temperature)}{d(volts)} \frac{d(volts)}{d(time)}$$

For the chromel-alumel thermocouple $\frac{d(temperature)}{d(volts)} = 23.65$

so that

$$MC_p = \frac{EC}{J} \times \frac{1}{23.65} \times \frac{d(time)}{d(volts)}$$

For Run 11

$$\frac{d(time)}{d(volts)} = \frac{3}{0.04} \left\{ 114 - \frac{1}{5}(228) + \frac{1}{45}(334) \right\}$$

$$= \frac{3}{0.04} \times 76.045$$

$$MC_p = \frac{0.94 \times 0.141 \times 3 \times 76.045}{4.18 \times 23.65 \times 0.04}$$

$$= 7.68.$$

It was found that difficulties still attended the measurement of the gradients even with the application of Taylor's Theorem.

(1). The curves sometimes intersected between two 0.01 millivolt divisions, say at 8.095. This did not matter so much when the gradient did not alter until well after the points used, for then the gradient could still be

Part (VII)

found from the actual experimental readings. At all times
the reading of values from the curves was avoided if at all
possible, because this is liable to error. As will be
seen from the curves, when the temperature of the specimen
became higher than that of the outer block the heating rate
of the specimen decreased while that of the block increased.
(2). The intersection of the two curves was sometimes not
sharp enough to enable a precision reading of the value at
the point of intersection to be made. If the gradient of
the heating curve of the specimen changed at all during the
range including this point then a large error could be
introduced.
(3). An examination of the formula for the gradient showed
that the accuracy was probably determined by the accuracy
with which $(t_1 - t_{-1})$ could be read. This was dependent
on the accuracy with which the time could be read. Allow-
ing that the maximum error in reading the watch would be
$\pm$ 0.5 seconds (it was actually much less), the maximum error
was then one second on $(t_1 - t_{-1})$ seconds. $(t_1 - t_{-1})$ had
then to be of the order of 100 to make this error 1%.
The smaller was $(t_1 - t_{-1})$ the larger was the percentage
error. This, therefore became the factor which governed
the amount of power put into the coil. The heating rate of
the coil had to be such that $(t_1 - t_{-1})$ was about 100
seconds.
Some of the curves are reproduced in figs. 59 - 64.
Fig. (59) shows a case where the temperature difference
before energising was about 12 ^{o}C. Note the sharp change
in slope of the specimen curve when the current was started
in the coil. Also note the convergence of the curves
after the intersection. It will be seen that the gradients
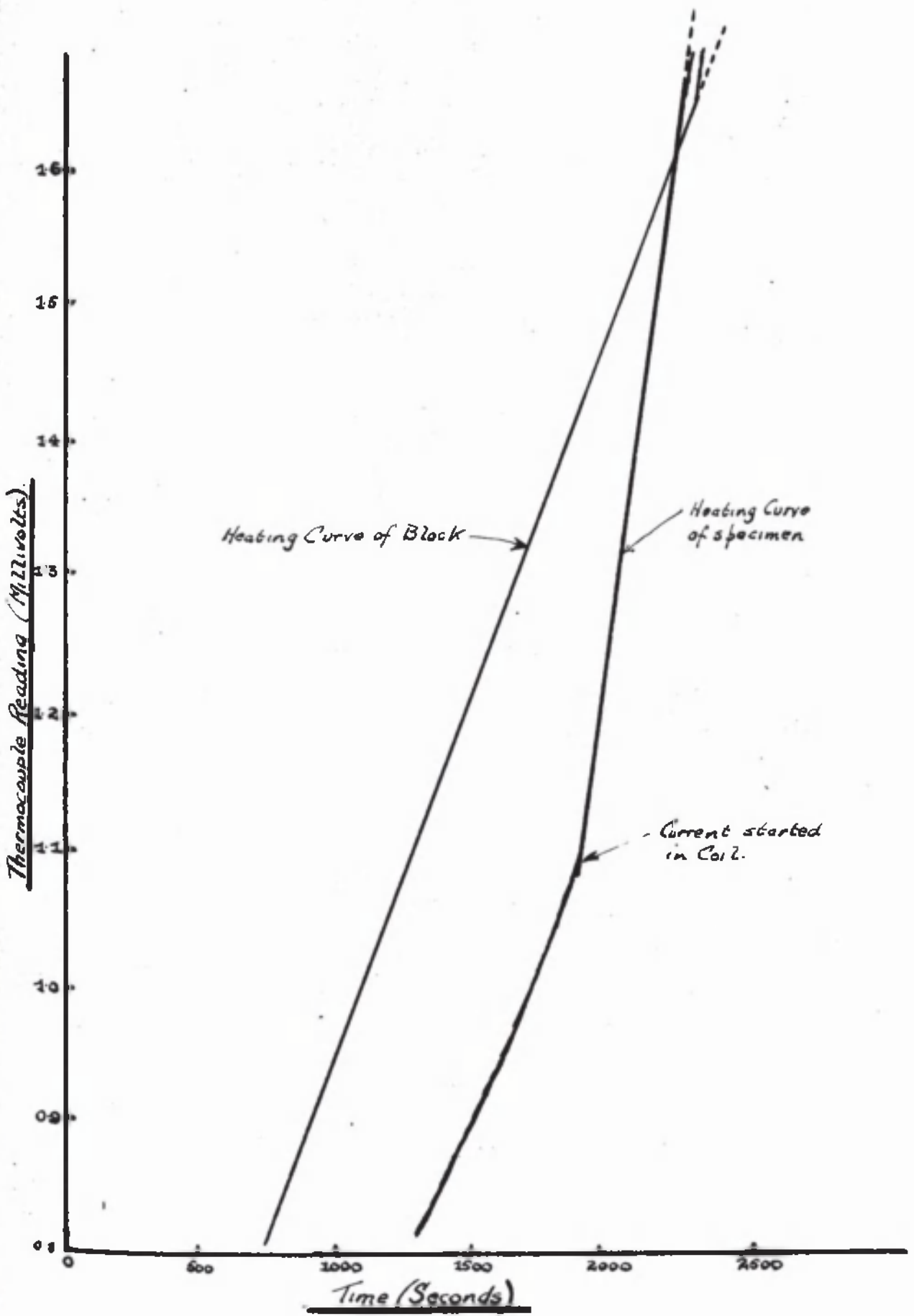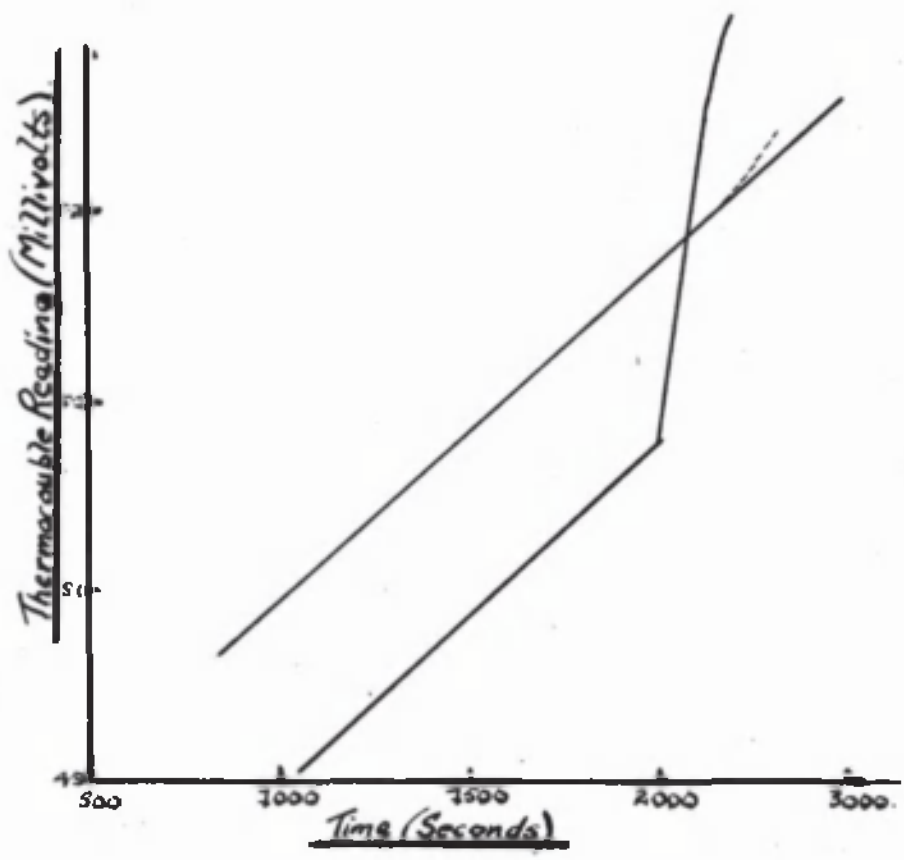change after this point.
Fig. (60) shows a case of a sharp intersection of the curves.
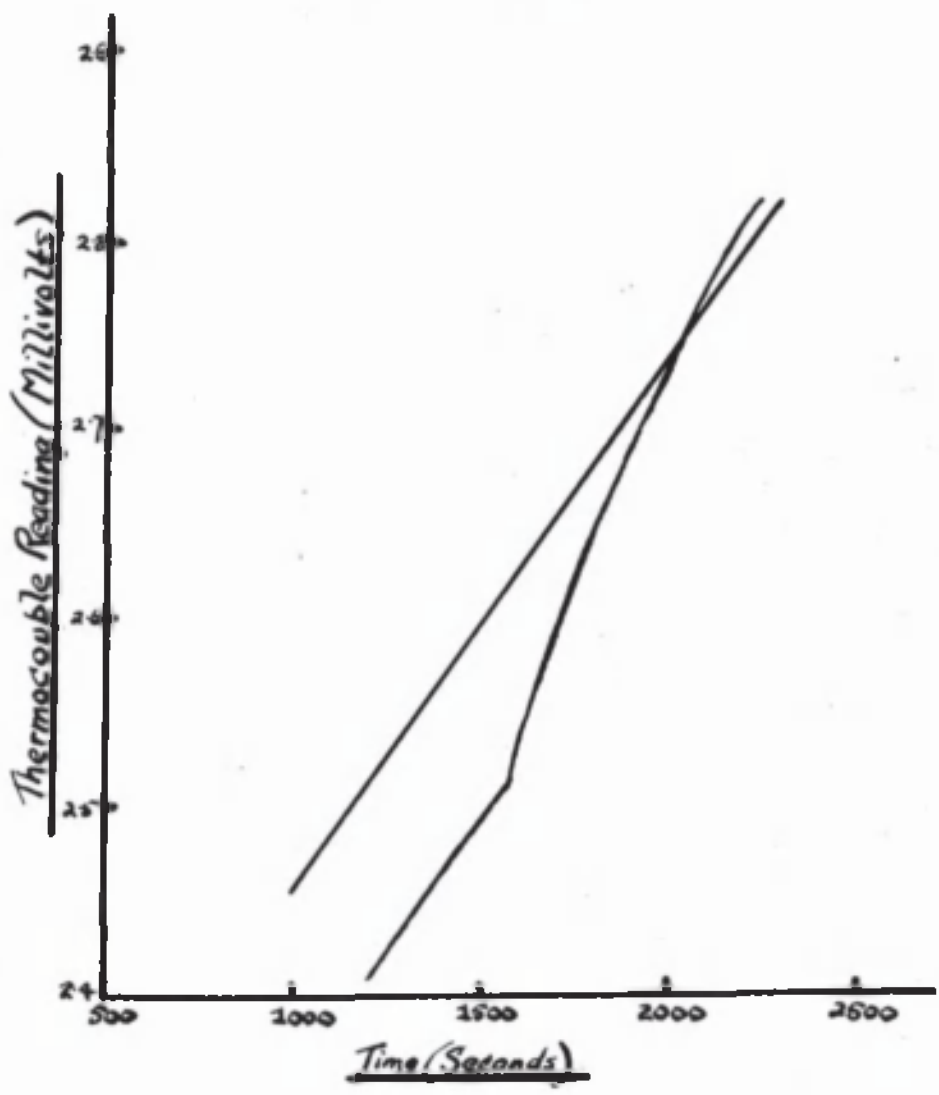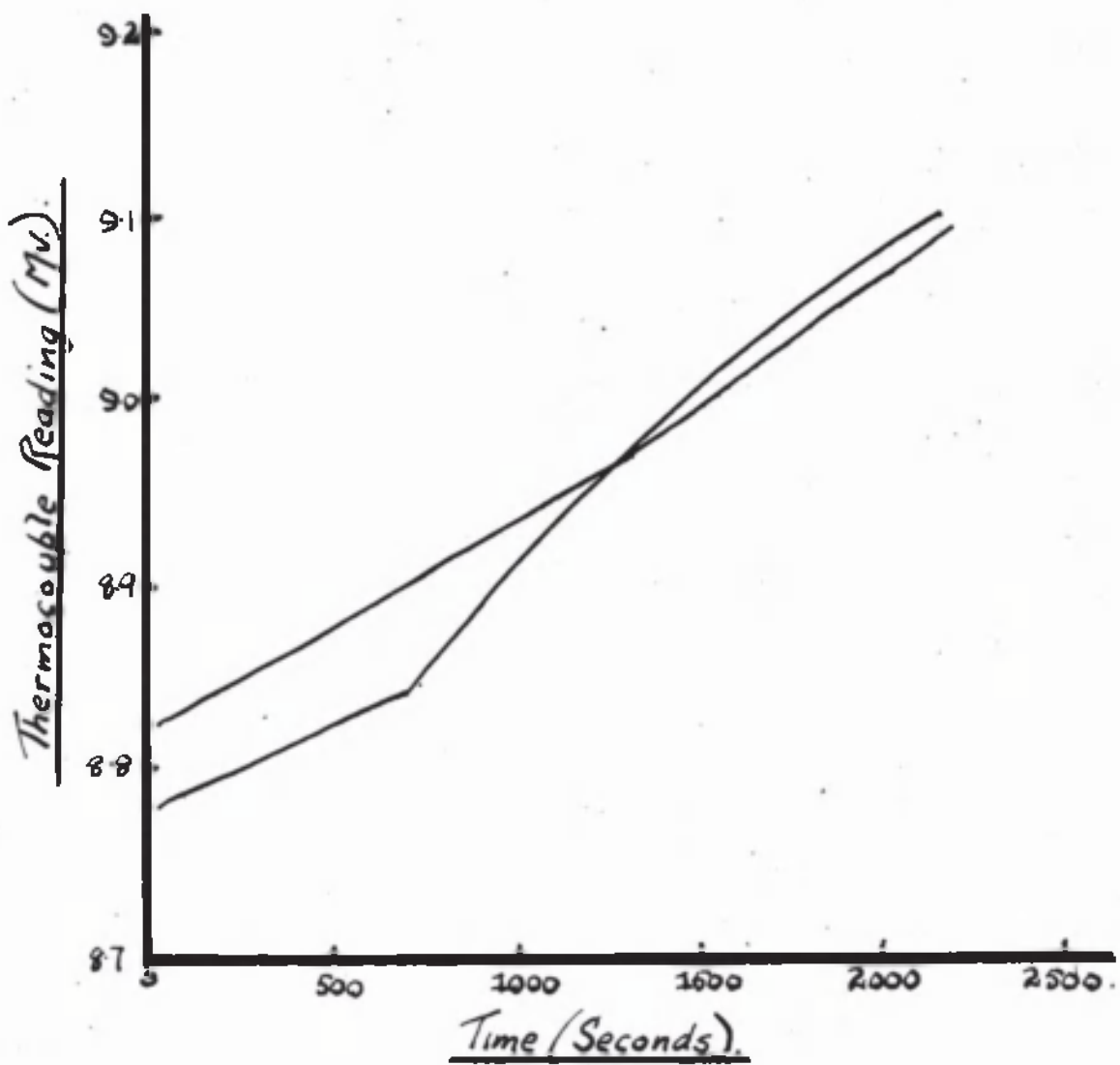
Fig. 59.

