

THE THERMAL EQUILIBRIUM DIAGRAMS OF THE OXIDES AND  
SULPHIDES OF IRON AND MANGANESE.

by

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## INTRODUCTION.

The problem of non-metallic inclusions in steel has become increasingly important in modern times, and has been aggravated by the need of high-class material to withstand the heavy strains that are now deemed necessary. It is surprising, then, that fundamental data, pertaining to this most vital branch of steel making, is either lacking or awaiting confirmation. Although an enormous amount of literature has been published on the solidification of steel ingots, and a number of theories have been elaborated on the processes of segregation in these ingots, very little is known of the properties of the non-metallics concerned.

Before any systematic consideration of the properties of non-metallic inclusions can be carried out, it is first necessary to know the type of non-metallic matter that is most common to steel. For this purpose, it might be well to consider the conditions that prevail during the working of a steel charge.

A possible source of non-metallic matter is that which is brought in with the raw materials. The most injurious materials of this type are the sulphides which remain in the metal from the beginning to the end of the process. This is particularly so in the case of the Acid Open Hearth where the sulphur is not removed even to a small extent. Soon after melting the metal is covered with a slag that is mainly a double silicate of iron and manganese. During the 'boiling period' when the bath of metal is in a violent state of agitation due to the removal of carbon as carbon monoxide, this covering of slag becomes intimately mixed with the metal. It is possible, indeed it is very probable, that some of the furnace slag will remain in a finely disseminated state throughout the steel bath. There does not seem any reason to suppose that this slag will have altered in composition to any marked extent. During this period

also, the metal is practically saturated with FeO, the amount of FeO present depending entirely upon the concentration of FeO in the slag. The relation between the concentration of FeO in the metal and the slag has been worked out by McCance (1) who has found that it is governed by a constant partition coefficient. Just prior to tapping, the slag has become impoverished in FeO and the steel now contains a concentration of FeO which is in equilibrium with that in the slag. Herty (2) has shown that, at this stage, the steel is generally 60% - 80% saturated with FeO with respect to the composition of the slag.

When the steel is 'tapped' from the furnace into the ladle, a certain amount of furnace slag is inevitably admixed with it. There is every possibility that a swirling action takes place just above the tap-hole of the furnace, which has the tendency of sucking particles of slag down, and out into the ladle. Near the end of tapping a stage is arrived at when slag and metal inevitably run into the ladle together. The extent to which they mix, however, would seem to depend on the viscosity of the slag in question. A fluid slag, that is, one with a low viscosity, would be more easily mixed than a slag with a high viscosity such as a highly silicious slag from an Acid open hearth furnace.

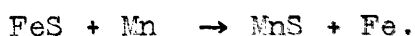
Another source of inclusion is the refractory material used in the furnace lining, the runner from furnace to ladle, and in the ladle lining. Undoubtedly, the refractories are worn away from the launder and ladle lining by the erosive action of a fast moving stream of metal, as well as by chemical corrosion.

However, the occurrence of furnace slag and refractory material in a steel ingot is rare. This is probably due to the fact that both the slag and refractory are present in the steel in relatively large sized particles which are removed by

rapidly rising to the top of the ladle provided the steel is allowed to remain at rest for some time before teeming.

The products of the reducing materials added to the steel bath just prior to, or during tapping, give rise to a much more troublesome type of inclusion which, owing to the fine state of division, is never completely removed. The deoxidants generally used are Mn, Si and Al and the products of the reduction of FeO in the steel are, MnO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. These primary products are capable of interaction one with another to form what might be termed secondary products. The secondary products would then be manganese silicate (MnO. SiO<sub>2</sub>), and ferrous silicate (2 FeO. SiO<sub>2</sub>). Since the reactions of reduction never proceed to completion the final inclusions will be a mixture of FeO, MnO, 2 FeO. SiO<sub>2</sub> and MnO. SiO<sub>2</sub>.

The sulphur, which is always present in greater or less amounts in the steel, exists before deoxidation in the form of FeS. When manganese is added as a deoxidiser the FeS is converted to MnS



In a properly deoxidised steel the manganese concentration has been increased to such an extent that it is problematical whether any FeS is present, that is, the reaction has practically proceeded to completion. Therefore, to the above probable inclusions present must be added MnS.

The solubility of these deoxidation products in steel is slight. Experimental determinations of the solubility of FeO in steel have been carried out by a number of investigators (3, 4). It is soluble to the extent of 0.94% at the melting temperature of iron. No determinations are available for the solubility of the other products, but from an analogy with FeO it is probable that the extent of the solution of MnO is about the same. MnS and the silicates are practically insoluble.

On account of their insolubility, then, they act as separate identities, so that it is only natural that they are easily detected by virtue of their distinctive characteristics. The usual methods used for detecting the presence of inclusions are those of etching, macro- and sulphur- printing and direct chemical analysis after separation. Whilst the first three processes serve admirably as methods of determining the distribution of the inclusions, they are practically useless in ascertaining the actual composition of the inclusions. The separation methods generally used are those of direct solution (5) of the steel in a weak acid in a current of air, and electrolytic solution (6). A comparison of the two methods shows that the direct solution method is apt to be misleading as it dissolves the greater part of the inclusion as well as the steel. As a result the inclusion amount by this method is always considerably lower than by the electrolytic solution method. It is worthy of note that the analyses of inclusions separated by the direct solution method are always high in silica which seldom falls below 45% - 50%. It would seem that the rest of the non-metallic matter had been dissolved away. Although these separation methods have their limitations and the results obtained may be erroneous, they do indicate, perhaps roughly, the nature of the inclusions. Analyses of non-metallic inclusions isolated from steel ingots have shown them to consist largely of silicates, sulphides and oxides.

Information regarding the melting temperatures of these inclusions is, however, lacking. It is obvious that non-metallic matter, which is solid and in a highly dispersed form at a temperature at which the steel is liquid, will have but a slight tendency to coalesce into larger particles and will, as a result, be entrapped in the solid ingot. On the other hand, non-metallic material which remains liquid to a temperature at

which the steel solidifies will have a greater tendency of coalescing into larger particles in the liquid steel, and will, therefore, stand a better chance of being eliminated by rising to the head of the ingot. This tendency to rise in the metal will increase with the size of the particle, which in turn depends upon the rate of coalescence, i.e., on the interfacial tension. These latter factors will increase as the melting points of the inclusions are lower with respect to that of steel. Further, the greater the degree of superheat of the liquid non-metallic particles, in relation to the melting point of the steel, the greater will be the tendency for them to rise to the head of the ingot. It is essential, therefore, to have some knowledge of the freezing temperatures of these non-metallic particles so that some methods for their elimination or for changing their compositions may possibly be devised.

The following binary systems were chosen for investigation being the most likely combinations to give useful results:

$\text{FeO} - \text{MnO}$ ;  $\text{MnO} - \text{MnS}$ ;  $\text{MnS} - \text{MnO} \cdot \text{SiO}_2$ ;  $\text{MnS} - 2 \text{FeO} \cdot \text{SiO}_2$ ;  
 $2 \text{FeO} \cdot \text{SiO}_2 - \text{MnO} \cdot \text{SiO}_2$ ;  $2 \text{FeO} \cdot \text{SiO}_2 - \text{FeS}$ .

FeO - MnO.

It was first necessary to prepare the pure compounds in sufficient quantity.

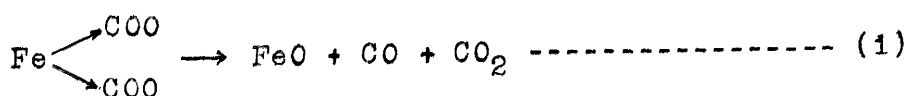
PREPARATION OF PURE FeO:

Very little help was obtained from the chemical literature on the subject for, whilst many references were cited no analyses of the products obtained were given. A number of methods were tried for the production of pure ferrous oxide.

Magnetic oxide, prepared by heating pure iron to bright redness in a current of air, was heated to 1050°C. in vacuo and maintained at that temperature for 6 hours. Although there was a marked increase in the amount of ferrous iron present, the resulting product was only approximately 50% pure.

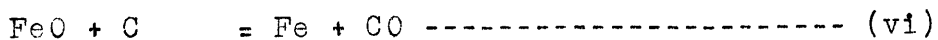
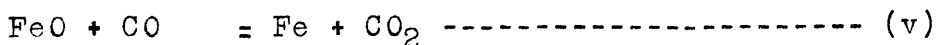
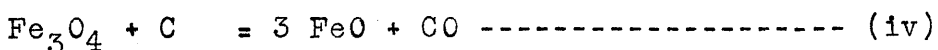
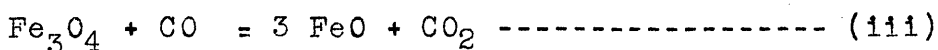
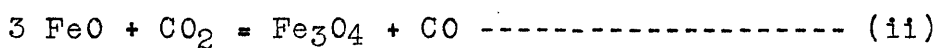
The product obtained by reducing Fe<sub>3</sub>O<sub>4</sub> with hydrogen at 500°C. whilst primarily FeO, was abandoned since the reaction was very difficult to control, and moreover, the purity varied from one lot to another.

FeO of a high degree of purity was finally prepared by decomposing pure ferrous oxalate in vacuo. At first very little attention was paid to the temperature to which the product was heated before all the gas had been withdrawn from the furnace tube. It was noticed that, according to the temperature to which the furnace had been heated, free iron, magnetic oxide and carbon accompanied the ferrous oxide. The decomposition of the oxalate takes place according to the following equation:-



If, however, there is a reaction taking place between the gases and the ferrous oxide when the oxalate decomposes, the following reactions are possible:-





During the decomposition of the oxalate an Edwards 'Hyvac' pump, capable of maintaining a vacuum of 0.01 mm. of mercury, was kept working continuously. It was evident, however, from the varied character of the product that the pump could not remove the gases quick enough to prevent them reacting together, and with the ferrous oxide.

To determine the correct conditions of temperature to obtain the pure product the following series of experiments were made:-

.5 gms. of pure ferrous oxalate was weighed into an alundum boat and placed in a porcelain tube in an electric furnace. A thermo-couple was inserted in the tube for the purpose of recording the temperature. The porcelain tube was evacuated by means of a mercury pump, prior to heating the furnace, and the tap between the furnace and the pump was then closed. The furnace was heated and allowed to remain for 1 hour at a predetermined constant temperature. A 50 c.c. gas sample was taken as the oxalate was decomposing, and another 50 c.c. sample after the furnace had remained at a constant temperature for 1 hour. The porcelain tube was again evacuated and the products were allowed to cool in vacuo.

Analyses of the solid and gaseous products were carried out over a range of temperatures from 500°C. to 1045°C. The analyses of the solid products are plotted against temperature in Fig.1, and the gas analyses, plotted similarly, in Fig.2. From the diagrams it can quite readily be seen that

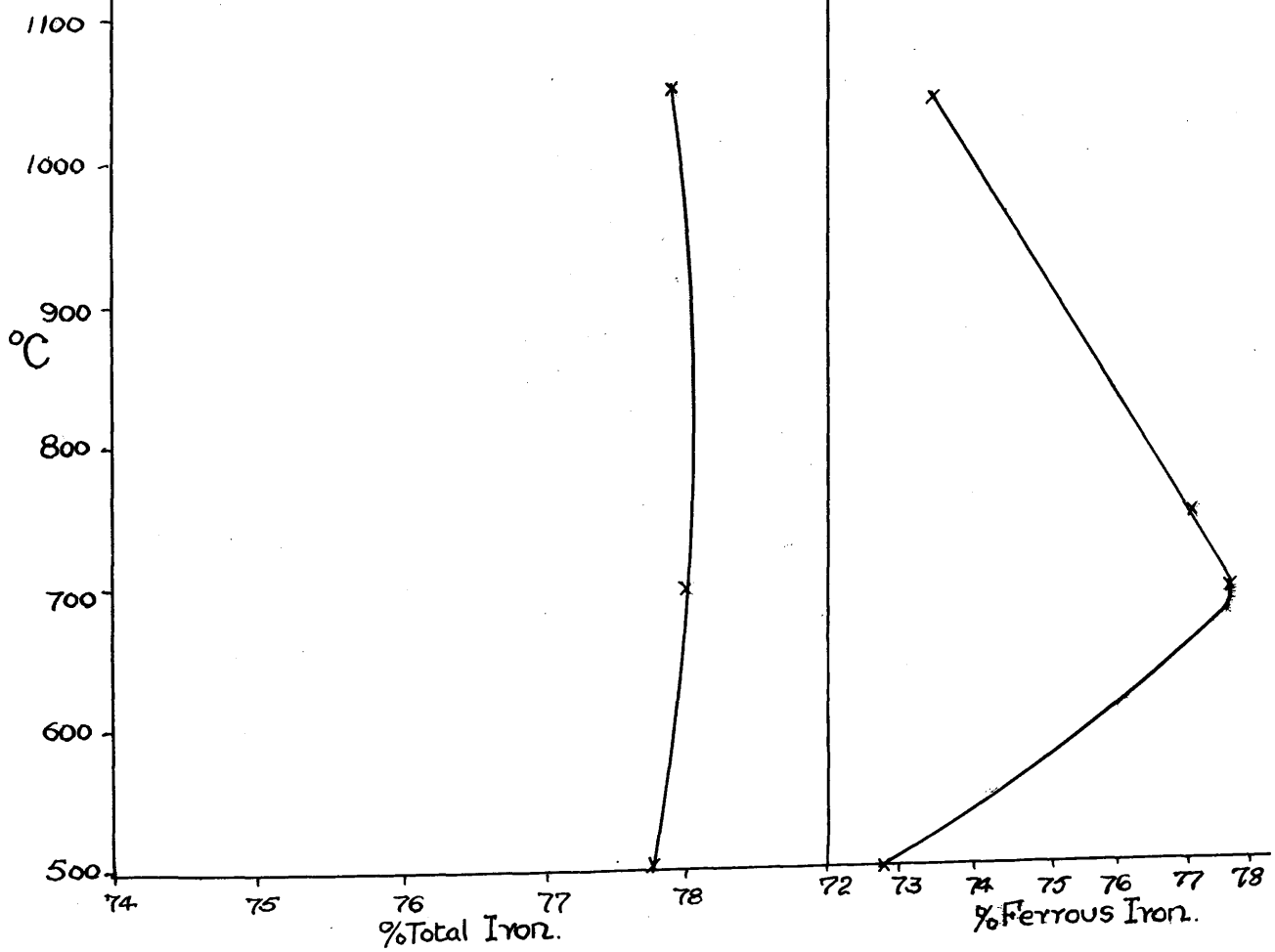
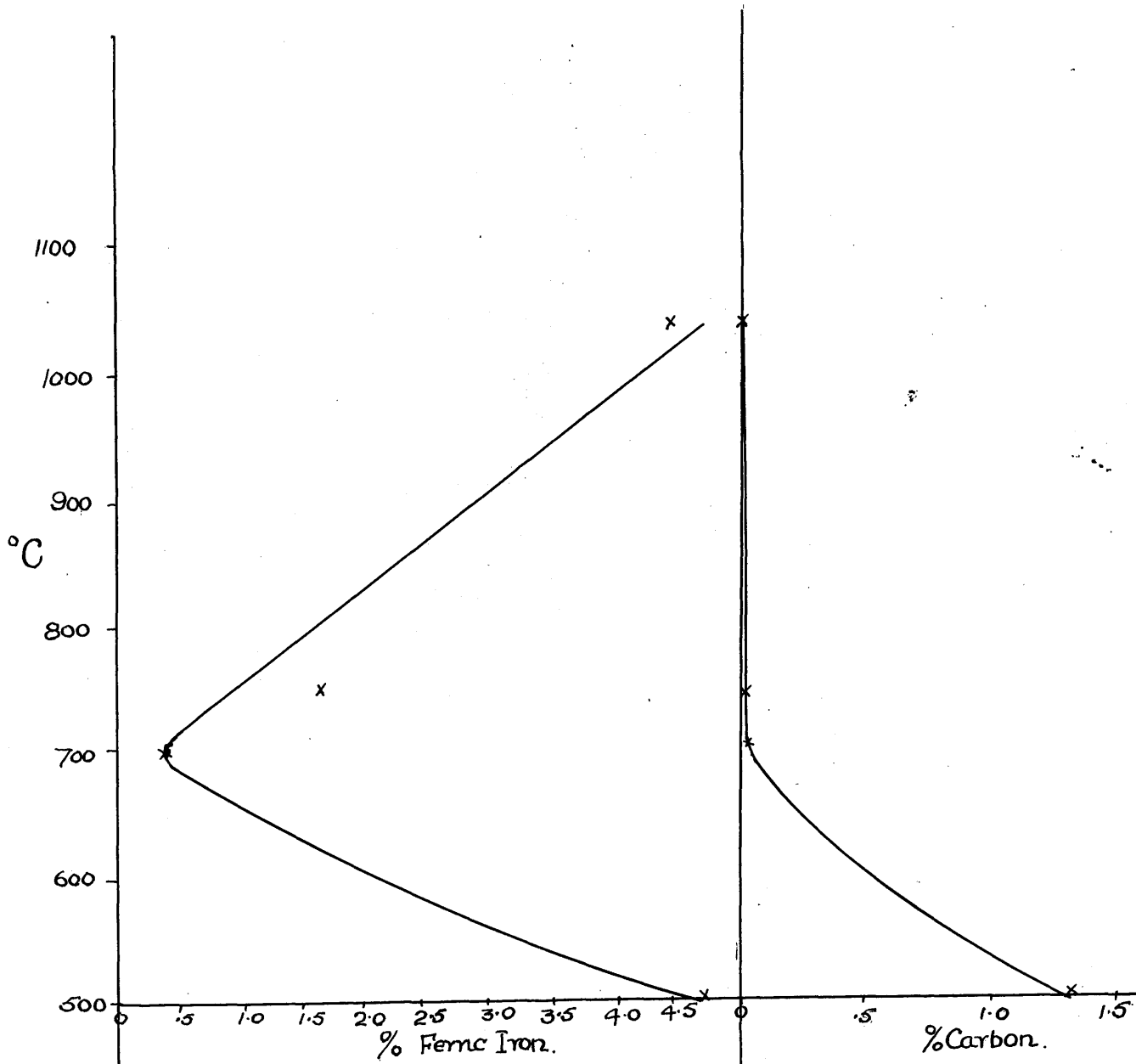


Fig. 1.

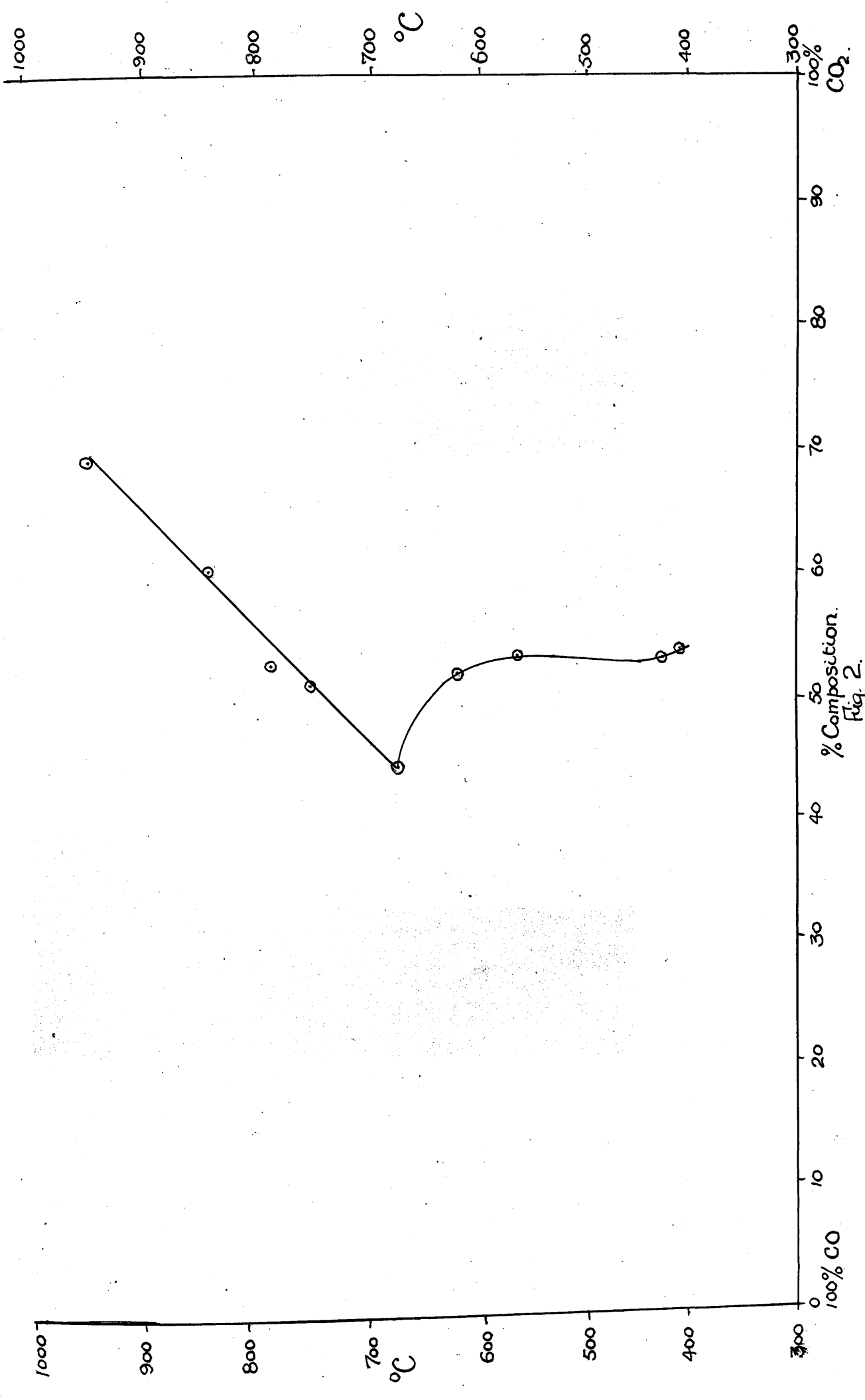


Fig. 2.

the purest product was obtained by soaking at a temperature of  $700^{\circ}\text{C}$ . The oxalate decomposed into equal volumes of  $\text{CO}$  and  $\text{CO}_2$ , and  $\text{FeO}$ , according to (1). If the temperature of the furnace were allowed to go above, or remain below,  $700^{\circ}\text{C}$ . free iron, or magnetic oxide and carbon respectively were found along with the  $\text{FeO}$ . The product obtained by soaking at  $700^{\circ}\text{C}$ . invariably analysed 99.0% pure.

When making the larger quantities required for the melts, the furnace was evacuated and the pump kept working continuously while the furnace was heating to, and at,  $700^{\circ}\text{C}$ . The amount of gas formed in the preparation of 200 gms. of ferrous oxide, which was the normal quantity made in one heat, is 200 gms., as will be seen from equation (i). This weight of gas at a temperature of  $700^{\circ}\text{C}$ . occupies a huge volume which the Hyvac pump could not reasonably be expected to remove in less than  $\frac{3}{4}$  of an hour. The gases and the products of decomposition were, of necessity, in intimate contact with one another. The products of decomposition were  $\text{FeO}$ ,  $\text{Fe}_3\text{O}_4$  and carbon. Even with the short time of contact between the gases and solid products, some gas-solid reaction must have taken place. The Carbon was probably dissolved in the  $\text{CO}_2$  as in equation (vii), whilst the magnetic oxide was reduced to  $\text{FeO}$  by the combined action of  $\text{CO}$  and carbon. Since the temperature was never allowed to go above  $700^{\circ}\text{C}$ . while the gases were being withdrawn, no free iron was produced. The furnace was maintained at  $700^{\circ}\text{C}$ . until all gas evolution had ceased. In this manner, non-magnetic, crystalline ferrous oxide was prepared which always showed a purity greater than 99.0%.

#### PREPARATION OF PURE $\text{MnO}$ :

The preparation of  $\text{MnO}$  of sufficient purity at first presented some difficulty. The higher oxides were difficult to reduce by means of hydrogen and the product was not pure.

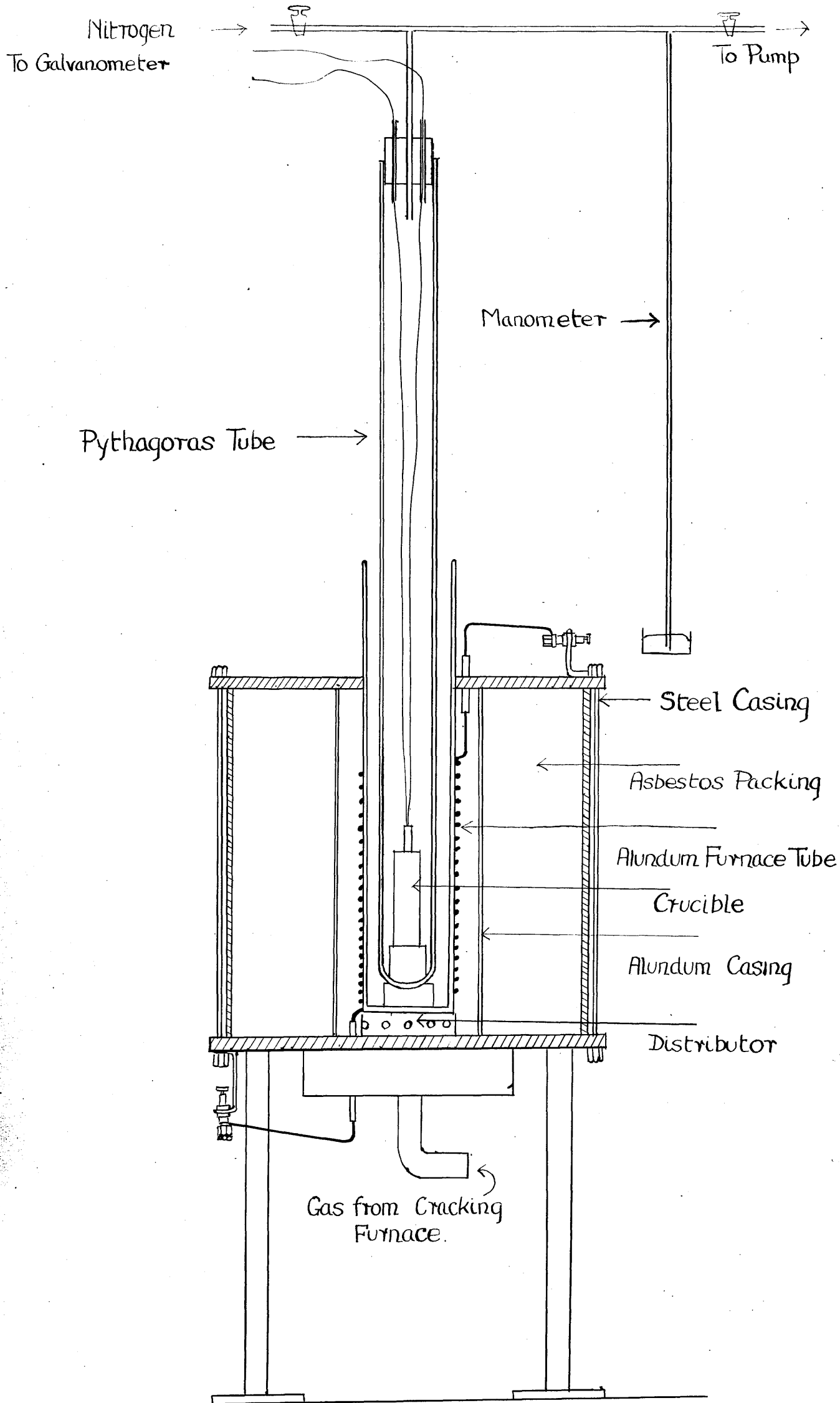


Fig. 3.

is delivered to the furnace.

The alundum tubes were made by coating an iron former, of the required size and previously wrapped round with two or three layers of brown paper, with an alundum cement. The cement was made up of 90 parts of coarse alundum and 10 parts of fine, moistened with water to the desired consistency for easy working. After air-drying the tubes were rubbed-down to shape with a coarse emery paper, and the former separated from the alundum tube by burning the brown paper at 400°C. - 500°C. The tubes were then baked at 1000°C. Tubes made in this manner have given excellent service both in respect of their strength and their ability to withstand sudden changes of temperature without cracking.

The furnace was operated on a 250 v. direct current electrical supply, 25 - 30 amps. being necessary to heat the furnace to a temperature of 1700°C. The heat-insulating material used in this type of furnace was asbestos wool.

#### REFRACTORY MATERIALS FOR CRUCIBLES:

A refractory material was necessary that would not react with either of the molten oxides and that would be sufficiently infusible to retain its shape at the very high temperatures employed. Owing to the success in making the alundum furnace tubes it was decided to make crucibles from the same cement mixture. The crucibles were moulded into shape by means of a wooden pattern, dried, and baked at the highest temperature available in the molybdenum furnace, that is, about 1650°C. The resulting crucible was exceedingly hard and showed a very fine fracture. However, it was found that as soon as the oxide melted it was completely absorbed by the crucible walls. Whilst there was certainly no chemical attack between the alundum and the molten oxides, the porosity of the crucibles was so great that this method had to be abandoned. By increasing the

proportion of fine alundum in the cement, crucibles were obtained that were much less porous but their susceptibility to form cracks after baking was so great as to make them useless.

Many unsuccessful attempts were made to make a satisfactory magnesia crucible. Although numerous types of bonds, such as magnesium chloride, magnesium nitrate, iron oxides, etc., were tried, it was practically impossible to make crucibles free from cracks. In addition, the time taken to prepare the magnesia and to dry the moulded crucibles, together with the very delicate skill needed in baking them, made their preparation on a large scale impossible.

An attempt to obtain the melting temperature of ferrous oxide with an iron crucible was next tried. A rod of Armco iron was drilled out to form the crucible and an iron sheath served to protect the thermo-couple from the molten oxide. Although the iron crucible withstood the temperature and in no way affected the composition of the oxide, it was very difficult to obtain a satisfactory temperature reading. At about 1300°C. the mirror galvanometer began to oscillate so badly that no readings could be taken. Replacing the iron sheath by one of alundum was no more successful. The iron crucible was insulated from the furnace by a large block of alundum; its outside walls coated with a thin film of alundum, even earthing the crucible, failed to remedy this condition. The iron crucible was abandoned.

By incorporating 10% of finely crushed and fully shrunk magnesia into the ordinary alundum cement mixture, a crucible was obtained that approached, more nearly, the properties required of it. It was still porous in parts but its texture was very much finer than that of the alundum crucibles. It was thought that if the magnesia were finer and more intimately mixed with the alundum, a crucible that would suit

the purpose, could be made. After a number of fruitless attempts, the following procedure gave the type of crucible that was required:

Alundum crucibles, made in the usual way, dried and baked, were soaked in a saturated solution of magnesium nitrate, in vacuo. The crucibles were soaked in the nitrate solution until all air bubbles, emanating from the pore-spaces of the alundum, had ceased to be given off. It was then evident that the magnesium nitrate had filled all the pores of the alundum completely. The crucibles were first dried and then baked at about 700°C. At this temperature the magnesium nitrate decomposed into magnesia which was very finely disseminated throughout the crucible. After this preliminary baking, the crucibles were fired at 1550°C., at which temperature they became glazed. The resulting material had a texture almost as fine as porcelain and had little power of absorption for the oxides melted in it. Above a temperature of 1550°C., they became very soft and began to lose their shape. Fortunately, however, the mixtures having higher melting temperatures than 1550°C., that is, mixtures rich in MnO, were not so readily absorbed by the crucible. For these melts the ordinary alundum crucible was quite satisfactory.

The thermo-couple sheaths were always made of the same material as the crucible and were moulded to shape in a wooden pattern. The crucibles and sheaths were, in all cases, made by hand.

#### THERMO-COUPLE:

In view of the high temperatures that it was necessary to record, and the unreliability of a platinum/platinum-rhodium couple used at these temperatures, it was decided to use a thermo-couple constructed of tungsten and molybdenum wires. The thicknesses of the tungsten and molybdenum wires were 0.4 mms. and 0.635 mms., respectively. The hot junction of the



couple from the furnace tube, to prevent the slightest electrical leakage, had no effect. As the only alternative explanation of the phenomenon, it was thought that the molybdenum heating unit emitted a stream of thermions at elevated temperatures. The obvious remedy, from a consideration of a thermionic valve, was the insertion of a grid between the heating unit and the thermocouple. The grid was constructed by binding a number of lengths of molybdenum wire along the length of an alundum tube which was insulated from the furnace. With the use of the grid the difficulty disappeared. The life of the wire grid, however, was very short. It ceased to function after two or three heats due, probably, to a superficial oxidation. Strip molybdenum, about  $\frac{1}{2}$  inch broad, instead of the wire was much more efficient and survived for a larger number of heats. Latterly a sheet of molybdenum was used as a grid and was found to be perfectly satisfactory in every way. Had alternating current been available, this difficulty would, naturally, not have arisen.