Fig. 60

Fig. 61

Fig. 62.

Fig. 63.

Time (Seconds)

Thermocouple Reading (Mv.)
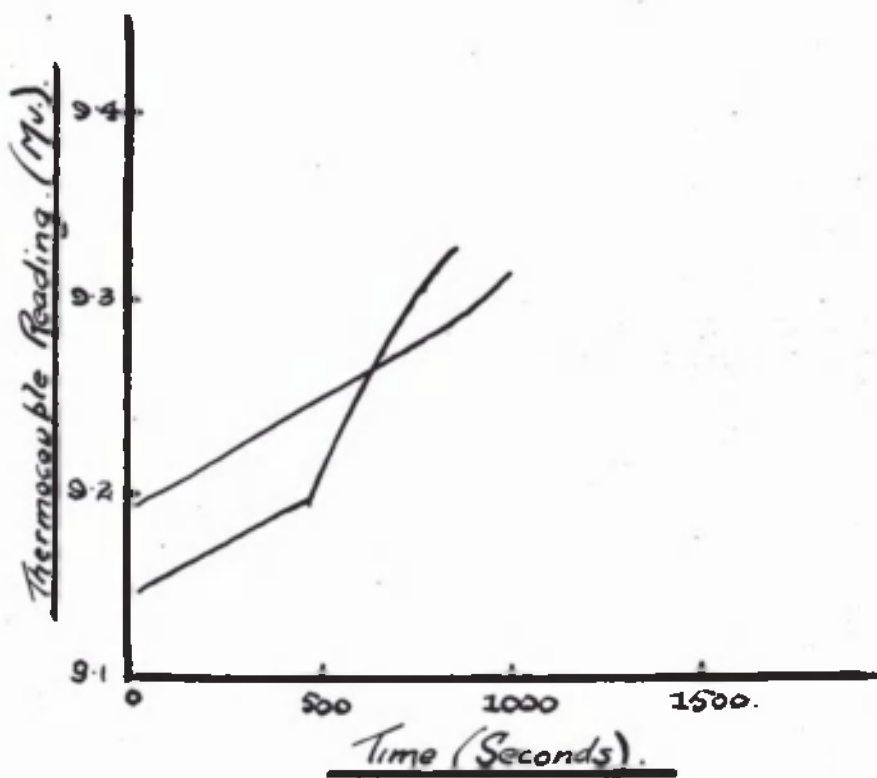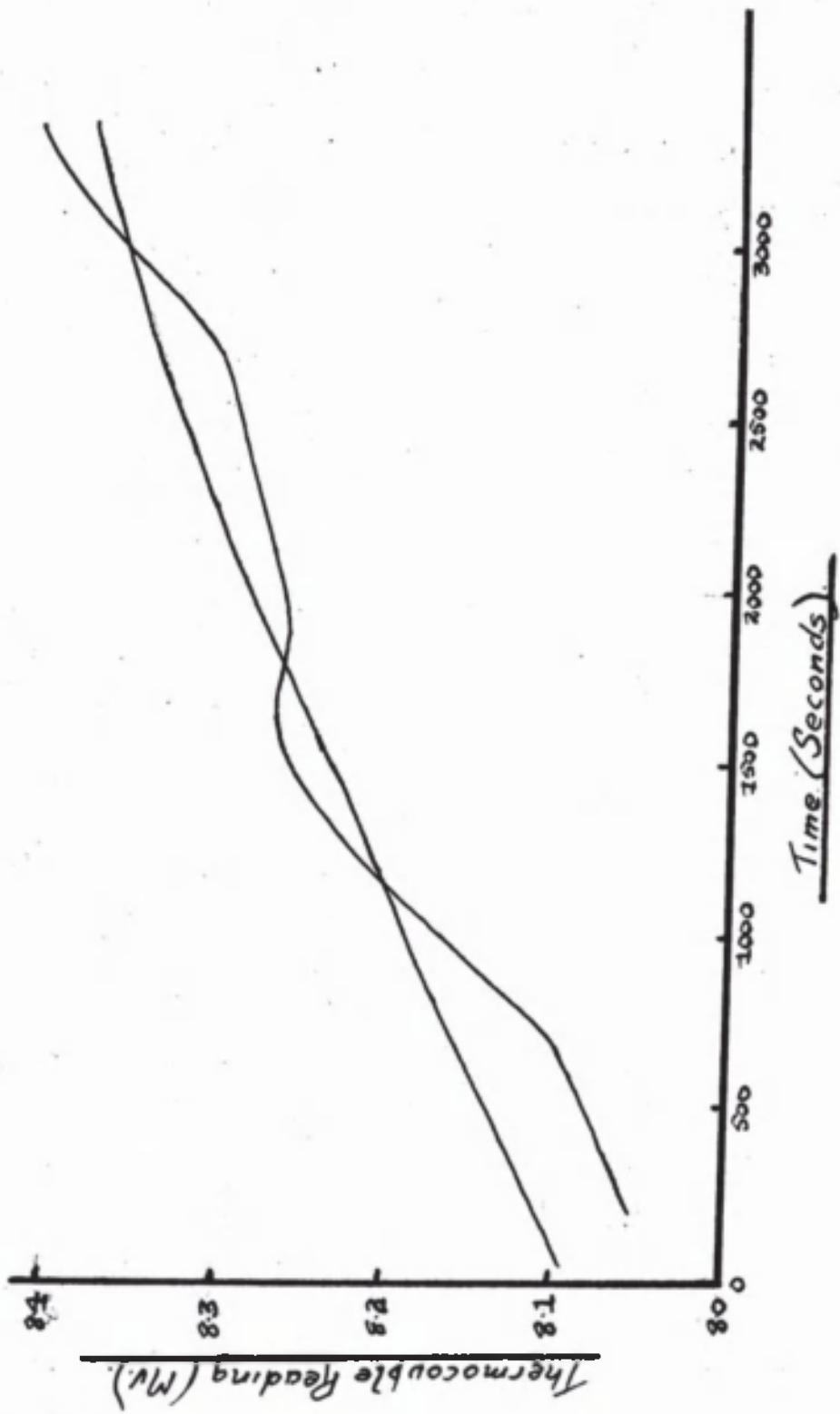
Fig. 64