Before any determinations of the melting temperatures of the oxides could be carried out, it was necessary to protect them from the air and from the furnace gases (hydrogen and nitrogen) owing to the ease with which they, especially ferrous oxide, were either oxidised or reduced. A tube of pythagoras material, closed at one end, was used for this purpose.

The oxides, or the particular mixture of oxides, were pressed as tightly as possible around the thermo-couple sheath in the crucible. The pythagoras tube was then evacuated by means of a Hyvac pump which was kept working continuously throughout the determination. After one or two heats the tubes collapsed completely. Although the pythagoras material was capable of withstanding a vacuum at  $1600^{\circ}\text{C}$ . the pressure difference between the outside and inside of the tube was too great for its diminished strength. The tubes were strengthened by placing

inside them a second tube of hard burned alundum with  $\frac{1}{8}$  inch thick walls. This, whilst prolonging the life of the tubes for one or two heats, did not prevent them from collapsing. In passing, it might be interesting to note the very destructive effect ordinary atmospheric pressure has on refractories. When one of the sagged pythagoras tubes was broken, the author was surprised to find the strengthening alundum tube and the crucible crushed into fragments. It might seem more surprising when it is said that it was difficult to break one of these alundum tubes with a hammer.

It was found impossible to melt the oxides under a vacuum because no refractory could be obtained that would stand up to the strain necessary. The only alternative was to melt under nitrogen. A stream of nitrogen passing over the heated oxides would have been objectionable, not only because it would have seriously affected the temperature readings, but also because it would have necessitated a purifying train for the large volume of gas that would be needed. Nitrogen at atmospheric pressure was open to the same objection since as the furnace heated it was blown out through the manometer arrangement thus creating a gas current. By the device shown in Fig.3 nitrogen at low pressure could be introduced into the pythagoras tube. The procedure, which was very satisfactory, and was adhered to throughout this investigation, was as follows:-

The tube was evacuated and a small amount of nitrogen was then admitted so that the pressure registered on the manometer was about  $\frac{3}{4}$  to  $\frac{1}{2}$  of one atmosphere. As the temperature of the furnace increased, the pressure inside the tube increased until at  $1600^{\circ}\text{C}$ . a pressure of very nearly one atmosphere had been attained. This device effectively prevented the buckling of the pythagoras tubes which could be used under these conditions for an indefinite number of times.

Great trouble was experienced, in the initial stages of the work, by the pythagoras tubes cracking after being heated to high temperatures. This feature was particularly prevalent if the tubes had been left unheated for periods of from four days upwards. Although a new tube gave off a considerable quantity of steam on its first heat, it never cracked. No explanation has been found for this peculiar behaviour and the only remedy was never to allow a tube to remain unheated for more than a week-end.

All temperature measurements given in these investigations were made on a Tinsley Vernier potentiometer. The method of obtaining the heating and cooling curves was to take readings of time for every increase or decrease in thermo-couple voltage of 20 micro volts. This was equivalent to a temperature difference of  $3^{\circ}\text{C}$ . The curves thus obtained were, in all cases, plotted as increase rate curves.

#### MELTING POINT CURVES FOR THE SYSTEM FeO - MnO:

The curves are shown in Fig.4 to Fig.7. FeO was found to melt at  $1410^{\circ}\text{C}$ . In order to obtain the melting point of pure FeO as accurately as possible, melting points were taken of every batch of oxide made. The melting curves thus obtained were found to agree perfectly and all showed an absorption of heat at  $1410^{\circ}\text{C}$ . On cooling the melted oxide no heat evolution was recorded until  $1170^{\circ}\text{C}$ . when a small transformation was seen to take place. The only point obtained on heating the same melt, immediately after cooling below the  $1170^{\circ}\text{C}$ . point, was at the melting temperature. If a cooling curve were taken of the fused oxide from  $1300^{\circ}\text{C}$ ., that is, below its melting temperature, the point on cooling still persisted. After annealing the oxide in vacuo for four weeks between  $1100^{\circ}\text{C}$ . and  $1150^{\circ}\text{C}$ . the change point on cooling had completely disappeared. The large difference of  $240^{\circ}\text{C}$ . between the melting and freezing temperatures, together with the disappearance of the cooling point on annealing,

Heating Curves

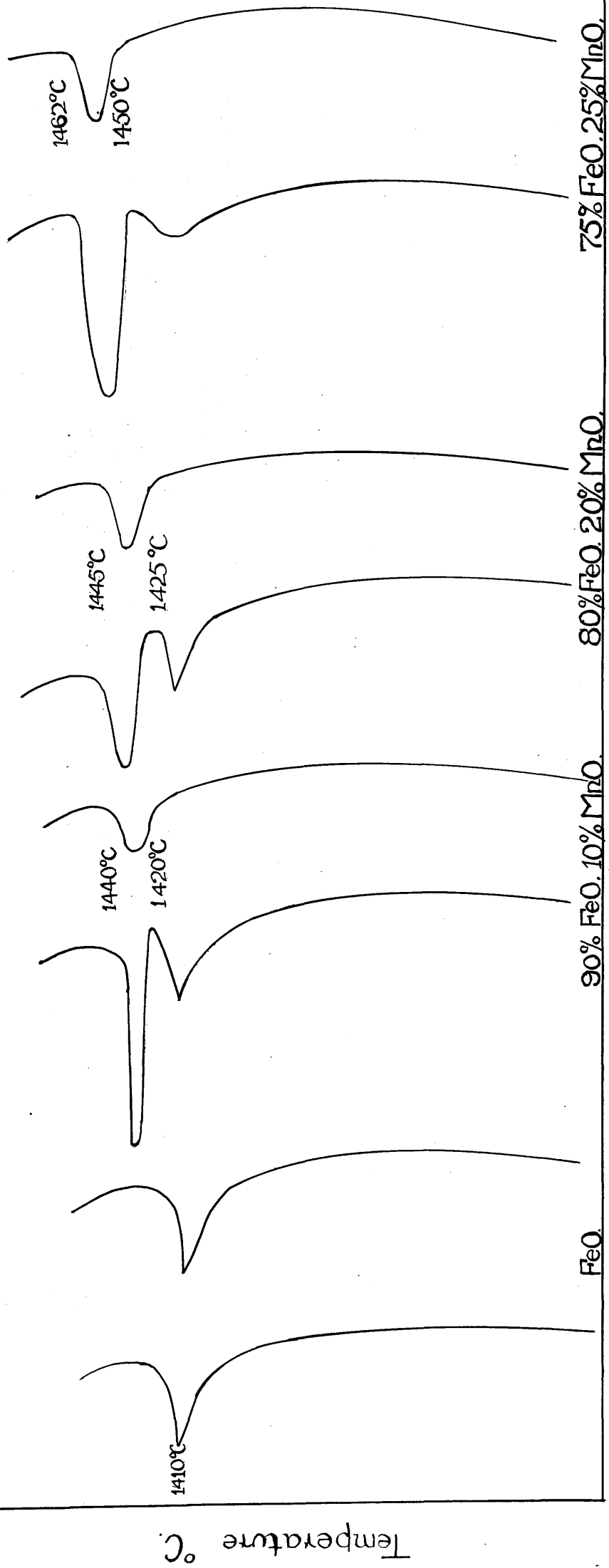


Fig. 4

Heating Curves.

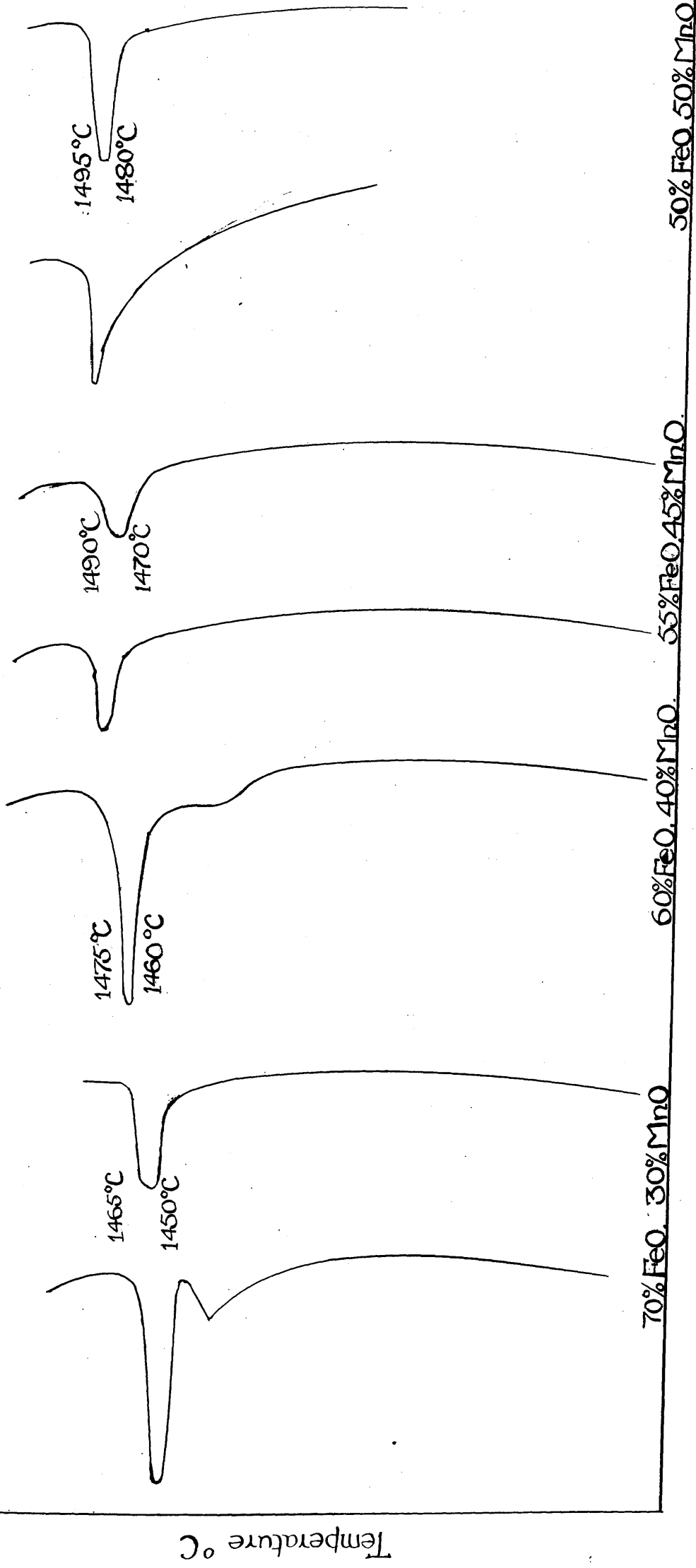


Fig. 5.

Heating Curves.

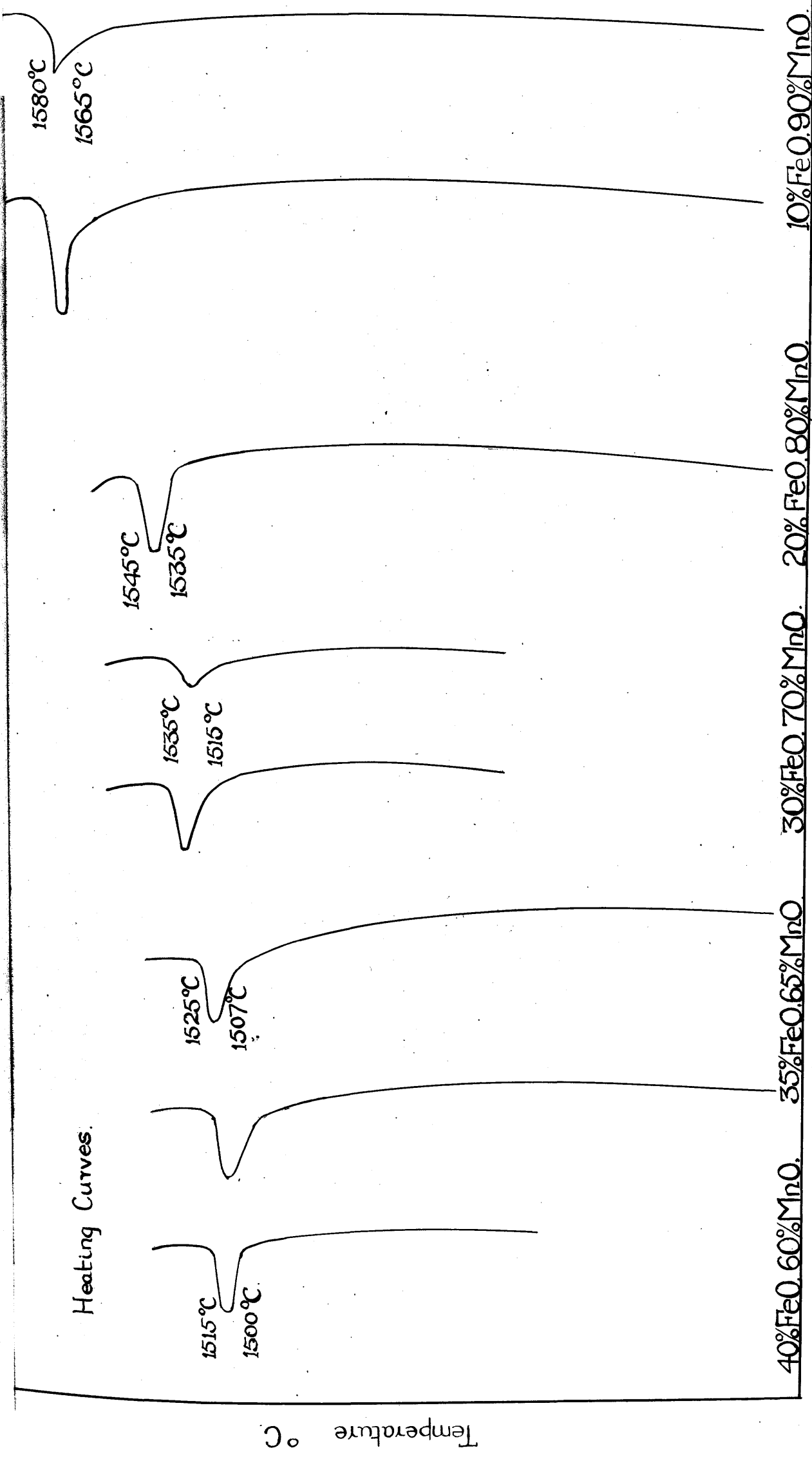


Fig. 6.

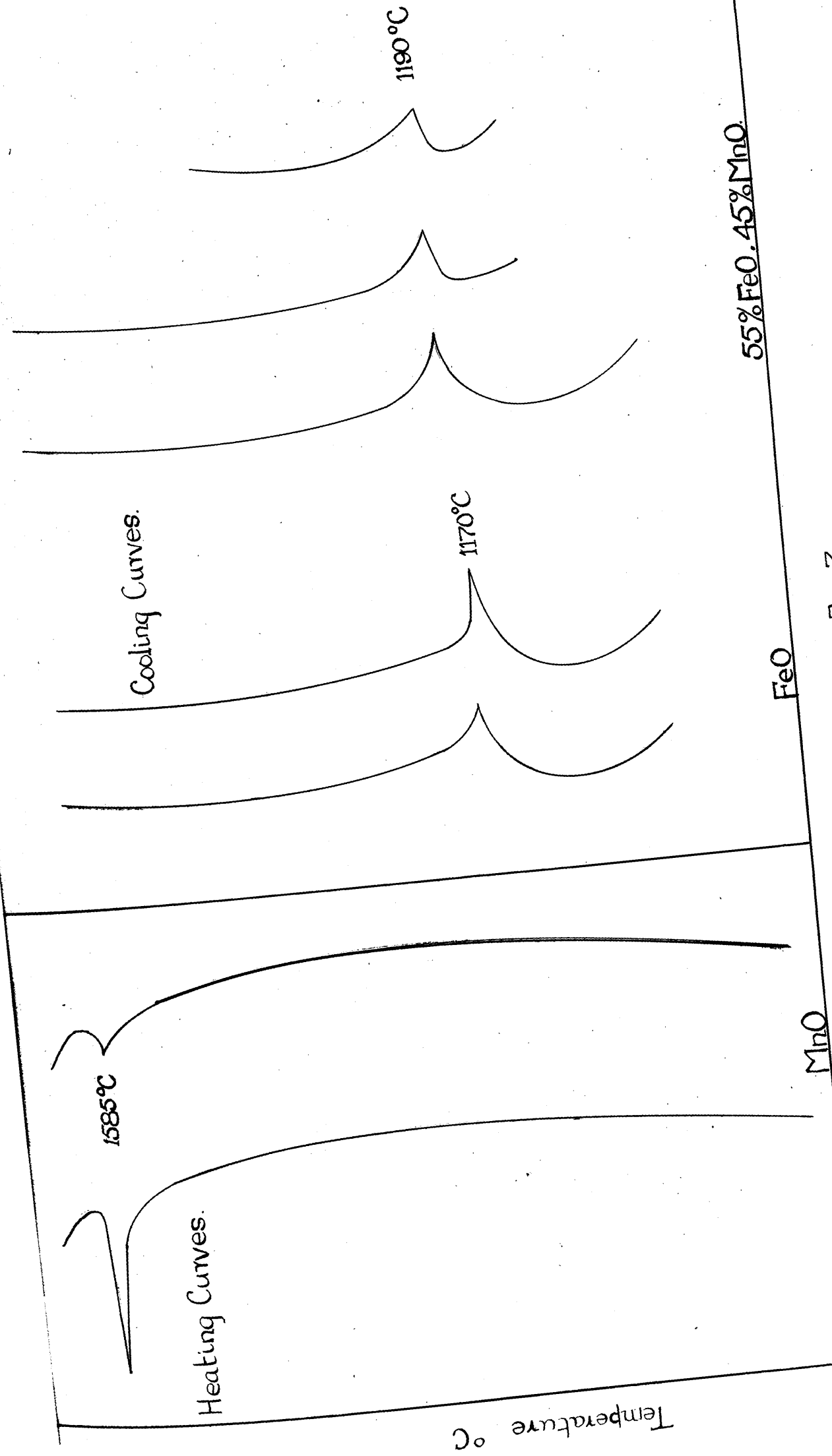


Fig. 7.

suggested that the large lag was due to supercooling. Micro-examination, as will be explained later, amply justified this view. The cooling curves of FeO are shown in Fig.7.

The mixture of the oxides up to that containing 50% MnO always showed two points on the first heating curves, the lower point occurring at about  $1410^{\circ}\text{C}$ . The second heating curve, however, only showed one heat absorption which corresponded in the majority of cases with the upper point in the first curve. Although the powdered oxides were mixed as thoroughly as possible before being placed in the crucible, it was evident that the FeO melted first at its normal temperature and then the MnO was dissolved in it giving rise to the upper point, which was the normal melting point of the homogeneous mixture. It was the second curve, however, which gave the true melting point of the homogeneous mixture. In the mixtures containing more than 50% MnO the lower point on the first heating curve was absent, and the melting points obtained in both curves were identical.

The cooling curves showed the same characteristics as those of pure FeO except in the case of melts containing more than 90% MnO when the change point on cooling was absent or at least it occurred at a temperature below the useful range of the molybdenum-tungsten couple. Fig.7 shows three cooling curves of the 55% FeO. 45% MnO melt which illustrates the persistence of the lower point after cooling from  $1250^{\circ}\text{C}$ . Fine mixtures of the two oxides were annealed for four weeks at  $1100^{\circ}\text{C}$ . and  $1150^{\circ}\text{C}$ ., and in every case the point obtained on cooling was entirely absent. The data obtained from the heating curves is plotted in Fig.8; the solidus line has been derived from the points in the curves at which they deviated from the normal.

The diagram differs considerably from that of Oberhoffer and Von Keil (7) but is similar to that of Herty (8). The melting temperatures of FeO and MnO given by Herty are  $1365^{\circ}\text{C}$ . and  $1610^{\circ}\text{C}$ .



FeO - MnO

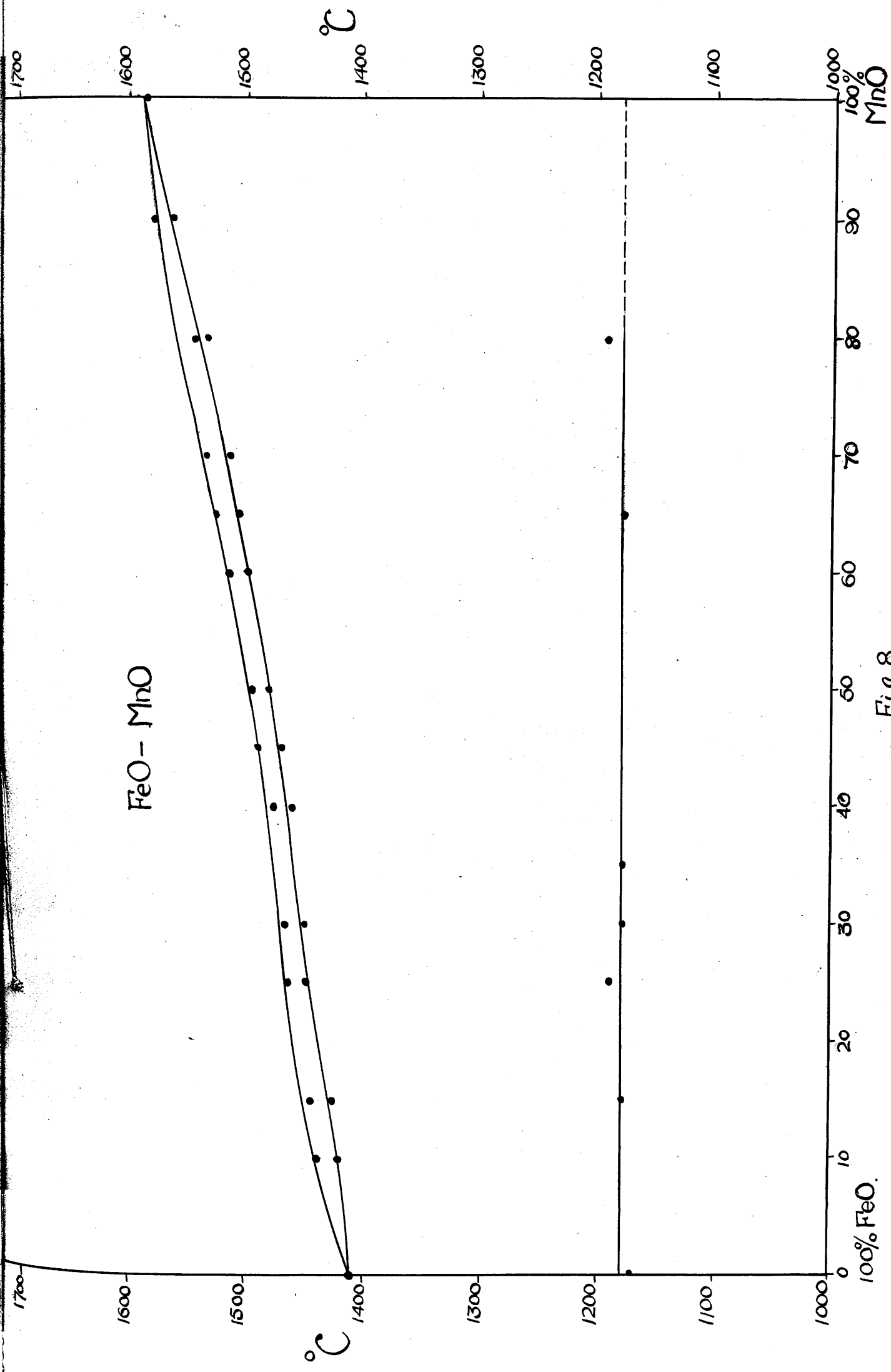


Fig. 8.

respectively, and the liquidus and solidus in his diagram are much further apart than in the diagram given by the author. Pfeil (9) states, in a recent publication, that FeO decomposes at 575°C. into Fe and Fe<sub>3</sub>O<sub>4</sub>, two strongly magnetic substances. The author has been unable to find any indication of a transformation at 575°C. and has produced FeO which is completely non-magnetic even when placed under strong electro-magnetic fields.

#### MICROSTRUCTURES:

Before polishing, the specimens were set in sealing wax in metal rings, as they were found exceedingly difficult to polish otherwise. They were all etched in dilute hydrochloric acid.

Every melt was sectioned and microscopically examined, typical examples being shown in Fig.9 to Fig.20.

Fig.9 shows FeO in the as cast condition. The acicular markings are in all probability due to the initial stages of crystallisation. After annealing for 6 days the structure becomes much more homogeneous and is shown in Fig.10. Fig.11 represents an area in the 80/20 melt in the as cast condition. The material around the crystal grains and penetrating into the grains, is probably some supercooled liquid that has not been able to crystallise. Fig.12 shows the same melt after annealing for 4 weeks at 1100°C. to 1150°C. The structure is practically homogeneous. Fig.13 was taken from a 50/50 melt in the as cast condition and shows a very well defined acicular structure which appears to be controlled by the position of the cleavage planes of the already crystallised material. After annealing for four weeks a structure similar to that shown in Fig.14 was obtained. It was perfectly homogeneous (the black markings shown are holes). A number of the melts show a marked eutectiferous structure that was not peculiar to a particular melt, but was associated

with every mixture in different degrees of distinctness. Fig.15 is an excellent example of this type of structure. This specimen on annealing became homogeneous. It points to the fact, then, that the structure is not a eutectic, but a stage in the devitrification of the supercooled liquid. Crystallisation has started from a point and has developed in at least six directions. Fig.16 shows an earlier stage in the devitrification of the glass. The supercooled liquid surrounding the crystal grains typical of most of the mixtures can be seen from Fig.17. The same specimen on annealing produced the structure shown in Fig. 18. Figs.19 and 20 represent pure MnO in the as cast and annealed condition, respectively.

No reactions in the solid were recorded by taking heating and cooling curves of the annealed specimens with a platinum/platinum-rhodium thermo-couple.



Fig.9. FeO  
x500



Fig.10. FeO  
x 200.

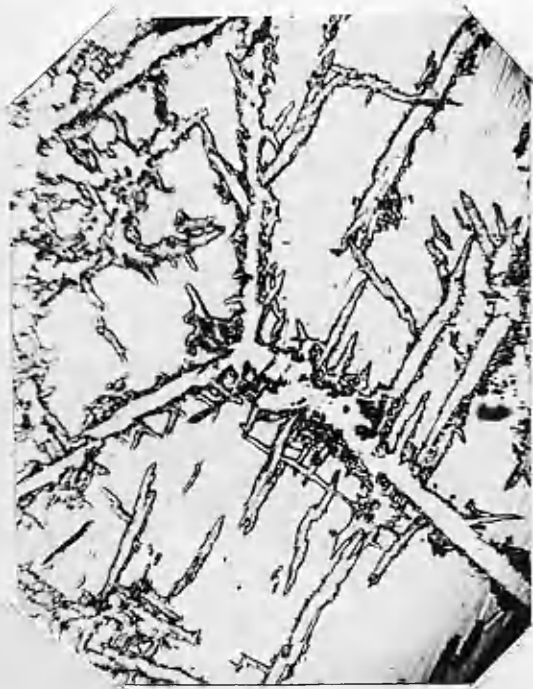


Fig.11. 80%FeO. 20%MnO.  
x500.



Fig.12. 80%FeO.20%MnO.  
Annealed x200.

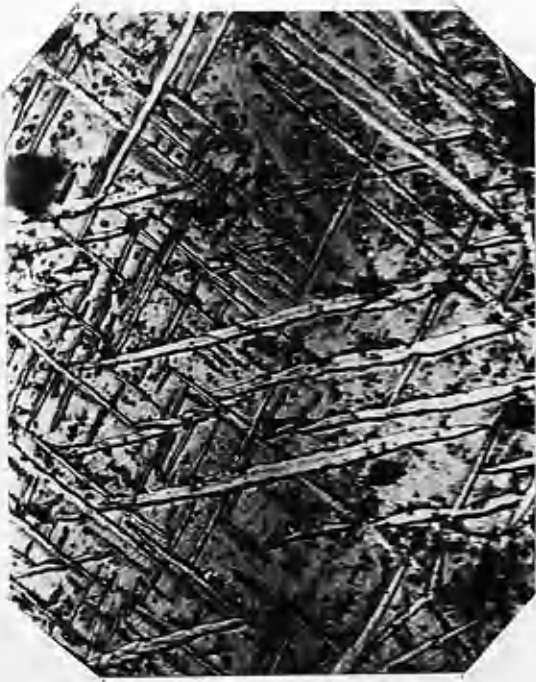


Fig. 13. 50% FeO. 50% MnO.  
x 500



Fig. 14. 50% FeO. 50% MnO.  
Annealed. x 500.

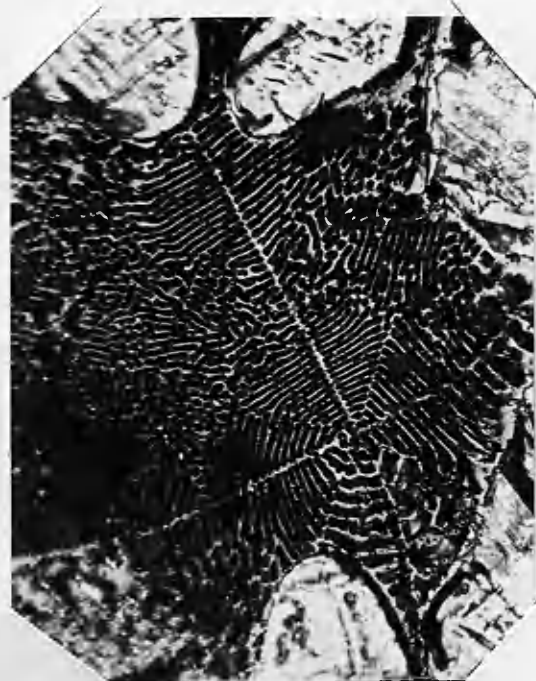


Fig. 15. 45% FeO. 55% MnO.  
x 500.



Fig. 16. 35% FeO. 65% MnO.  
x 500.



Fig. 17. 20% FeO. 80% MnO.  
x 500.

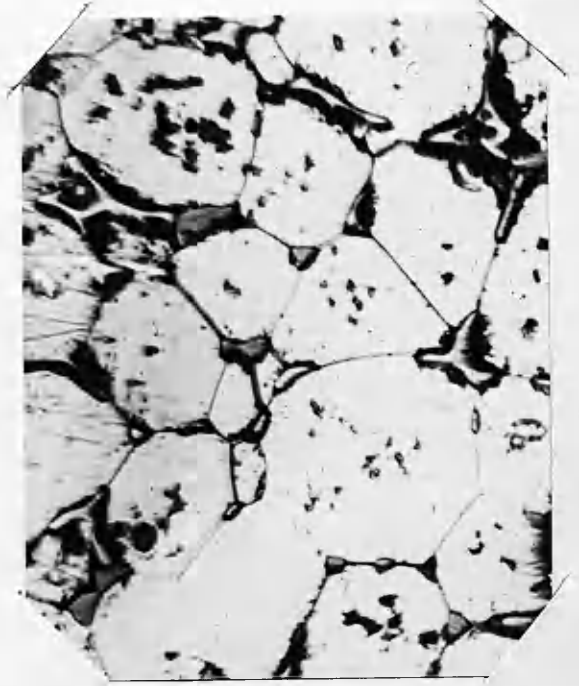


Fig. 18. 20% FeO. 80% MnO.  
Annealed x 500.



Fig. 19. MnO  
x 500



Fig. 20 MnO. Annealed.  
x 500.

MnO - MnS.

The determination of the system MnO - MnS presented no new difficulties from those that had been satisfactorily solved for the system FeO - MnO. The method of melting the mixtures and of taking their melting temperatures were identical in both cases, and have been adhered to throughout these investigations.

PREPARATION OF PURE MANGANOUS SULPHIDE:

A number of wet methods were first used for the preparation of MnS, but none were successful owing to the large volumes of solution that had to be filtered and to the ease with which the sulphide oxidised when exposed to the air. Although attempts were made to filter under neutral gases, the time taken to produce large quantities of sufficient purity was too great, and an easier and cheaper method was sought. Eventually, manganese sulphide, free from foreign impurities, was purchased. It was found that this sulphide contained an excess of manganese, probably as an oxide. After much experimenting, the following procedure gave MnS of the required purity by means of a simple, though efficient, process.

The impure sulphide was heated for 1 hour at 850°C. in a stream of hydrogen sulphide generated in a Kipp's apparatus. After this period the temperature was allowed to fall to 500°C. when the H<sub>2</sub>S was displaced by a stream of hydrogen. Any excess sulphur present with the sulphide after its first treatment was thus removed. The product was cooled in an atmosphere of hydrogen. The sulphide prepared in this way was a yellowish-green powder and always showed a purity greater than 99%.

MnO was prepared in the same way as in the preceding investigation.