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Note, however that the curves are convergent again after the point of intersection, but that the gradient of the specimen curve does not change for some distance after the point of intersection.

Fig. (61) shows a case where the intersection was not sharp and where the gradient of the specimen curve was changing before and after intersection. The difficulty of finding the gradient of this curve at the point where the temperature difference is zero will be appreciated.

Fig. (62) shows a similar case, and Fig. (63) is of the same type as Fig. (60).

Fig. (64) represents one of the runs where the curves were continued after the current was stopped in the coil and then was started again. The difficulties of measuring the gradients of the specimen curve are again apparent and it will be noted that the gradient of the block curve was not constant throughout the whole experiment. For that reason, each run was after that done independently.

While the experimental work was being done the weight of the specimen was not known so that all opinions of the method were formed on the product MC_p which was some sixty times the magnitude of C_p, the errors seeming bigger in the same ratio. When the apparatus was dismantled the specimen was weighed and the values of C_p were then found. These are tabulated below along with the values of MC_p.

Milli-volts.	Temper-ature	MC_p	C_p	Remarks.
1.61	70.6°C	6.56	0.1059	
2.75	97.5	6.50	0.1050	
3.54	116	6.56	0.1059	Block was stationary in temperature at intersection.

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Milli-volts.	Temperature	MC_p	C_p	Remarks
5.19	165	7.23	0.1156	
8.19	226.5	7.45	0.1200	
8.34	229.5	7.57	0.1220	
8.99	243.5	7.68	0.1240	
9.26	251.5	7.47	0.1210	
11.59	307.5	8.85	0.1420	Block and specimen curves practically coincided.

The results of C_p are plotted against temperature in fig. (65) and on the same graph is shown the relationship of C_p against temperature for an $\propto \beta$ brass as found by Sykes and Wilkinson (The transformation in the β brasses Month. Journ. Inst. Met. July 1937) which was after the work which is being described was done. It will be seen that the author's results are higher than those of Sykes and Wilkinson, but that they show the same trend. Judging from the values of MC_p as found during the work, it was felt that there was not sufficient accuracy in the measurement of this product, e.g. at 226.5°C this was 7.45, at 229.5, 7.57, and at 251.5°C, 7.47.

It was felt that the measurement of the gradient could not be improved. The vacuum was not a perfect one, and so it might have been that the small residual pressure of gas in the tube varied from day to day, and even from run to run, for the evacuating pump was kept running all the time. The presence of some gas in the tube would not alter the basic theory of the work, in that when there was no temperature difference between the specimen and the block, there would be no transfer of heat between them. There could, however, be losses from both. But, once there was a temperature difference, transfer of heat would take place more readily, and thus, the convergence of the curves after the intersection
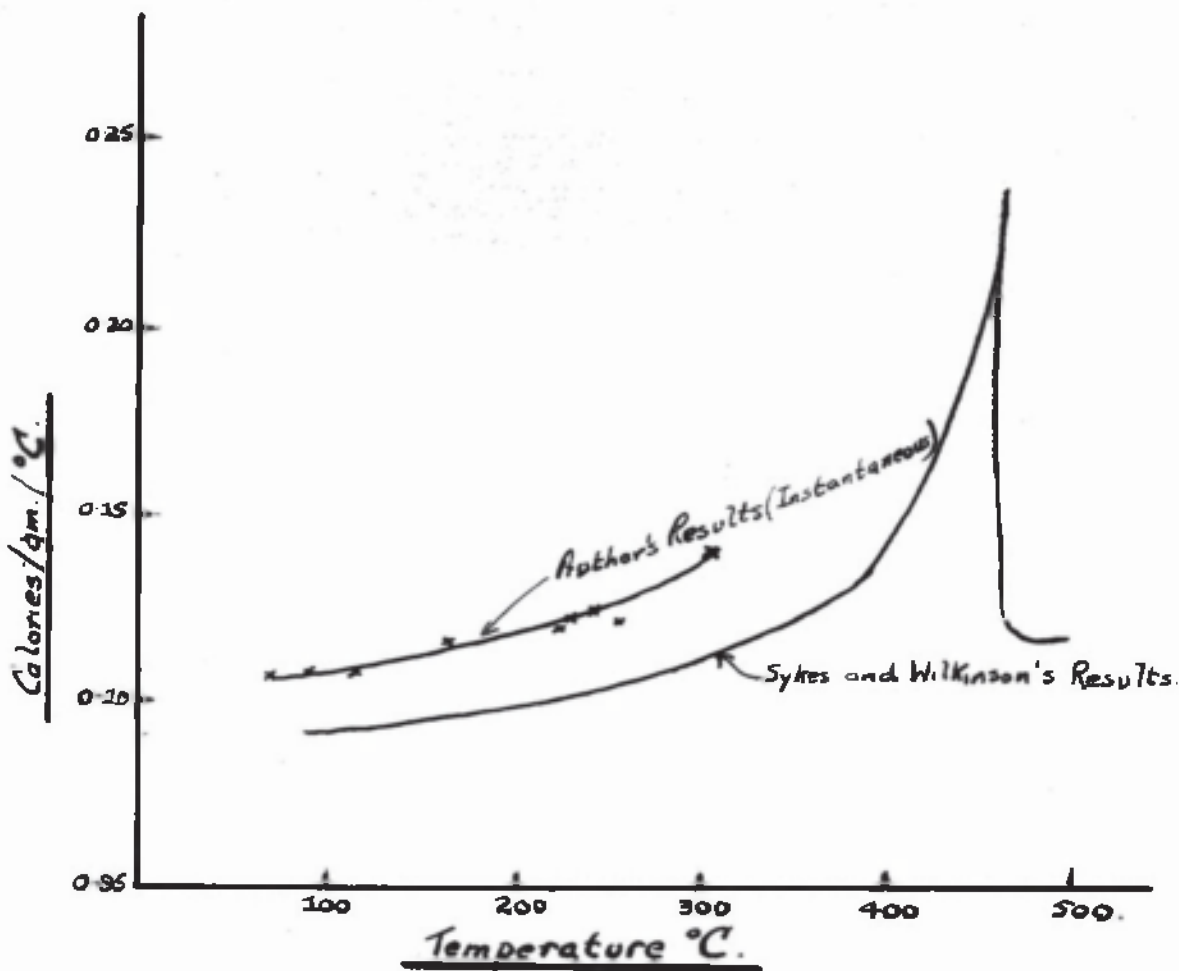
Fig. 65.

would be dependent on this and so the difficulty in the
measurement of the gradient.   The residual gas could
have been the cause of the difference between the curves
in fig. (65), provided this gas increased the losses.
Since for the determination of specific heats at high
temperatures with the use of a Pythagoras tube the pres-
ence of a gas is necessary to prevent the collapse of the
tube, it was decided to find out if the presence of a gas
influenced the results and if so, to what extent.
Some determinations were therefore done in an atmosphere
of nitrogen which was oxygen-free.   Figs. (66), (67),
(68) show some curves taken in the presence of nitrogen
and it will be seen that the convergence of the curves is
greater.   Fig. (65) is reproduced again in fig. (69) and
the crosses represent the determinations done in nitrogen.
As will be seen, the results are not in agreement with
those found in almost a vacuum, provided the relationship
as drawn holds.   On the other hand another relationship
could be drawn as shown dotted.   The results, as found
in the gas, were more in agreement with those found by
the other workers.

        As has been mentioned before, the great difficulty
in the work was the measurement of the gradient of the
curve, and this was more so in the case of the nitrogen
because of the greater convergence of the curves, when
the temperatures of the specimen was greater than that of
that block.   Again there was the difficulty, when the
curves did not cross on a 0.01 millivolt division.   Since
the gradient of the block changed less than that of the
specimen it was decided to change over to the differential
system as described by Sykes (loc. cit.).

        The differential galvanometer scale had to be
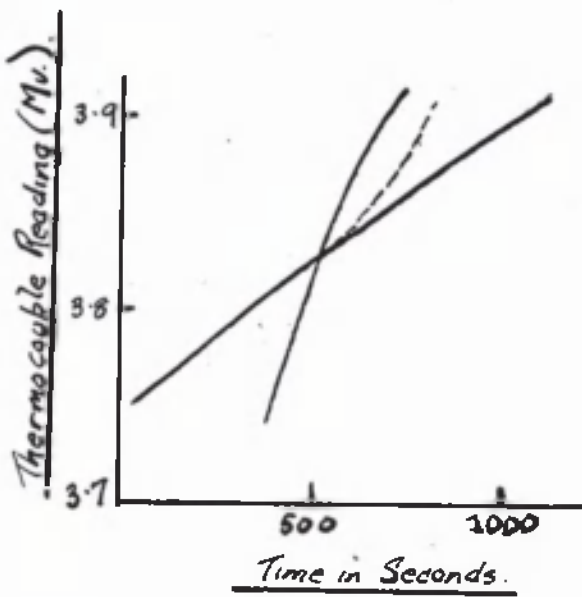calibrated.   This was attempted by putting the selector
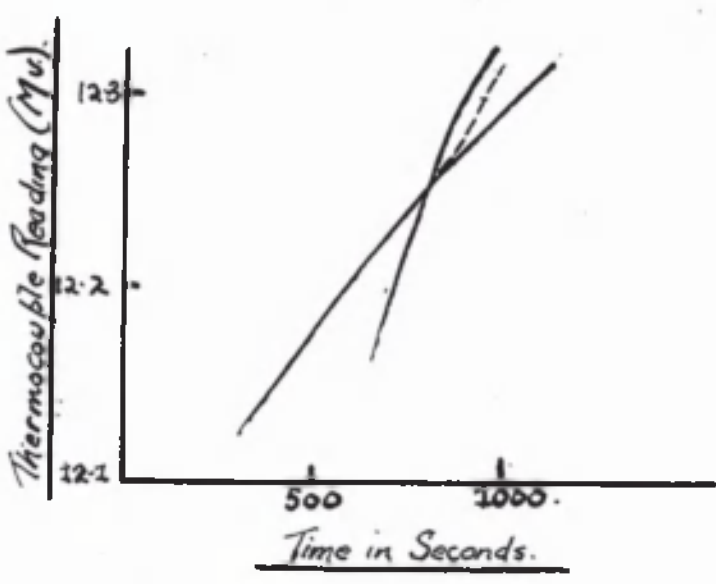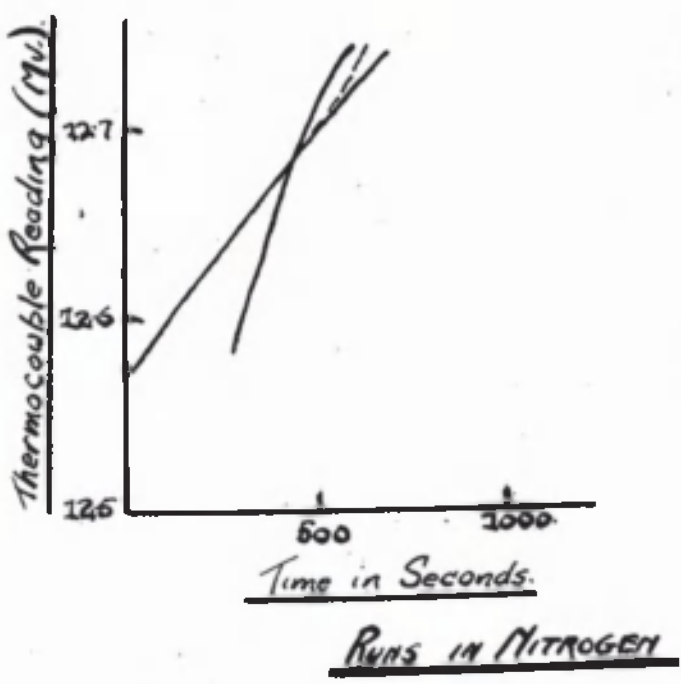
Fig. 66.

Fig. 67.

RUNS IN NITROGEN

Fig. 68.

x   Determined in Nitrogen.

Calories / gm. / °C.

Temperature °C.
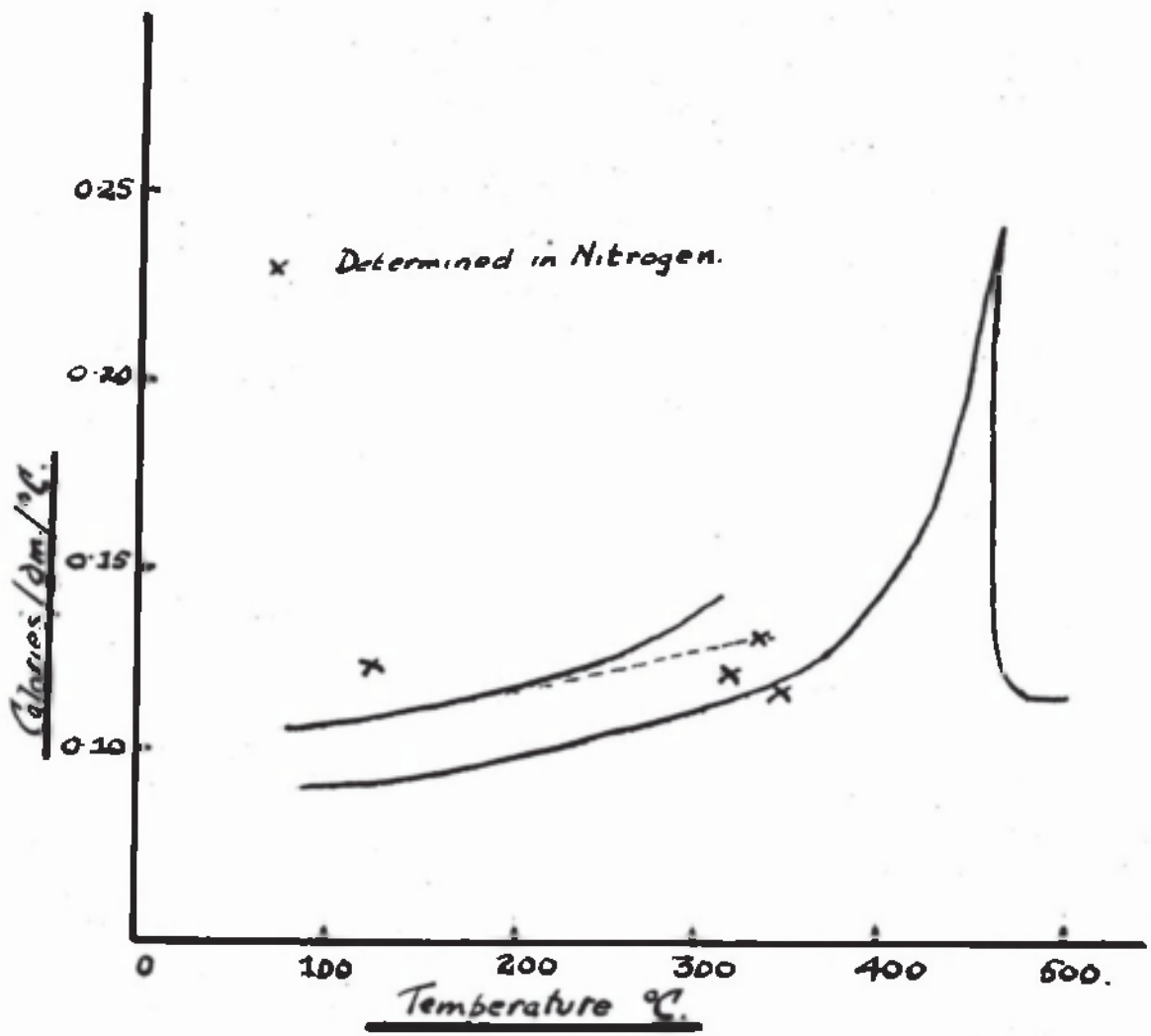
Fig. 69.

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switch of the Vernier Potentiometer at the Standard cell and standardising the potentiometer. Then, by tapping off from the studs of the potentiometer, known voltages of 2, 4, 6, 8, up to 20×10^{-2} millivolts were applied to the differential galvanometer and the deflections to the right hand side were found. The same was done for the left hand side, and a graph was plotted giving the voltage represented by deflections to either side of the zero of the galvanometer. These when multiplied by 23.65 gave the temperature difference existing between the specimen and the block.

The theory of the determinations was as follows:

$$\frac{IV}{J} = MC_P \frac{dT}{dt} S_{S=B}$$

$$\frac{DT}{dt}S = \frac{dT}{dt}S - \frac{dT}{dt}B + \frac{dT}{dt}B$$

$$= \frac{dT}{Dt}B + \frac{d}{dt}(T_S - T_B)$$

$$= \frac{dT}{dV}B \times \frac{dV}{dt} + \frac{d}{dV}(T_S - T_B)\frac{dV}{dt}$$

Thermocouple Millivolts	Two thermocouples	Differential
0.44	-----	8.60
1.61	6.56	----
5.19	7.23	----
8.19	7.45	----
8.30	----	10.75
8.34	7.45	----
8.99	7.68	----
9.26	7.47	----
10.58	----	9.40
11.59	8.85	----

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It will be seen that the results by the differential
method in no way agreed with those of the two thermo-
couples.   The following difficulties were noted.

(1).   Although the maximum deflection of the differential
galvanometer was only 6cm. the suspension of the galvan-
ometer was affected so that the zero shifted some 2 - 3 mm.
Actually therefore the gradient of the block curve was
being measured not when there was zero difference of
temperature but when the specimen was at a temperature
corresponding to this zero shift above the block.   This
zero shift could not be forecast nor controlled.

(2).   The difficulty of measuring a gradient was still
present.   In only a few cases was it possible to correctly
apply Taylor's Theorem.

(3).   Another difficulty was introduced due to the cali-
bration of the galvanometer.   This was the inaccuracy with
which the calibration curve could be derived, plotted, and
read.   The reading of the curve was especially difficult
when only small deflections were involved.

The differential system was given up and it was
decided to go back to the two thermocouples but this time
to use two potentiometers and two watches and so to derive
the curves with greater accuracy at the critical period.
The results were in agreement with those found already with
two thermocouples but the difficulties were not diminished
in any way.

The measurement of a gradient is necessary for the
determination of instantaneous specific heats, so to
eliminate this, it was decided to attempt the measurement
of mean specific heats over very small temperature ranges
and to assume that this value would be the true specific
heat at the average temperature of the range.

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Theory of the Method.