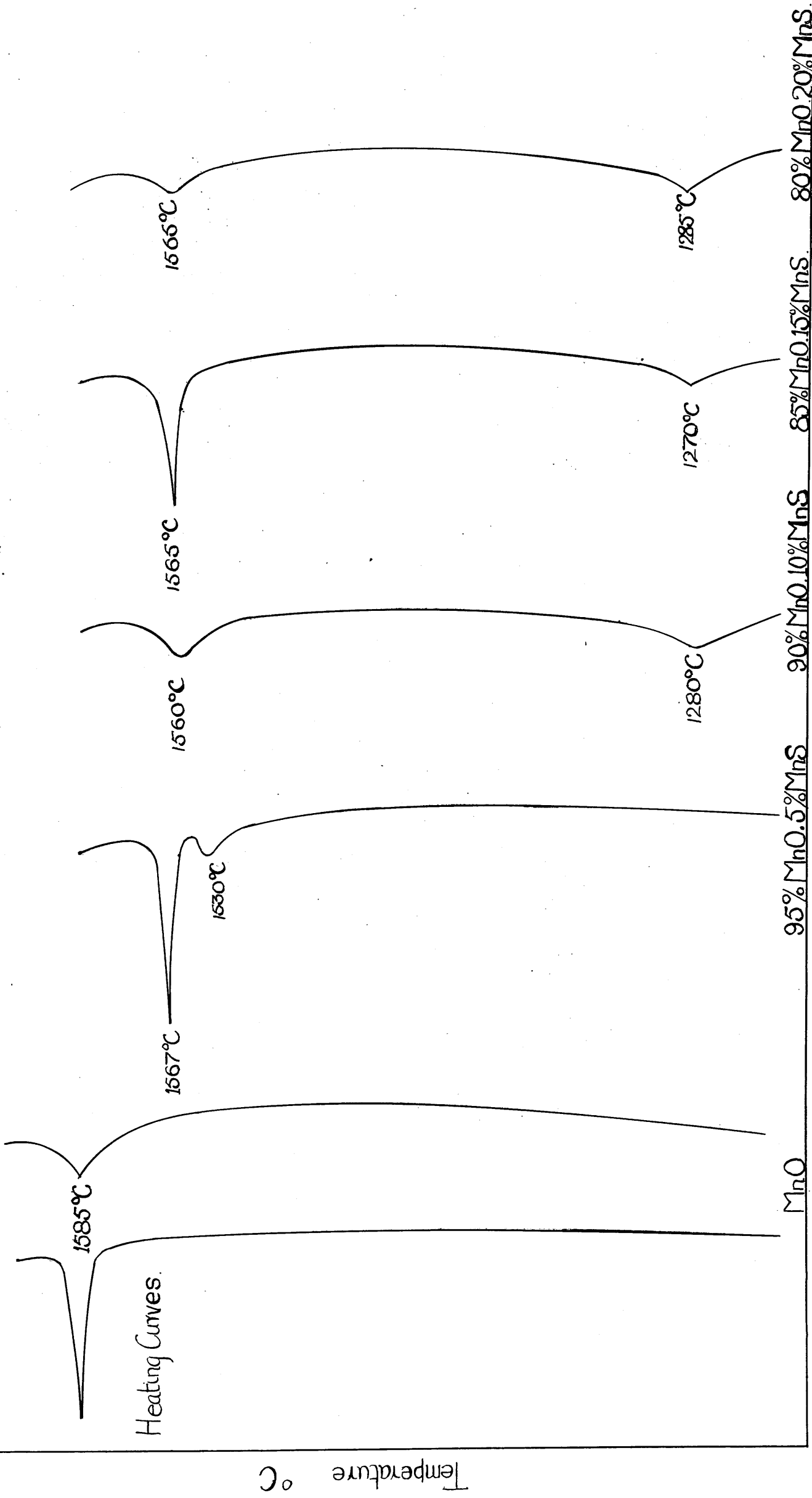


Fig. 21.



Heating Curves.

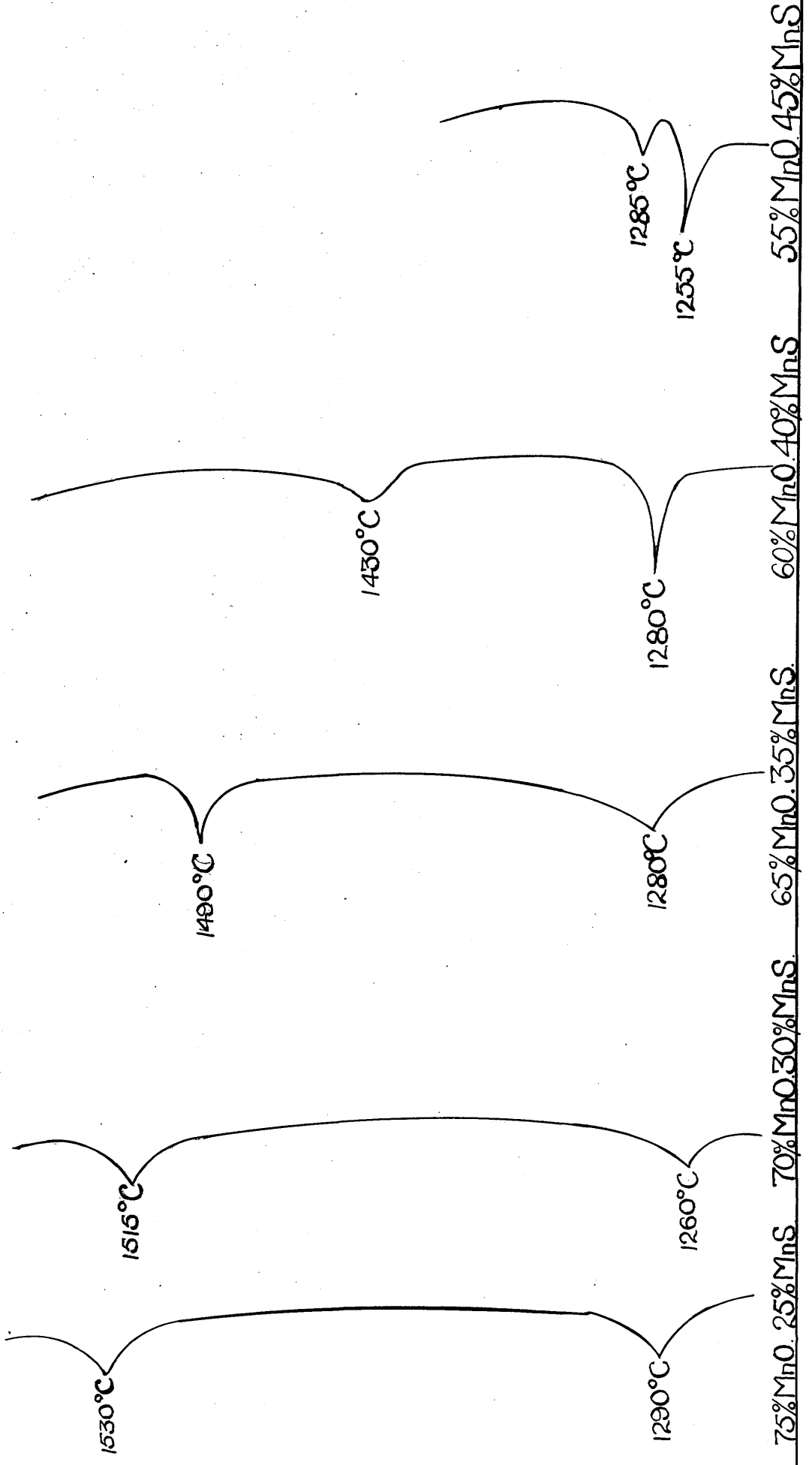


Fig. 22

Heating Curves

Temperature °C

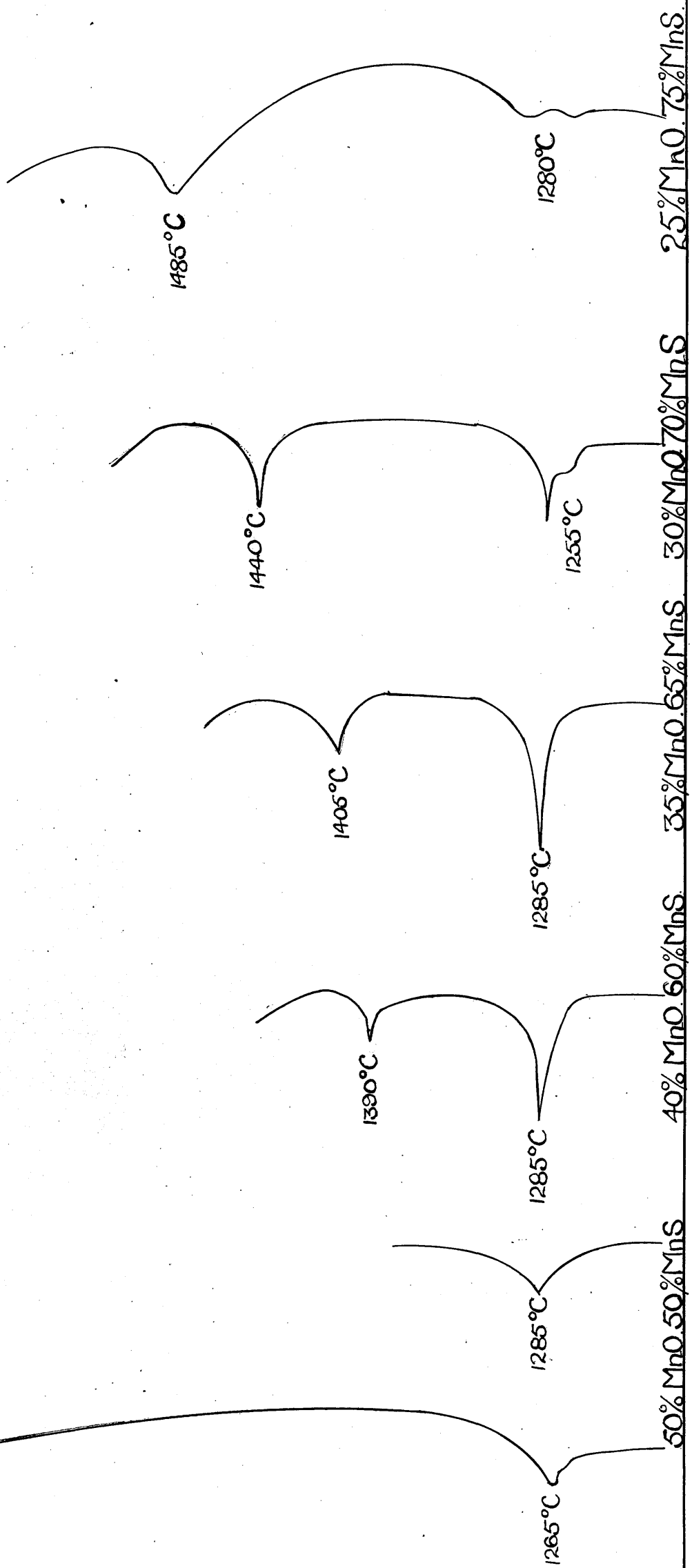


Fig. 23

Heating Curves.

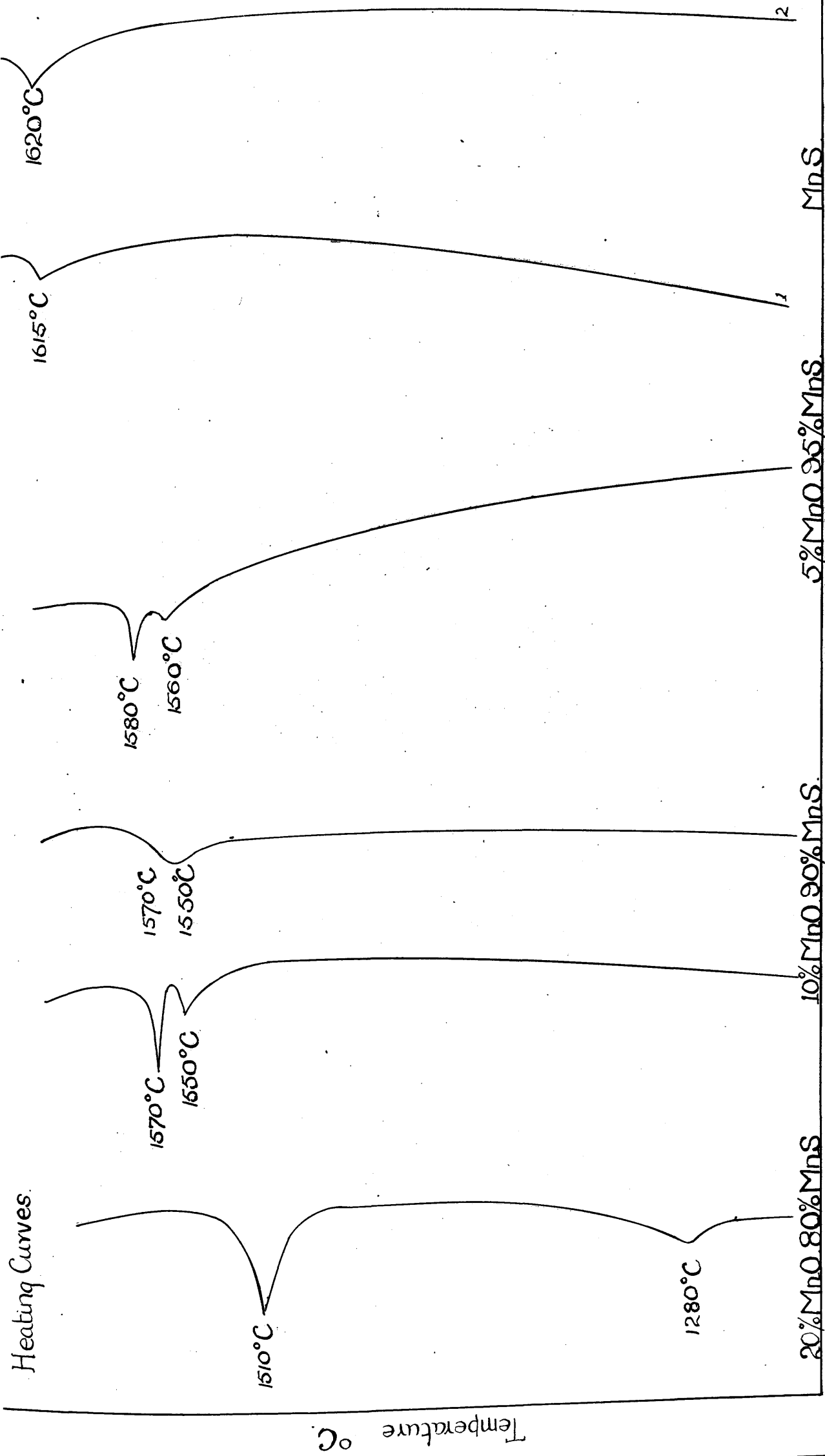


Fig. 24.

MELTING POINT DETERMINATIONS FOR THE SYSTEM MnO - MnS:

The heating curves for this system are given in Fig. 21 to Fig.24.