If E is the e.m.f. in volts applied to the coil and C is the current generated in amperes, then in time t seconds the energy produced is ECt joules. If M is the mass of the specimen and C_P the mean specific heat over the range d_T through which the temperature of the specimen rises then

$$\frac{ECt}{J} = MC_P dT$$

The measurement of the time t and the current was avoided by connecting a copper voltameter in series with the coil, so that the same current flowed through both for the same time. By Faraday's Laws of Electrolysis, the mass w of copper liberated in time t seconds by the passage of a current C is given by

$$w = z \times C \times t$$

where z is the electrochemical equivalent of copper. Therefore, by dividing the increase in weight of the copper cathode by the electrochemical equivalent of copper the product Ct was found.

The copper cathode used had a depositing surface of 10x15 square centimetres, and the electrolyte had the following composition:

Copper sulphate	150 grams.
Sulphuric Acid	50 grams.
Alcohol	50 grams.
Water	1000 grams.

Measurement of the Voltage.

Every time the coil was energised, the voltage was read every ten seconds, while the current was flowing in the coil. In the first few determinations these readings were added and the mean value found. It would have been much better to have used an integrating voltmeter, for the addition of fifty to a hundred readings was tedious. Finally the mean voltage was judged visually from the list of readings, and it was found that the maximum error which

could appear from this procedure was not greater than 0.5%.

The apparatus was assembled for the differential system of thermocouples, for since only very small deflections were used there was no change of the zero.

The ideal method would have been to get the temperature of the block rising at a certain rate, and then to pass sufficient energy through the coil to enable the specimen to rise at the same rate and always to be at the same temperature as the block. This was not possible, but, by putting a mercury switch in the circuit, it was possible to manipulate this switch on and off by hand so that the differential galvanometer spot could be kept quite easily within 0.3 cm. on either side of the zero. According to the calibration of the differential galvanometer, mentioned above, this was equivalent to 0.003°C. above or below the temperature of the block.

Experimental Procedure.

The temperature of the block was brought quite quickly to the temperature at which the determination was to be made, and then the furnace was gradually steadied in temperature, and kept steady for some time to enable the temperature to become uniform throughout the apparatus. During this time the differential galvanometer was not in circuit, because the deflection was very large due to the specimen's lagging behind the block in temperature, and this large deflection would have caused the zero to shift. When the furnace was steady in temperature the voltameter was short circuited, and by passing a current through the coil, the temperature of the specimen could be brought above that of the block. The outer furnace was arranged to heat very slowly at about $1-1.5^{\circ}$C/minute. The specimen was kept about 0.05°C above it by manipulating the mercury switch. The Vernier Potentiometer was adjusted to the

x 0.01 scale and by slowly rotating the lowest dial of the
instrument the temperature galvanometer could be kept at
zero.   By then opening the switch of the Potentiometer
and leaving the indicator in position the temperature at
which a determination was begun was easily obtainable.
The method of beginning a determination was to pass a
current through the coil and let the specimen get about
0.1°C above that of the block and then switch off the coil
current.   This gave ample time for the voltameter to be
placed in circuit.   The temperature was followed up on
the Potentiometer, and when the differential reached the
zero the temperature was noted simultaneously with the
switching on of the current.   The voltage was measured at
equal intervals of time as has been described above.   By
careful manipulation of the switch the differential galvan-
ometer could be kept within 0.3 cm. of either side of its
zero.   The range of temperature used was determined by the
weight of the copper deposit.   This had to be of such a
magnitude that any small error in weight would be negligible.
At first the ranges were about 50°C.   In the case of a
large specific heat the range could be cut down.   At the
termination of a run, the Potentiometer was read when there
was no current in the coil, otherwise the coil would have
been stored energy capable of still raising the temperature
of the specimen.   While the measurement of the current was
not necessary for any of the calculations, the current was
measured at least once every run so that the power could be
computed, for observations on the life of the coil, for
purposes of design of new coils, etc.

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The following are specimen runs:

	Run 15	Run 16	Run 17	Run 18
Cathode After	127.3834gm.	127.4568gm	127.5270gm.	127.5998gm.
Cathode Before	127.3154gm.	127.3834gm	127.4568gm.	127.5270gm.
Cu Deposited	0.0680gm.	0.0734gm.	0.0702gm.	0.0728gm.
E.E. of Cu	0.0003293	0.0003293	0.0003293	0.0003293
ct.	206.2	222.8	213.5	221.0
Average Volts	4.64V	4.765V	4.73V	4.85V
Current	0.68A	0.69A	0.68A	0.70A
Final Potentiometer Reading	5.236 mv.	8.303 mv.	9.720 mv.	11.732 mv.
Initial Potentiometer Reading	3.820 mv.	6.934 mv.	8.336 mv.	10.354 mv.
Temperature Range	1.416x23.65 = 33.5	1.369x23.65 = 32.4	1.384x23.65 = 32.7	1.378x23.65 = 32.6
$MC_P/^{\circ}C$	6.83	7.85	7.38	7.87
Mass of Specimen	62gm.	62gm.	62gm.	62gm.
C_P	0.110	0.127	0.119	0.127
Initial Temperature	$123^{\circ}C$	$196.5^{\circ}C$	$229^{\circ}C$	$277^{\circ}C.$
Average Temperature	$139.75^{\circ}C.$	$212.7^{\circ}C.$	$245.35^{\circ}C.$	$293.3^{\circ}C.$

The method of calculation was as follows:

For
Run 15.

Temperature range $= 1.416 \times 23.65$ $33.5^{\circ}C$

$$MC_P = \frac{4.64 \times 206.2}{4.18 \times 33.5}$$

$$= 6.83.$$

Part (VII)

The results are tabulated below

Initial Temp. °C	Temp. Range.	Average Temp.	MC_P	C_P
123.	33.5	139.75	6.83	0.110
125.7	46.1	148.75	7.08	0.114
147.	21.75	157.9	6.33	0.102
163.95	36.8	182.35	7.41	0.120
160.95	44.8	183.35	7.66	0.124
176.95	51.7	202.8	7.72	0.125
188.5	41.6	209.3	7.50	0.121
196.5	32.4	212.70	7.85	0.127
215.45	46.25	238.58	7.80	0.126
229.	32.7	245.35	7.38	0.119
244.3	40.02	264.31	7.35	0.119
264.45	29.9	279.4	7.98	0.129
261.45	39.4	281.15	7.63	0.123
267.45	37.5	286.2	8.00	0.129
277.	32.6	293.3	7.87	0.127
316.45	32.	332.45	8.18	0.132

The following results were taken in nitrogen

36	43.25	57.63	6.61	0.107
64.5	33.2	81.1	6.4	0.103
151.25	72.5	187.5	7.46	0.120
657.5	24.84	669.92	12.05	0.194
702	14.8	709.4	13.3	0.275

These results are plotted in fig.(70), and the
curve obtained by the instantaneous method is drawn also
on the graph.   It will be seen that these results obtained
by the mean specific heat method agree fairly well with
those of the other method, and since the mean specific
heat was less tedious it was decided to use this method in
future.   Some results were obtained in nitrogen and those
are also plotted on fig. (70).   It will be seen that the
presence of nitrogen did not noticeably influence the
results.   Two results are given in the region of 700°C,
but these are not plotted in fig. (70).   These were
done /
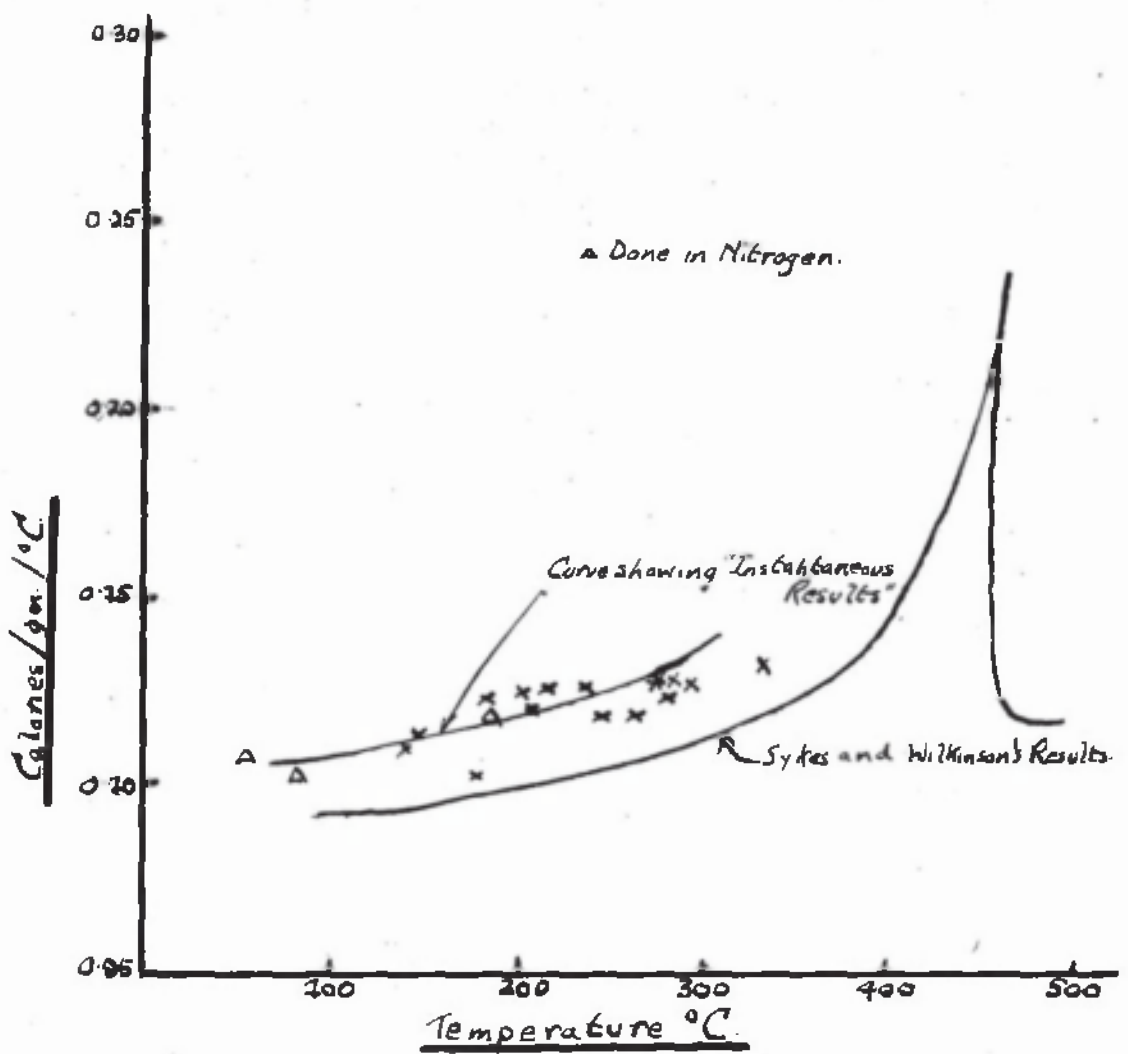
Mean Specific Heat Determinations.

Fig. 10

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for the leads and the thermocouples.

The Container.

The work was intended to be carried out at
temperatures exceeding 1000°C, so that copper could not
be used as a containing substance.   Chromium has a
melting point of 1830°C (Adcock, Chromium-Iron Constitut-
ional Diagram Journal Iron and Steel Institute, 1931,
No.2, P.122), and is a substance which would probably not
react with the slags.   It was not possible to obtain
chromium in sufficient amount to make a container.
Platinum would have probably been satisfactory, but until
it had been proved that the method was capable of giving
results of sufficient accuracy the expense of platinum
was not justified.   Iron shows no allotropic changes
between 900°C and 1400°C, and with most of the slag
substances would have little or no action, so that this
metal was suitable for determinations between say 950°C
and 1350°C.   The material finally chosen because of its
convenience was 0.08% C steel, which between its A_3 and
A_4 transformations is austenite and behaves like pure
iron, for unless the slag substance was of a very oxidising
nature there would be no reaction with the small carbon
percentage.   The outer block was made of the same material
and in fig. (71) the essential parts are shown.   In this
figure the thermocouple leads are not shown.   The differ-
ential system was used as has been just described.   The
holes for the thermocouples were drilled in the outer wall
of the specimen, or container.

The container.

The size of the container was determined by the
smallest dimension, i.e. that of the heating coil.   The
scale of fig. (71) is full size.   The lids of both the
outer block and the specimen were made each in two parts,
to facilitate the assembly.   To insulate the specimen
from /

Part (VII)

from the block a recessed ring of baked alundum was used,
as shown in the fig. The design of the container lid
will be described together with the coil. The screws
which held the lids in place, as well as the grub screws
were of the mildest steel obtainable. The specimen in-
side the outer block was placed inside the outer steel
piping, and held in position with grub screws. This was
to be accommodated in a "Pythagoras" tube of a suitable
size, but as will be described below the first few experi-
ments were done in the train gases because of the delay in
getting a suitable tube.

The Heating Coil.

The temperatures at which it was hoped to work
were to be about $1000^{\circ}C$-$1400^{\circ}C$, so that the actual temper-
ature of the coil would be above this. For that reason,
it was decided that it would not be safe to use Nichrome,
because it would probably burn out. Through the courtesy
of Messrs. Aurora Lamps Ltd., Old Kilpatrick, the author
was able to procure some 12 volt 12 watt lamp filaments
of molybdenum. These had to be attached to electrodes.
The method adopted in lamp filaments is to flatten the ends
of nickel electrodes and to bend these over the ends of the
filaments and pinch them tight.

The electrodes.

In the previous work these had been of stout
Nichrome, and this was replaced by 18 S.W.G. nickel, which
of course, meant that great care would have to be exercised
with temperatures in the neighbourhood of $1400^{\circ}C$. The
attaching of the molybdenum filaments to these nickel
electrodes was difficult. Spot welding was tried unsuccess-
fully. It was hoped that the nickel would solidify round
the molybdenum and hold it in place. Flame welding also
proved unsuccessful. Finally, following the method used
in lamp filaments, the ends of the nickel electrodes were

flattened /

Part (VII)

flattened and then bent over the molybdenum filament and pinched tightly. This was a very delicate operation for the molybdenum filaments were so fragile. It was not practicable to do this operation with more than three or four inches of the nickel wire, so that these electrodes had now to be attached to the current and voltmeter leads.

The insulation of the electrodes.

The electrodes had to be insulated from the lid of the specimen and at the same time had to be given a rigid support so that any move of the current or voltmeter leads would not cause the fragile filament to break. This was finally done as is shown in fig.(72). The nickel wire was given a small U bend and this was embedded in alundum cement. The alundum was dressed down to a tri- angular shape as shown and then baked. This had to be done before the filament was attached, otherwise it would have oxidised. When this was baked the filament was attached as has been described. The lid of the specimen was shaped to correspond to this triangular shape. The alundum rested on top of the main body of the specimen and when the lid was screwed down the baked alundum was held tightly. Any strain was thus taken by the alundum and not by the electrodes and filament. This is shown in fig.(73). Above this the electrodes were insulated from the lid of the outer steel block by means of silica sheathing. The lid of the outer steel block was made in two portions and these two pieces fitted over the silica sheathing as is shown in fig. (74).

The other ends of the electrodes had still to be attached to the current and voltmeter leads. These were now also made of 18 S.W.G. nickel. Spot welding was tried. This was unsuccessful because even if a weld was obtained, it was so brittle that it ruptured before the apparatus could be assembled. Flame welding with a very small /
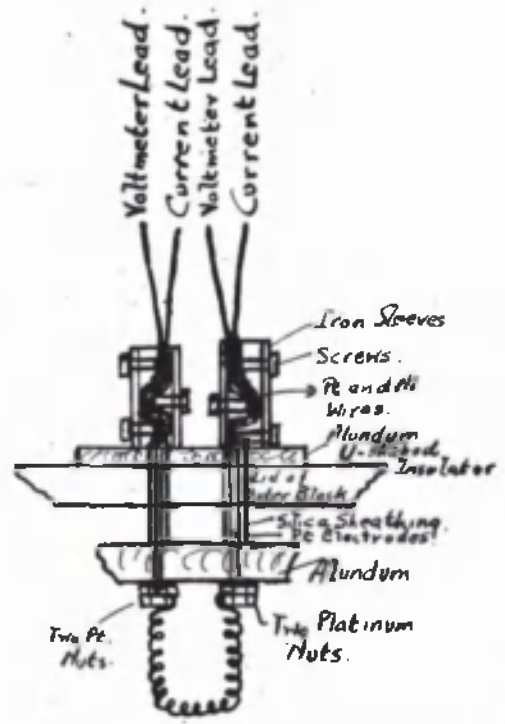
Holes for Electrodes

Annular Space for Slag.

Scale

Voltmeter Lead.
Current Lead.
Voltmeter Lead.
Current Lead.

Iron Sleeves
Screws.
Pt and Ni Wires.
Alundum U-shaped Insulator
Lid of Outer Block
Silica Sheathing
Pt Electrodes
Alundum
Two Pt Nuts.
Two Platinum Nuts.

Fig. 74.

Specimen

Annular Space for Slag

Space for Heating Coil.

Outer Block.

Alundum Ring

Steel Piping

Alundum Container Lid.

Fig. 73.

Alundum
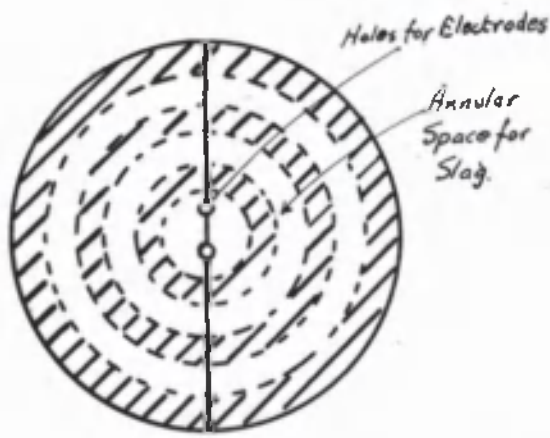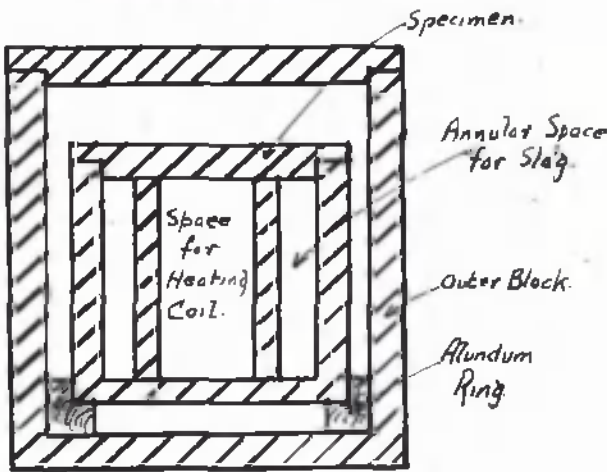
Fig. 72.

Scale :- Full Size   Fig. 71.
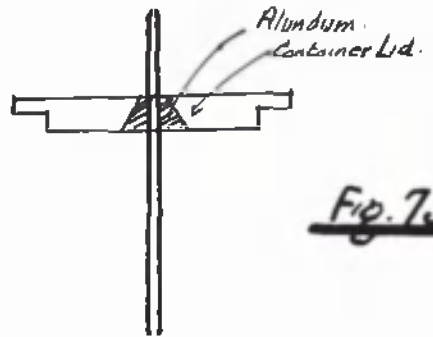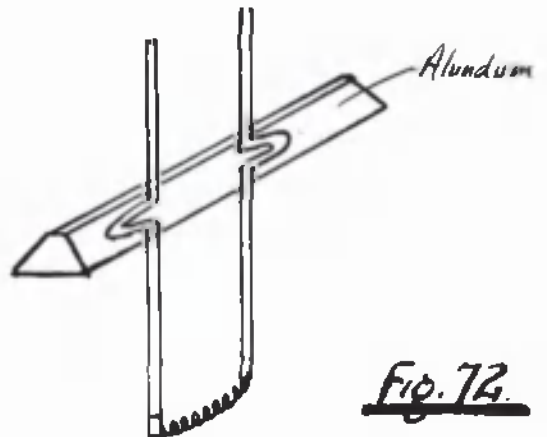
Part (VII)

small jet was next tried and this was moderately successful.
The apparatus was assembled and on the first run the weld
broke.   Every time the apparatus was heated to an elevated
temperature it became increasingly difficult to dismantle,
due to the screws becoming soft.   Also, every time the
apparatus was dismantled, the nickel electrodes worked
loose in the alundum, so that the fragile molybdenum
filament was broken very easily.