The mixtures were melted in alundum crucibles using alundum sheaths as a thermo-couple protection. It was found impossible to obtain a cooling curve of the mixtures. This was explained by the fact that the melted mixtures formed extremely mobile liquids which sank to the bottom of the crucible in which they eventually became absorbed, thus breaking contact with the thermo-couple sheath. In such cases the only cooling curve obtained merely showed the rate of cooling of the furnace with no heat evolutions apparent. This was particularly so in the region of the eutectic which only remained in contact with the sheath long enough for its melting temperature to be recorded. The smallness of the eutectic point shown in Fig.23 is directly attributable to this fact. The powder mixtures no matter how tightly packed into the crucible showed a very large contraction on heating, and if it were not for the fact that they shrank on to the thermo-couple sheath, it is doubtful whether even heating curves could have been obtained. This contraction allowed a fairly accurate determination of the solidus in mixtures where the eutectic was absent. As soon as the first portion of the mixture had melted, it ran down the sheath in intimate contact with the thermo-couple, giving a greater heat absorption than would normally be expected. The curves in Fig.21 and Fig.24, for mixtures at each end of the diagram, show this quite clearly. Two points are obtained where normally there would only have been one. In the two mixtures 85% MnS. 15% MnO, and 7.5% MnS. 92.5% MnO it was found that when a temperature of 1420°C. and 1400°C, respectively, was attained, the heating curve became very irregular until their respective melting temperatures had been passed, when the normal curve was again obtained. At first

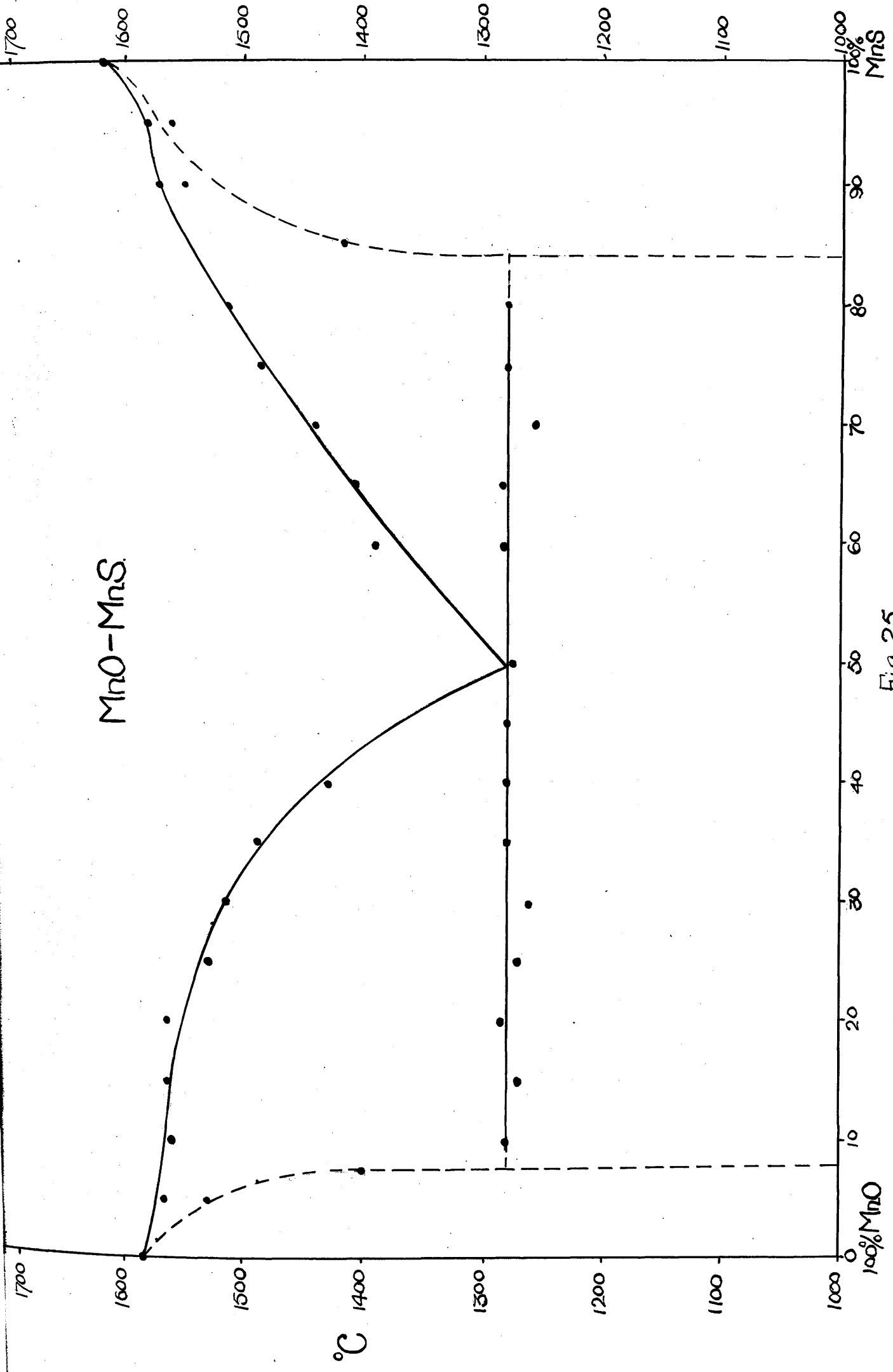


Fig. 25.

The dendrite situated in a matrix of eutectic bears a striking resemblance to the structure shown in Fig.15. It is very probable that the markings in both cases are due to the same action, that is, devitrification. Distinct signs of the dendrite reverting to a more crystalline form are shown in the lower portion of Fig. 27. Figs.28 and 29 show the microstructure of the 50/50 melt which appears to be composed completely of the eutectic. Incidentally, Fig.28 shows the eutectic obtained from the alundum crucible whilst Fig.29 represents the melt of eutectic proportions made in the platinum crucible. The well defined dendrites of the MnS rich solution in a matrix of eutectic are seen in Fig.30. Fig.31 shows the structure of pure MnS, which is perfectly homogeneous and crystalline.

All the micro sections were etched in dilute HCl.

The equilibrium diagram conforms very closely to the qualitative figure given by Benedicks and Löfquist (10) except in the small difference in melting points and of the solubility ranges.

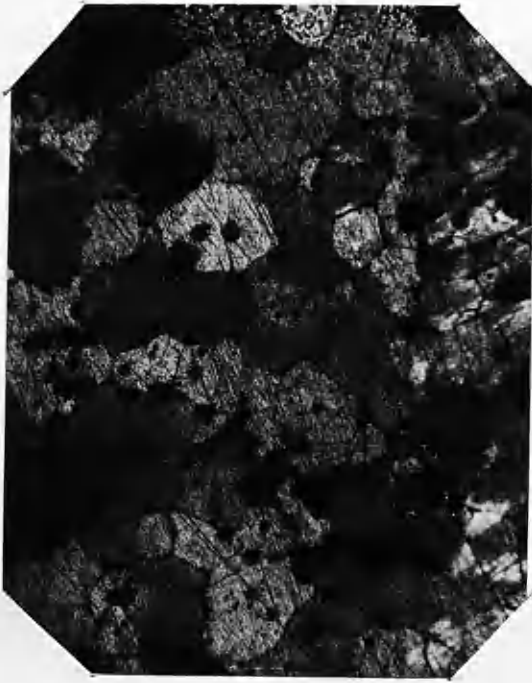


Fig. 26. 93%MnO.7%MnS.

×200.



Fig. 27. 70%MnO.30%MnS.

×200.



Fig. 28. 50%MnO.50%MnS.

×200.



Fig. 29. 50%MnO.50%MnS.

×300.



Fig. 30. 30% MnO.70% MnS  
× 250.



Fig. 31. MnS.  
× 250.

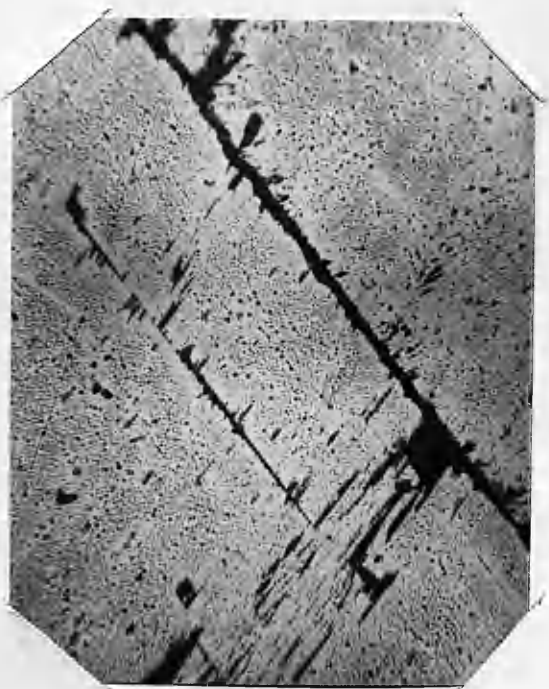


Fig. 38. MnO.SiO<sub>2</sub>  
× 200.



Fig. 39. MnO.SiO<sub>2</sub>.  
× 200.



MnO. SiO<sub>2</sub> - MnS.PREPARATION OF MnO. SiO<sub>2</sub>:

Pure manganous silicate, that is, rhodonite, was prepared by fusing together pure silica sand and manganous oxide in a molybdenum furnace in an atmosphere of hydrogen. Manganous oxide was prepared in the same manner as had already been described. A salamander crucible was found to be entirely satisfactory for making the fusion and in no way did it affect the composition of its contents. The silica sand and the oxide were accurately weighed in the respective gram-molecular proportions necessary for the formation of MnO. SiO<sub>2</sub>. At about 1350°C. - 1400°C. the two components combined to form the liquid silicate. The silicate was allowed to cool in the furnace in hydrogen. It was a strongly crystallised reddish-brown mass which, on analysis, was found to agree with the theoretical composition to within 0.5%.

Manganous sulphide was prepared as before.

MELTING POINT DETERMINATIONS FOR THE SYSTEM MnO. SiO<sub>2</sub> - MnS.

It was obvious, after the first attempt to melt the silicate in an alundum crucible, that some other refractory had to be found. The silicate readily attacked the alumina with the result that the temperature readings taken were irregular. In addition to this, the rhodonite was contaminated with impurities and its correct melting point could not be obtained.

After several attempts to produce a more satisfactory crucible it was decided to use one of pure graphite. The protective covering for the thermo-couple was also of graphite. These graphite crucibles and thermo-couple sheaths were found to be most satisfactory since the carbon in no way reacted with the contents.

The heating curves are given in Figs.32 and 33, and

Heating Curves.

Temperature °C

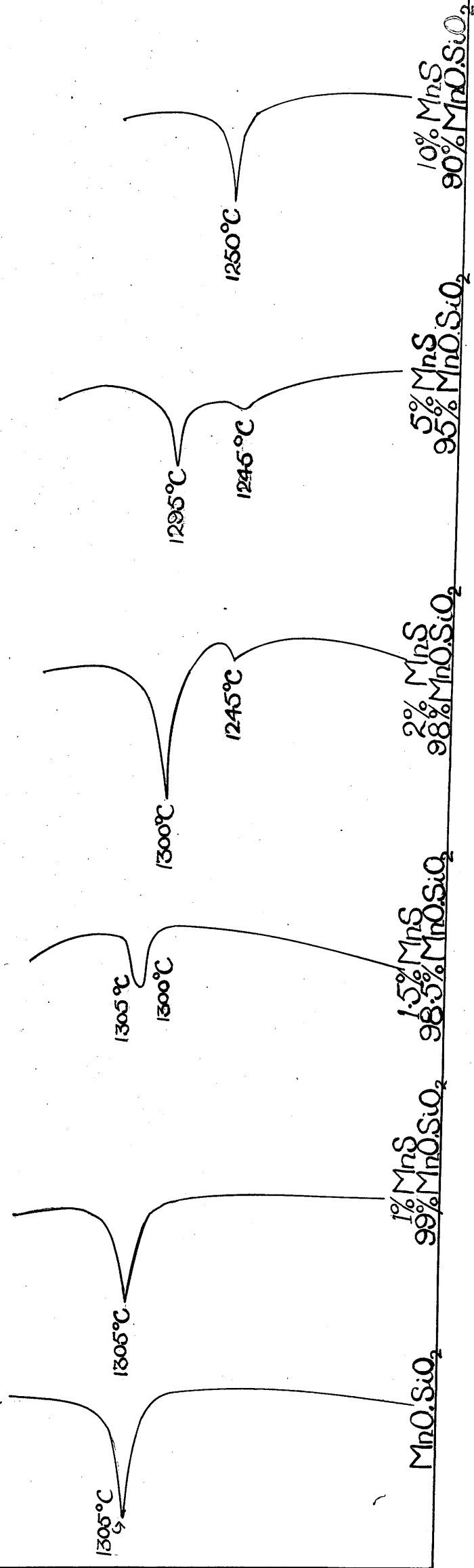


Fig. 32

Heating Curves.

Temperature °C

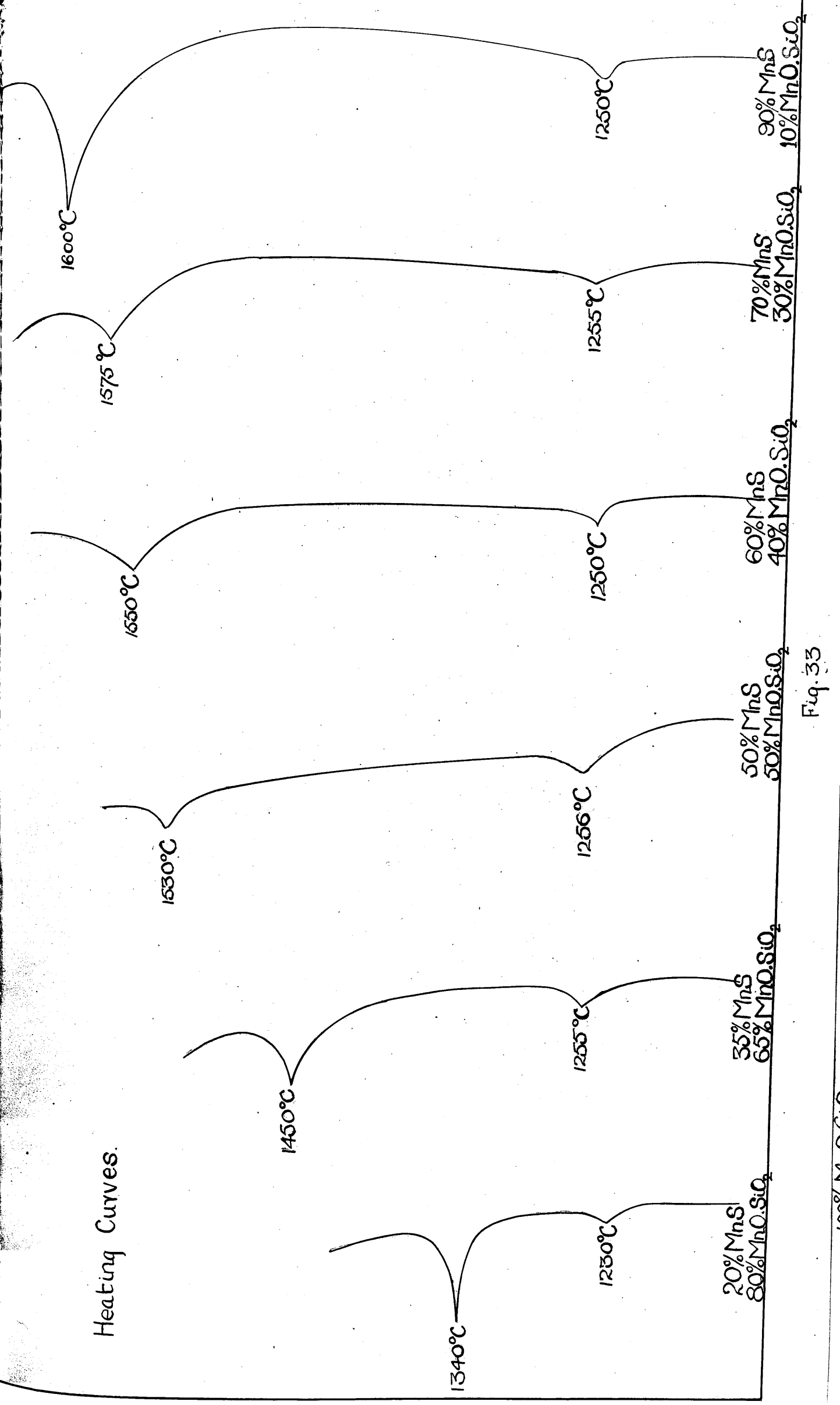


Fig. 33

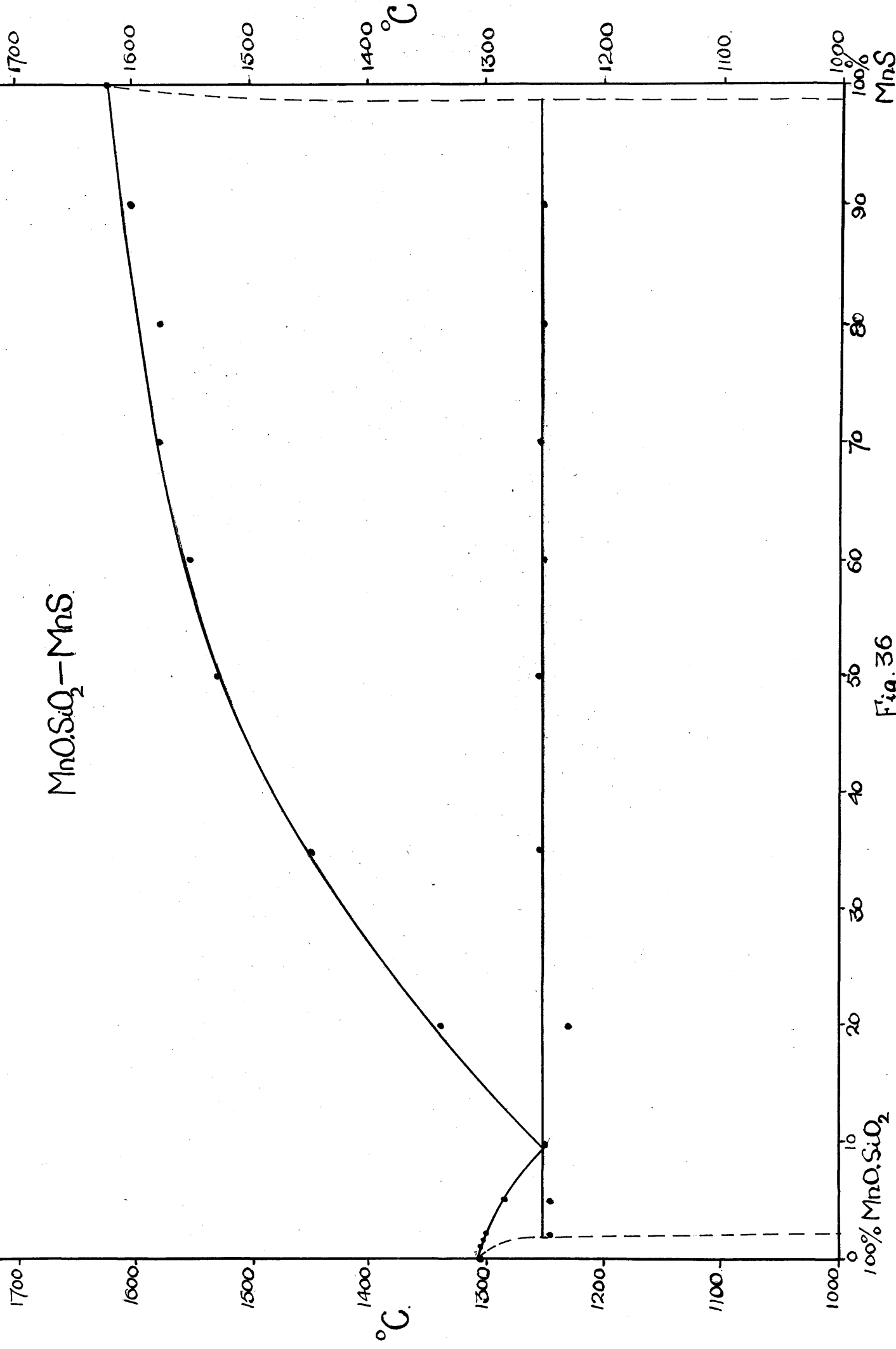


Fig. 36

the melting points thus obtained are plotted in the form of an equilibrium diagram in Fig.36. Again, as in the previous systems, the first heating curve of any mixture always corresponded to within very narrow limits with the second heating curve. Since the crucible did not absorb either of the constituent materials, this system gave much less trouble than those formerly described. The same mixture was always heated and cooled twice but it was always found that the heat absorptions on both curves corresponded exactly, in spite of the fact that the materials were mixed together in the powdered form for the first determination.