The work became punctuated with a succession of
welding, setting up, breaking of the joint, rewelding, and
breaking of the filament.

The molybdenum filaments introduced another difficulty.
The apparatus was designed to be used in a "pythagoras"
tube but since these have to be obtained from abroad, there
was difficulty in obtaining one of such large dimensions,
without a delay of several months.

From the sketches of the apparatus it will be seen
that the specimen and block were well enclosed, and so it
was decided to attempt the measurements in the train gases,
especially as in the previous work nitrogen had been found
to have very little effect.   However the train gases contain
small quantities of water vapour and this was sufficient to
oxidise the filaments.   It was possible to get one or two
determinations from the filament before it burned out.
Naturally the train gases were allowed to run for some time
before a current was passed through the filament, otherwise
it would have burned out.   It was decided to abandon the
use of the molybdenum filaments, and even though platinum
absorbs hydrogen, to attempt to use a coil of this metal.
Platinum- 10% rhodium was chosen because of its superior
mechanical strength.

The dimensions of the coil were fifteen centimeters
developed length by 0.008 ins. in diameter.   The coil was
wound in the same way as was the coil of Nichrome, but there
were /

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were no radiation tags. The ends of the coil were welded
to the nickel electrodes, and these were supported in the
alundum as has been described before. The ends of the
electrodes were welded to the ends of the nickel voltmeter
and current leads; this latter joint was the weakness of the
set-up, and finally the nickel electrodes were flattened
out, and pinched round the ends of the electrodes. This
was unsatisfactory because these pinched joints opened
at the high temperatures. With the dismantling of the
apparatus, the nickel electrodes worked loose in the alundum
and on the next heat the coil broke where it had been welded
to the nickel electrodes. This happened with such
frequency that it was decided to replace the nickel electrodes
by platinum ones. On inspection of the coil it was found
that the platinum was in perfect condition, but that it had
sagged at the high temperature, and that the winding had
welded together at points. It had been noted during the
work that there had been sudden drops in the voltage which
were now explainable as due to the short circuiting of the
parts of the coil due to the sagging.

The following has been adopted as the method of
making the coil. 20 S.W.G. platinum electrodes have been
used. The coil instead of being an open design as before
was made as shown in fig. (74) i.e. with a smaller diameter
of coil. This has been found not to sag at the high temper-
atures. Welding has been avoided by threading the ends of
the platinum electrodes. Nuts of platinum were made from a
larger diameter wire and these fitted on to the ends of the
electrodes, two on each. It was found that even after
heating to 1300°C, these nuts could be easily loosened, and
kept tightly screwed at the high temperatures. The method
of support in the alundum has been unchanged but the method
of attachment to the nickel electrodes has been modified to
avoid /

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avoid welding or pinching.

This was done by providing a sleeve for each electrode, as shown in fig. (74) which shows all of the modifications of the coil. The nickel leads were squeezed together and passed through the sleeve from the top to the bottom, while the platinum was passed up from the bottom to the top of the sleeve. When the three screws were tightened up a satisfactory joint was made. This design has withstood repeated heating to $1200^{\circ}C$ without failure. However another difficulty was found at these high temperatures, which is commented upon below.

Experimental Work at High Temperatures.

The thermocouple used was still the chromelalumel couple. This is not probably trustworthy at temperatures exceeding $1100^{\circ}C$, but the purpose of these experiments was to explore the difficulties and so develop a method by which results could be obtained with a fair degree of accuracy. The differential thermocouple system was used, and the method of taking mean specific heats over a small range was employed.

Theory of the Method.

The specific heats of the iron container were to be found throughout the range from say $950^{\circ}C$ to $1350^{\circ}C$. With the same container or one made of the same material, determinations were to be done over the same range with the slag in the annular space.

Thus, using the same symbols as before.

$$\frac{ECt}{J} = (M_1 C_P + M_2 C_S)dT$$

where M_1 is the mass of the iron container, and M_2 the mass of the slag. C_S is the required specific heat of the slag, over the range dT. C_P is already known from the blank determinations on the iron container, and is the specific heat of the iron container at the mean temperature of the range. /

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range.   No actual correction was made at this stage for the
alundum in the lid of the container.   This would be practically
constant, and it was intended to find the thermal capacity of
the complete container, including alundum at a later stage.
The same copper voltameter was used, and also the same volt-
meter and ammeter.

Difficulties Experienced.

        The first difficulty was that mentioned above in
connection with the coil.   The thermal expansion of the
various parts was a constant source of trouble.

1) The expansion of the leads caused the iron sleeves connect-
ing the electrodes to the leads to short circuit on to the lid
of the block.   This was finally cured by inserting a U-shaped
piece of baked alundum below the sleeves as shown in fig.(74).
The seat of the trouble was now shifted to the leads where
they came out of the outer steel piping.

2) The expansion of the leads caused the leads to press
against the metal lid of the outer steel piping and thus caused
the silica sheathing to break with consequent short circuiting
of the leads with the lid of the piping.   This was cured by
drilling the holes in the lid larger, and grouping the wires
from the specimen together in twos or threes and enclosing
these in a piece of thick silica sheathing.   The leads were
separately sheathed inside this.   This thick silica sheathing
stretched only for about an inch above and below the lid of
the piping.   The silica sheathing used was a piece of a
pyrometer tube.

3) The greatest trouble was however the embrittlement of the
leads and thermocouples.   The merest trace of sulphur in the
train gases would have caused the embrittlement of the nickel, and
there is always a trace of sulphuric acid vapour present in
these gases.   The hydrogen, too, would probably have an em-
brittling effect.   These leads were finally replaced with
iron wire leads and these behaved better, and although these
became brittle at the high temperature, they were not so prone
to fracture.

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fracture.

4) If during a run the leads did not fracture the thermo-
couple did.   On beginning a run, one could never be sure
that the leads would last out long enough to enable a
result to be obtained.

5) A difficulty was experienced which has not been explained
satisfactorily.   At the high temperatures, whenever the
current circuit of the coil was made or broken there was a
kick in the differential galvanometer.   This only happened
if the outer current in the furnace was running at the time.
If the coil current were running, and the outer furnace
circuit was made or broken the same thing happened.   This
was worse at some times than at others, and may have some
connection with the shorting or with the breaking of the
leads, because it was always worst just before the leads
broke.   The kick produced on the differential scale was
sometimes only two centimetres and at others it was more
than a full scale.   When it was only about two centi-
metres the work could still be continued, and this kick
allowed for.

The following results were obtained for the iron container.

Mean Temp.ºC	Temp. Range.	C_P	Remarks.	
319	31.8	0.175	Mo Filament.)	The oxidation
372.25	33.6	0.161	Mo Filament.)	of the
404	24.65	0.267	Mo Filament.)	filaments might
426.6	32.2	0.125	Mo Filament.)	have influenced
459	18.95	0.436	Mo Filament.)	the results.
485.45	32	0.134	Mo Filament.)	
532	19.22	0.443	Mo Filament.)	

These results show no agreement and when the diffi-
culties which have been recounted above are considered it
is not surprising.   With the new platinum-rhodium coil,
the first four runs were done to see if the determinations
could be repeated.   The results of these are reproduced
next. /

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Mean Temp.$^{\circ}$C	Temp. Range.	C_P	Remarks.
408	19.42	0.182	Pt-Rh Open type of coil
407	19.50	0.178	Pt-Rh Open type of coil
407	14.20	0.184	Pt-Rh Open type of coil
407	17.50	0.184	Pt-Rh Open type of coil

Thus it will be seen that the results seemed to be repro-
ducible to within about 3%. However results at other
temperatures did not agree at all well, although it must
be noted these results were obtained just before the coil
failed.

Mean Temp.$^{\circ}$C	Temp. Range.	C_P	Remarks.
452	14.05	0.24	Pt-Rh Open type of coil
465	9.36	0.191	Pt-Rh Open type of coil
494	19.75	0.200	Pt-Rh Open type of coil

On the strength of the four results which agreed
so well it was decided to try the method at higher temperat-
ures. The following were the results obtained.

Mean Temp.$^{\circ}$C	Temp. Range.	C_P	Remarks.
910	16.3	0.362	Pt-Rh Open type of coil
982	18.9	0.518	Pt-Rh Open type of coil
926	17.42	0.562	Pt-Rh Coil of small section
927.1	15.22	0.522	Pt-Rh Coil of small section
927.5	20.08	0.578	Pt-Rh Coil of small section
1061.0	7.14	1.525	Pt-Rh Coil of small section
+ 1163.4	5.85	3.60	Pt-Rh Coil of small section
1164.5	7.53	2.25	Pt-Rh Coil of small section
1165.2	5.46	2.39	Pt-Rh Coil of small section

These results are shown in fig. (75), but cannot be
said to be satisfactory. The result marked + is probably
due to some cause which was not noted at the time, however
it is plotted along with the others.