As can be seen from Fig.36 the system conforms to the simple eutectiferous type with a limited solubility at either end of the series. Manganese silicate melts at  $1305^{\circ}\text{C}$ . but the addition of 10% MnS lowers the melting point to  $1250^{\circ}\text{C}$ . which is the eutectic temperature. The limits of solubility occur at compositions approximately equal to 1.5% MnS, 98.5% MnO.  $\text{SiO}_2$  and 1.3% MnO.  $\text{SiO}_2$ , 98.7% MnS. The diagram is similar in form to those given by Woloskow (11) and Levy (12).

The use of the graphite crucibles gave a very big improvement in the conditions of melting and, as a result, it was found possible to determine the freezing temperatures. These are given in Fig.34 and 35. From these curves a cooling diagram can be drawn and is shown in Fig.37, superimposed upon the diagram obtained from the melting points. It can be seen that there is considerable supercooling of the system. Rhodonite, for example, freezes at a temperature  $50^{\circ}\text{C}$ . below that at which it melts, namely at  $1257^{\circ}\text{C}$ . In the zone of the eutectic the degree of supercooling is decidedly irregular whereas outside this zone the eutectic freezes at a constant temperature, i.e.  $1110^{\circ}\text{C}$ . It should be explained that the melted mixtures were allowed to freeze without any type of inoculation or mechanical disturbance, and that the rates of cooling in all cases were

Cooling Curves.

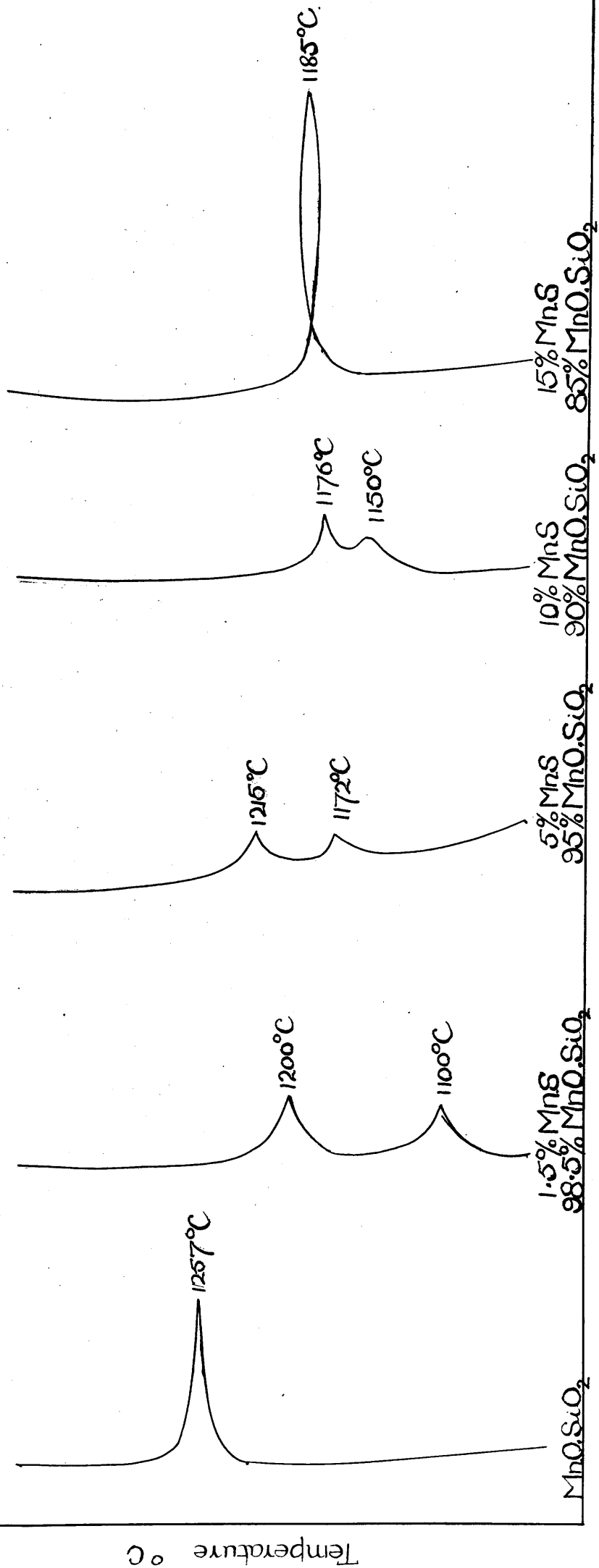


Fig. 34

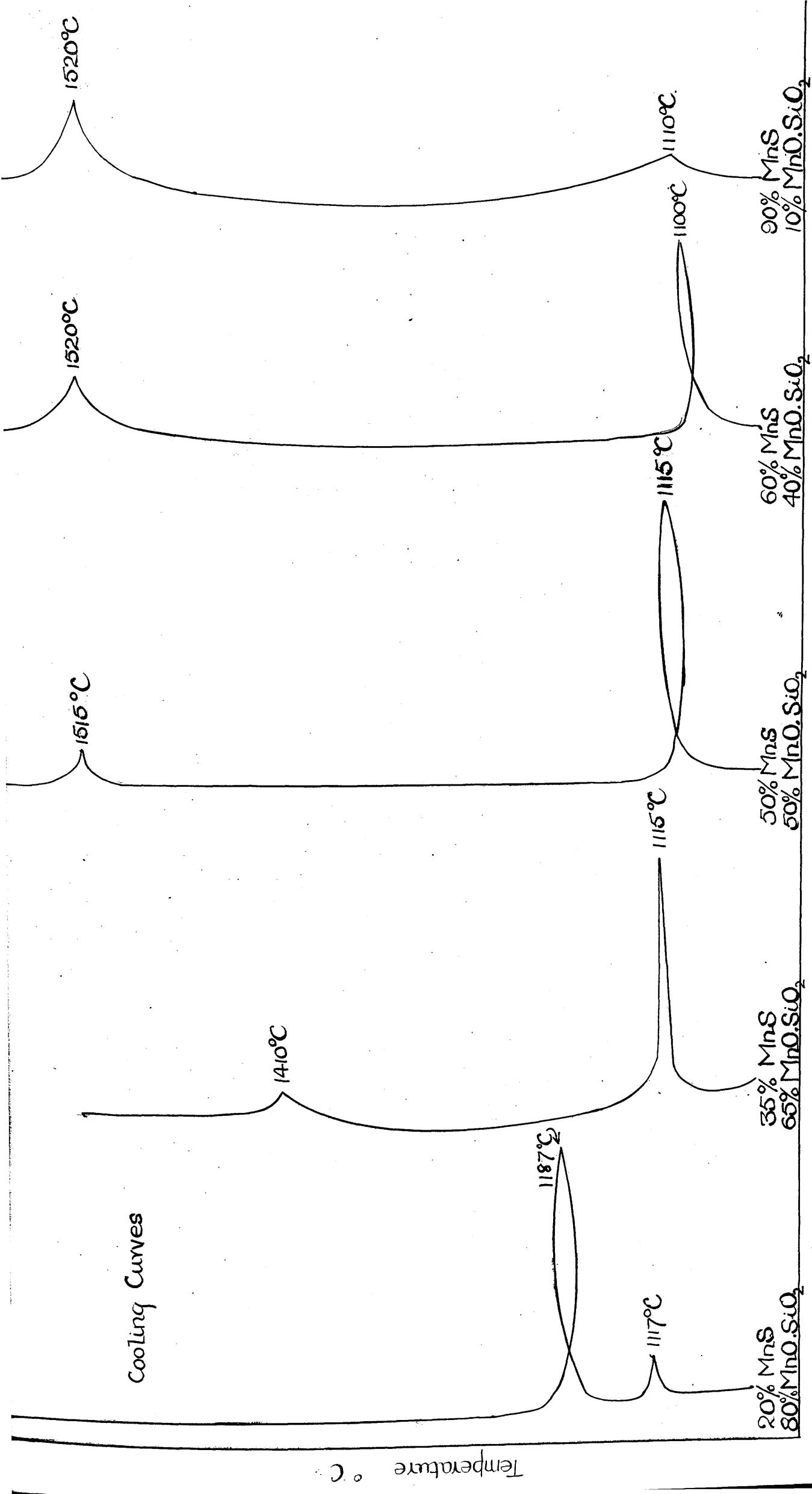


Fig. 35

$MnO \cdot SiO_2 - MnS$

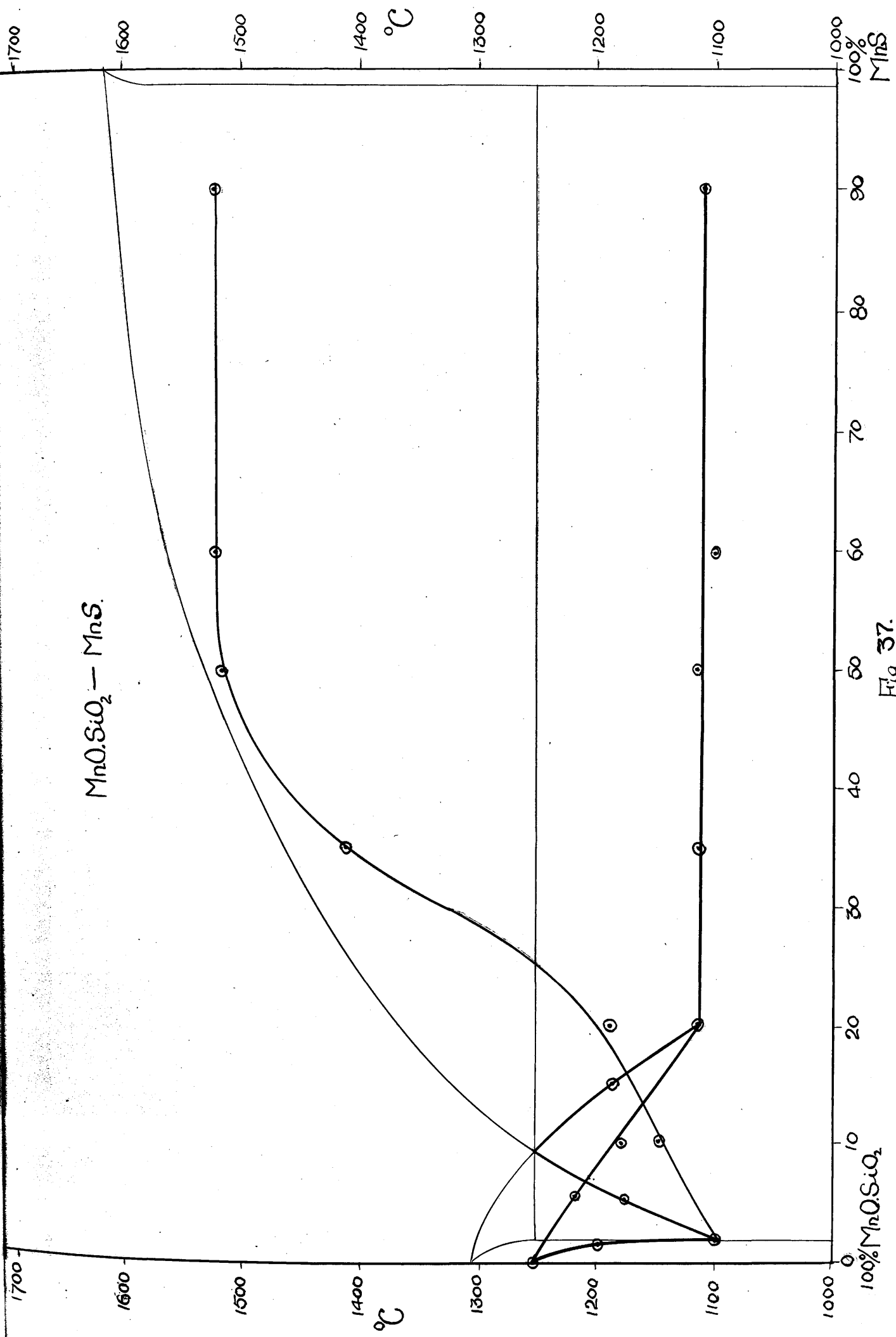


Fig. 37.



practically identical. The mixture containing 5% of MnS, then, on cooling does not precipitate the solid primary phase at its melting temperature but supercools to a temperature of 1220°C. when MnO. SiO<sub>2</sub> crystallises from the liquid. The separation of MnO. SiO<sub>2</sub> proceeds until the supersolubility curve of MnS is reached when MnS begins to separate, and the whole of the mother liquor solidifies at the constant temperature of the hypertectic point. The effect on the microstructure would then be to cause the MnO. SiO<sub>2</sub> to occupy too large an area, the area of the eutectic being correspondingly reduced. Fig.40 shows the effect of supercooling this mixture and the small amount of eutectic present can thus be accounted for.

On cooling the eutectic mixture crystals of MnO. SiO<sub>2</sub> separate first and when the hypertectic point is reached MnS is precipitated and the remaining liquid solidifies as the hypertectic. The eutectic mixture should, thus, show two heat evolutions on cooling as is shown in Fig 34. The microstructure should also reveal the effects of this supercooling. Massive MnO. SiO<sub>2</sub> and MnS should be present, in amounts depending on the extent of supercooling, as well as a typical eutectic structure. This is precisely the structure that is obtained from the eutectic mixture as can be seen from Fig.41.

Outside this eutectic zone the inoculation by the separation of the primary phase is not so marked and the eutectic is supercooled to its maximum degree.

#### MICROSTRUCTURES:

The microstructures of the synthetically prepared rhodonite are shown in Figs.38 and 39. The typical rhodonite markings are well brought out in Fig.39. With the addition of 5% MnS the rhodonite loses its flesh-coloured appearance and becomes green. In this melt the rhodonite crystallisation still persists but there is also a small amount of eutectic present



Fig. 40. 95% MnO.SiO<sub>2</sub>.  
5% MnS.  
x 200.