With one determination it was found that the outer
block cooled a little, and yet energy had still to be supplied
to the coil. This should not have been so, because on
cooling the specimen should have been at a higher temperature
than the outer block. The next experiment was therefore to
see if, when the outside furnace was kept steady, was any
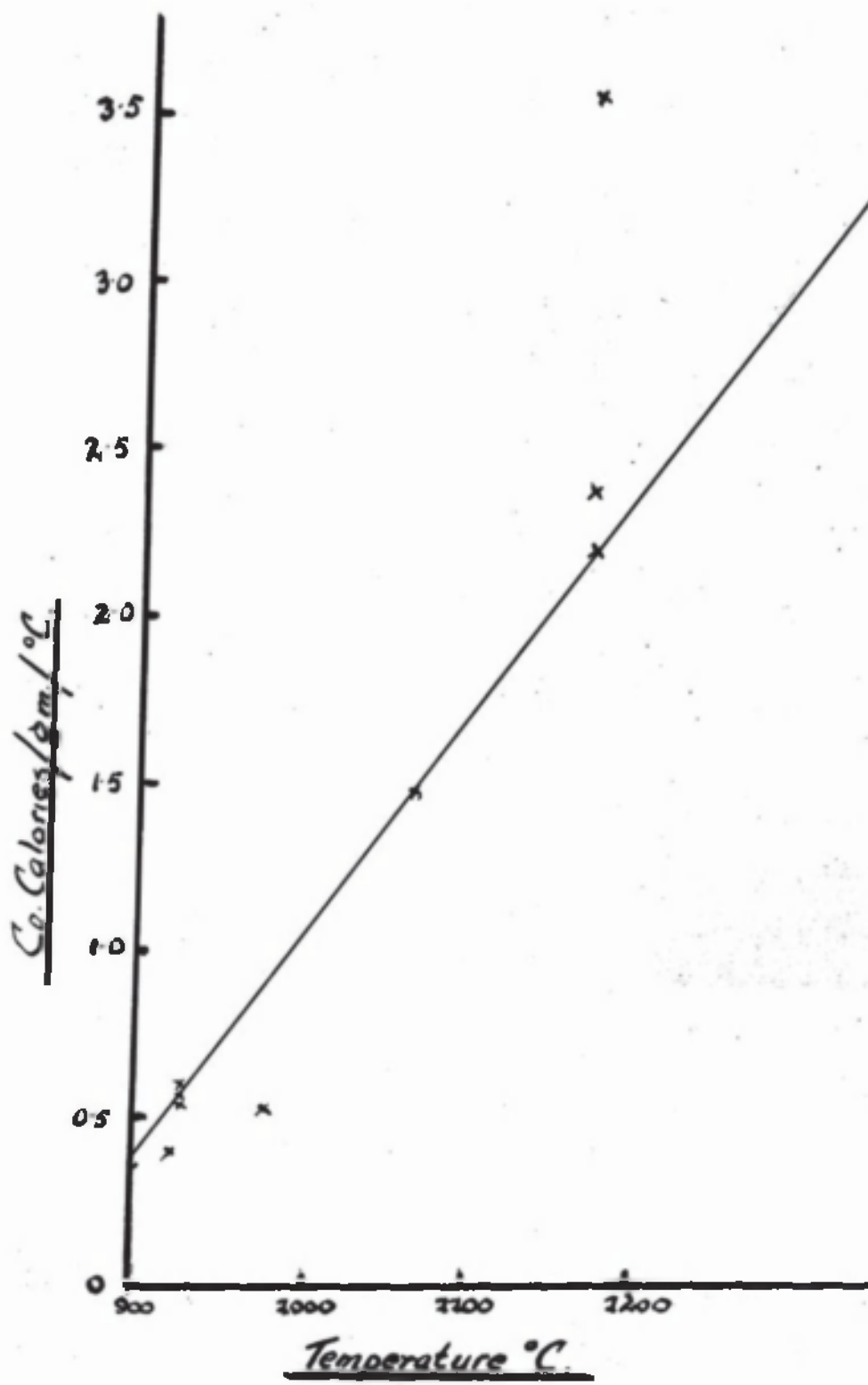current required in the coil to keep the specimen steady.

1) /

Fig. 75

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1) When the furnace was kept steady a current was necessary to keep the specimen steady.

2) With no current in the coil, the outer furnace was dropped in temperature, and it was found that the specimen became increasingly lower in temperature than the outer block.

The only explanation of this was that the leads were conducting away heat and that the specimen was in turn loosing some of its heat to the coil, this heat being conducted away along the nickel leads. The thermocouple leads would have affected the outer block more than the specimen because there were three leads from it and only one from the specimen. The whole loss was probably due to working in the train gases. The next step was therefore to shield the leads from the train gases. For this purpose, a hole was drilled in the lid of the outer steel piping to take a one inch Morganite tube. The lid of the outer steel block was recessed so that the Morganite tube rested firmly in the recess. The leads were brought out of this Morganite tube which came right out of the lid of the molybdenum furnace. The tube was cemented with alundum to the lid of the outer steel piping. The top of the tube was plugged with asbestos. However with this advance it was found that there was a greater strain on the thermocouple wires and the leads, and also that the differential galvanometer kicked very violently whenever the current was switched on in the coil. It was not possible to get any determinations done at all with the apparatus in this form. The work is still being continued, but from the experience obtained above the following points are to be observed.

1) The apparatus will be made larger. The mechanical difficulties of any apparatus of this nature are numerous especially at these high temperatures, but these were magnified greatly by using such a small specimen.

2) Even though the train gases do not seem to affect the specimen /

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specimen much, since it is so well enclosed, these affect
the leads and give a source of losses, which are unknown
and which cannot be estimated.

3) The work will therefore be done in a vacuum within the
temperature limits of a pythagoras tube, and since the effect
of a still atmosphere of nitrogen was found to have little
effect at low temperatures, attempts will be made to extend
the temperatures of the determinations by using an atmosphere
of nitrogen.

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CONCLUSIONS.

The term deoxidation is not strictly accurate,
unless the deoxidation products are removed from the bath
of molten steel.   If this is not so, then the total
content of oxygen in the steel is unchanged, although the
form of that oxygen is changed from an oxide which is
soluble in the molten steel and which is reducible by carbon,
with the production of carbon monoxide, to an oxide which is
practically insoluble in the molten steel, and which is
irreducible by carbon at these temperatures.   Aluminium has,
for that reason, been found to be very useful in the
production of sound ingots, because of the success with which
it changes the form of the oxygen to an aluminate, which is
insoluble in the steel and irreducible by carbon.   The
cause of blowholes is thus removed.

From that standpoint, the use of aluminium is
commendable, but difficulties arise due to the nature of the
resultant products of the deoxidation reactions.   The nature
of these inclusions, as shown by the work, of this thesis, is
directly against their easy elimination.   e.g. their low
surface tension means that two slag grains do not readily
amalgamate with diminution of surface, to form one larger
grain with a higher rising velocity.   The coalescence of
these grains depends, in the first instance, on their melting
point.   MnO and Al_2O_3 have high melting points and do not
coalesce readily.   FeO has a relatively low melting point,
and the effect of additions of FeO to either MnO or Al_2O_3 is
to lower the melting point and so increase the power for
coalescence.   However, from the ternary model as shown in
fig. (44) it can be seen that the zone of low melting
inclusions is confined to the high FeO, low MnO, low Al_2O_3
region in the FeO corner of the system.   If the conditions

of /

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of deoxidation could be controlled so that the composition of the resulting inclusion always fell on the eutectic trough there would be little difficulty in eliminating aluminate inclusions, provided that the MnO content were not too high.   However, a small deviation from the compositions on this trough, causes the liquidus temperature to rise to such an extent as to be soon above the temperature of the steel, with the exception of those inclusions in the high FeO corner.   The inclusions are therefore produced in a finely dispersed state throughout the bath and since the rising velocity depends on the square of the radius of a slag grain the chance of their rising in the bath is very small indeed, unless helped by some other agency such as stirring followed by a period of rest, or by the formation of a gas, for bubbles of gas have a power of concentrating slag grains around them.

As an example of inclusions formed by the use of aluminium as a deoxidation agent, Treje and Benedicks (Jour. Iron and Steel Inst. Sept. 1933) found in Armco Iron of the following composition

C   0.02% Mn   0.09% Si   0.01% P   0.017% S   0.028%

inclusions having the following analysis

FeO	50. 9%	to	68. 1%
MnO	0. 8%	to	1. 8%
Al$_2$O$_3$	48. 3%	to	30. 1%
	100. 0%		100. 0%

From fig. (45) it will be seen that the liquidus temperature of these inclusions will be between 1650-1750°C which is above the temperature of the liquid metal.

From what has been said it can be concluded, therefore that the deoxidation products of aluminium will, for the most part, remain in the steel after complete solidification.

This is accord with the experience of the works, that   /

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that it is possible to tell with a high degree of
certainty, whether aluminium has been used in the deoxi-
dation of the cast or not.   While the steel is acknowledged
to be sounder, it is found to contain a number of small
hard inclusions which do not become plastic at the temperat-
ure of working.   The latter fact is again explainable from
the work of this thesis.   The lowest solidus temperature
of the ternary system is that of the $FeO-Al_2O_3$ system and
this is at $1305^{\circ}C$, a temperature which is above the usual
temperatures of hot fabrication.   It has been found also
in the works that even if an aluminium-killed steel were
drawn to very fine wire these inclusions retained their
angular shape, and gave rise to a trouble called "holing
out".   In the work described in this thesis it has been
shown how the characteristic shape of these spinels is an
angular one.   It has also been shown how exceedingly hard
they are, thus confirming in a systematic way the works'
experience with "sand-spots".   The brittleness of these
inclusions probably is the cause of this trouble of "holing
out", which is caused by the abrasive action of the
inclusion on the dies.

The problem of slag inclusions has received greater
prominence in recent years with the development of the
higher tensile steels for aircraft, automobile, and general
structural steels.   In particular is the problem of major
importance with steels which have to be subjected to
alternating stresses.

The presence of a slag inclusion has an effect
approximating to that of a notch.   Mailänder (Z. Ver.
Deutch. Ing. V77, 1933) has shown how a notch on a polished
specimen of steel will lower the endurance limit.   The
amount of this lowering is shown to be greater for the
higher tensile steels.   Gough when discussing the key-way
problem in his book on "The Fatigue of Metals", concluded
that /

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that in the case of a milder steel which can yield by local overstress without propagating a crack it will, when stressed above its yield point, yield locally, while in a high tensile steel with an endurance limit far below its yield point, the yield point is not reached and the crack propagates. Thus with the higher tensile steels the importance of getting uniform stress distribution is greater than with the lower carbon mild steels. Slag inclusions, especially those which do not deform during the working of the steel have thus a more detrimental effect in a high tensile steel than in an ordinary mild steel. For that reason, steels killed with aluminium have a grave disadvantage for high duty alternating stress work.

The work which has just been described, also gives useful information of the behaviour of high alumina refractory materials towards slags. The behaviour is explained by the presence of the eutectic trough, with the liquidus surface steeply sloping on either side. In the case of a slag containing MnO, and FeO the melting point of the alumina will be lowered perhaps to the eutectic trough. However, since the concentration of the alumina rises as we leave the slag-brick interface and go into the brick, the melting point of any mixture will rise very sharply. For this reason, any attack of the slag in fluxing the brick will be confined to the surface in contact with the slag.

The position with respect to the specific heat determinations is not such as to warrant any conclusions being drawn, from that part of the work.