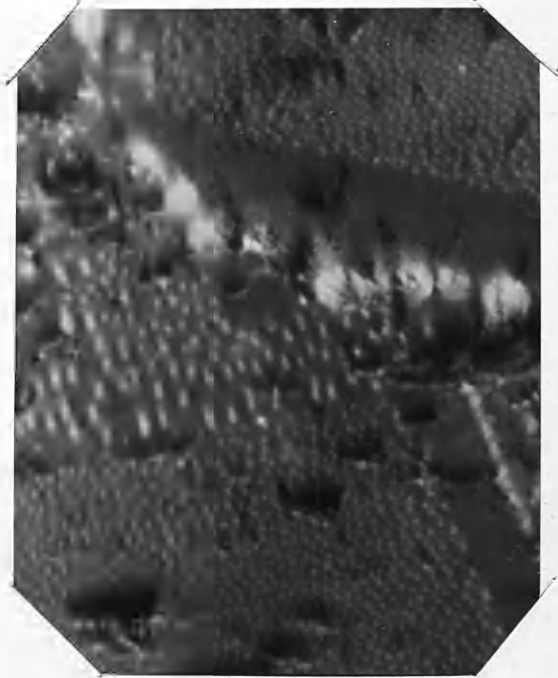


Fig. 41. 90% MnO.SiO<sub>2</sub>  
10% MnS  
x 600.

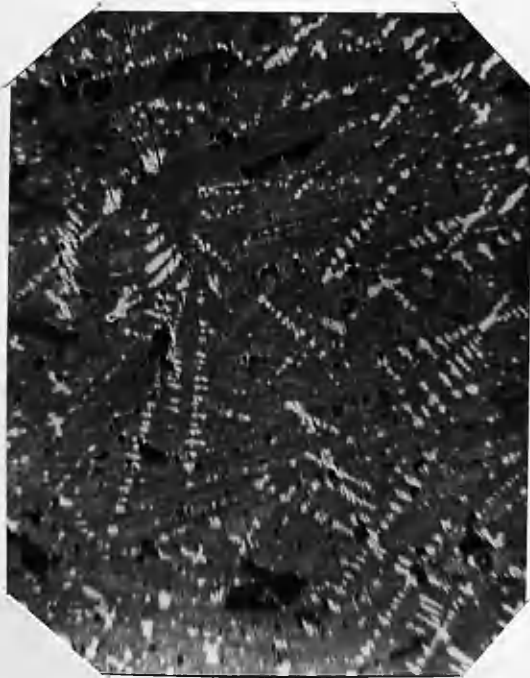


Fig. 42. 85% MnO.SiO<sub>2</sub>  
15% MnS.  
x 200.



Fig. 42 a. 80% MnO.SiO<sub>2</sub>  
20% MnS.  
x 250.

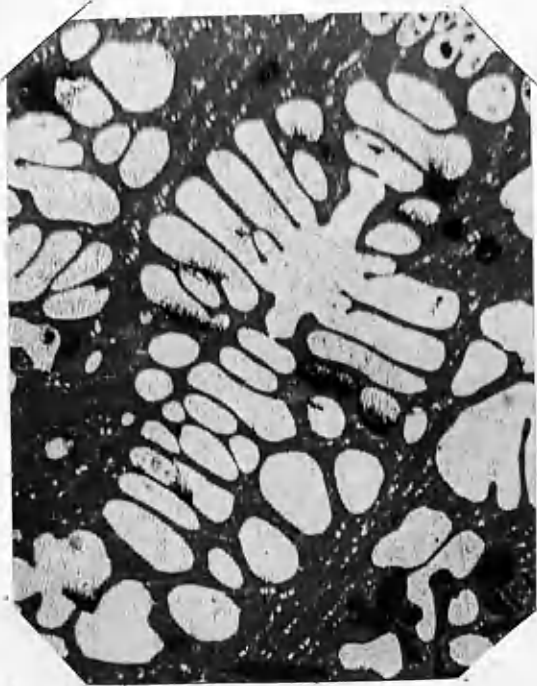


Fig. 43. 50% MnO.SiO<sub>2</sub>  
50% MnS x 250.



Fig. 44. 20% MnO.SiO<sub>2</sub>  
80% MnS. x 200.

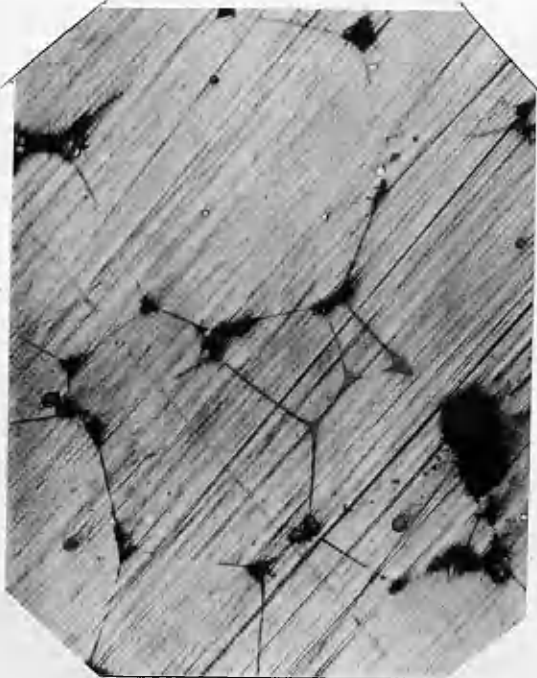


Fig. 45. 1.5% MnO.SiO<sub>2</sub>  
98.5% MnS. x 250.

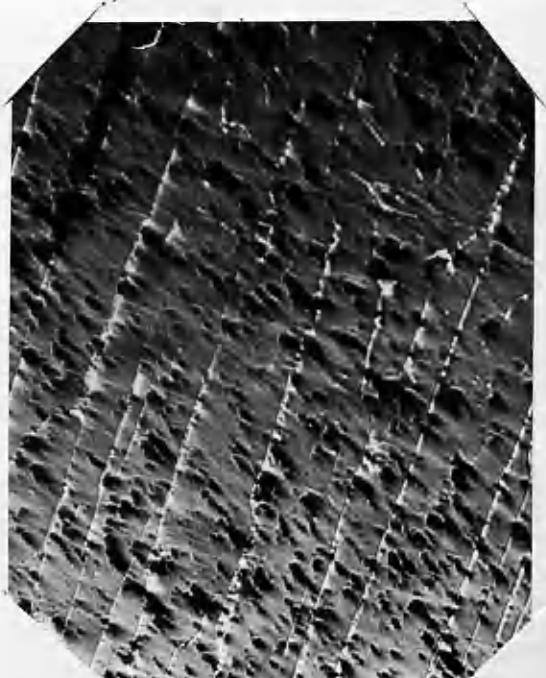


Fig. 46. 98% MnO.SiO<sub>2</sub>  
2% MnS. x 250.



Fig. 47. 98.5% MnO.SiO<sub>2</sub>  
1.5% MnS x 200

(Fig.40). It is extremely difficult to interpret correctly the microstructures of the melts in the eutectic range owing to the variable amount of supercooling that occurs. The pure eutectic is shown in Fig.41. It is interesting to note the massive silicate and sulphide that occurs around the very fine eutectic. This, again, is directly attributable to the supercooling of the melt.

With increasing amounts of MnS, the amount of eutectic present decreases (Figs.42 to 44). Fig.45 represents the melt containing 1.5% of MnO. SiO<sub>2</sub> and which is seen to be practically homogeneous. This then is approximately the limit of solid solubility of MnO. SiO<sub>2</sub> in MnS. The melt containing 98% of MnO. SiO<sub>2</sub> and 2% MnS can be seen (Fig.46) to contain an excess of MnS which separates as eutectic whilst Fig.47 shows the homogeneous melt of 1.5% of MnS and 98.5% of MnO. SiO<sub>2</sub>.

It was found practically impossible to polish these last three specimens sufficiently well for micro-photographic reproduction; however, they demonstrate approximately the solid solubility limit.

2 FeO. SiO<sub>2</sub> - MnS.

The ferrous silicate was made by melting pure silica sand and pure ferrous oxide in the correct gram-molecular proportions. The ferrous oxide was prepared as already described on page 6. The melting was carried out in a salamander crucible in a gas injector furnace. The silicate produced was not noticeably crystalline and had a bluish-green colour.

Mixtures rich in silicate gave considerable trouble on melting since they either attacked the crucible chemically or became absorbed in it. As a refractory alundum, alundum crucibles coated with zinconia and graphite, were tried, but without success. The zinconia coated alundum crucibles could not be given a satisfactory test because the coating cracked badly on firing and actually only covered a part of the alundum. Graphite crucibles, as was expected, reduced some iron from the silicate and had to be abandoned.

Eventually it was found that an ordinary Morgan fireclay crucible served the purpose best. It was found that the absorption was very small indeed and any chemical attack that took place was confined to a thin skin on the outside of the melt. In this skin it was quite frequently noticed that skeletal crystals of cristobalite developed, the excess silica in this skin being presumably dissolved from the crucible. Another difficulty that arose in this system was the penetration of the thermo-couple protection tubes by the liquid mixtures. The penetration was not through the wall of the sheaths but from the closed end. It appeared that the bottoms of these sheaths became loose on heating to a high temperature, with the consequent formation of cracks through which the liquid silicate flowed immediately after melting. On this account the thermo-couple wire was contaminated and eventually broke.

It was only possible, then, with the adopted method of

working to obtain one heating curve for a mixture and cooling curves could not be attempted. This was not considered a serious objection in so far as the melting temperatures were concerned in view of the fact of the exact correspondence between the first and second heating curves in the other systems examined.

The melting point curves are shown in Figs.48 and 49, and the melting points thus obtained are plotted in diagram form in Fig.50. It will be seen that the system is eutectiferous the eutectic occurring at temperature of  $1060^{\circ}\text{C}$ . and containing 10% of MnS. The solubility limit at either end of the diagram is approximately 1.5% in each case. The similarity between this diagram and the  $\text{MnO} \cdot \text{SiO}_2 - \text{MnS}$  system is interesting.

It was found impossible to prepare microsections of this system which were free enough from scratches to allow of photographic reproduction. Sections were, however, taken of every melt and the points given in the diagram were confirmed by micro-examination.

# Heating Curves

Temperature °C

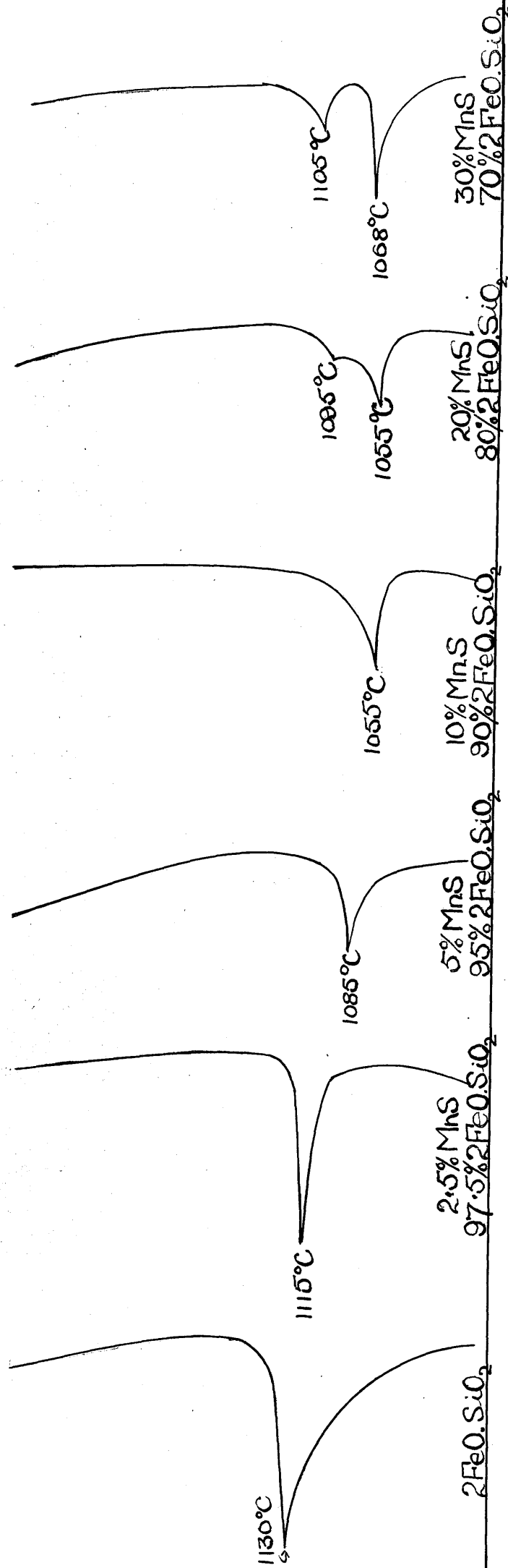


Fig. 48

Heating Curves

Temperature °C

1552°C

1388°C

1185°C

1100°C

1060°C

1060°C

50% MnS  
50% 2FeO.SiO<sub>2</sub>

70% MnS  
30% 2FeO.SiO<sub>2</sub>

85% MnS  
15% 2FeO.SiO<sub>2</sub>

Fig. 49



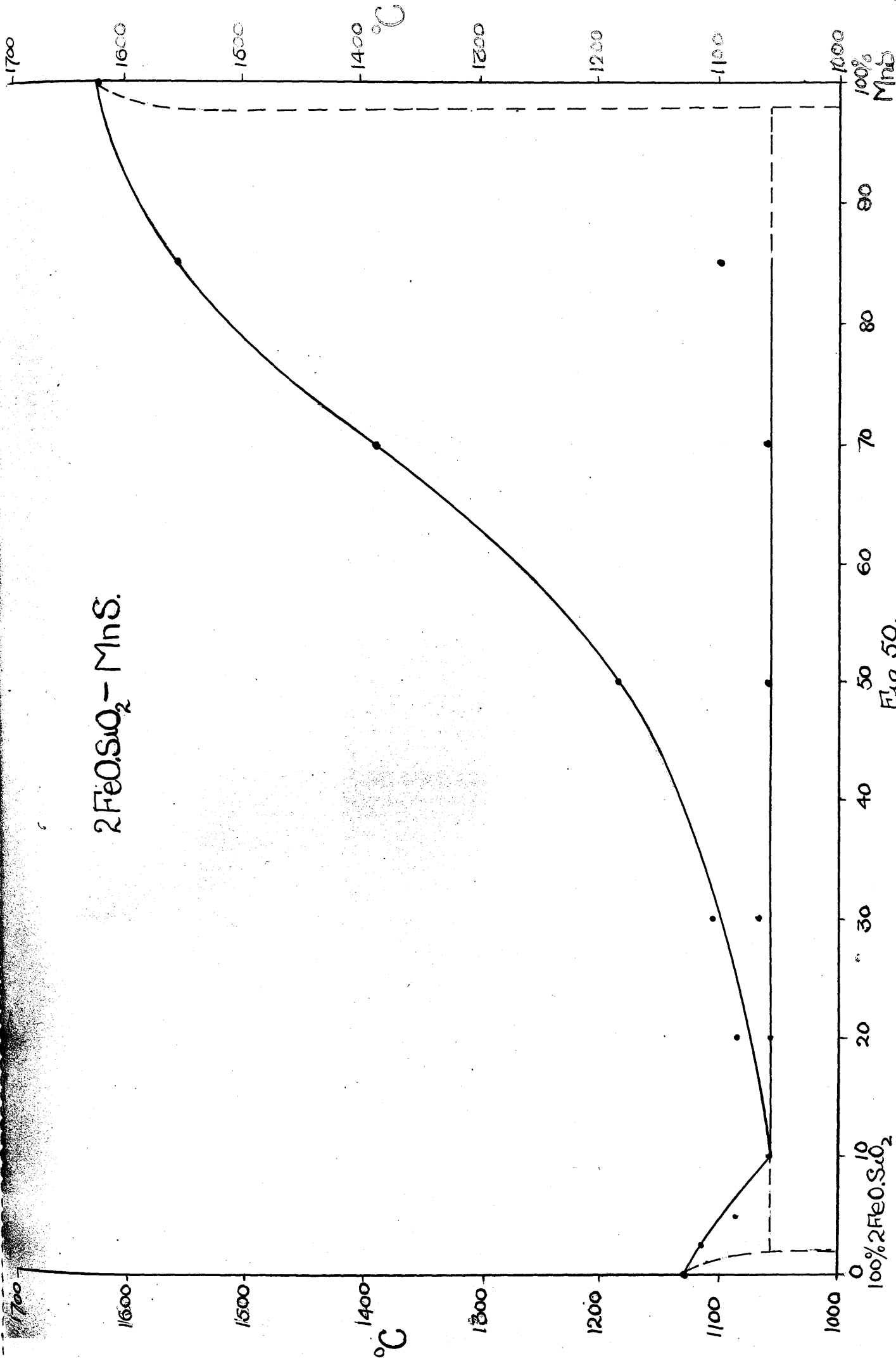
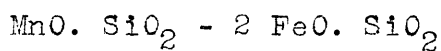


Fig. 50.



A slight deviation from the usual method of determining the melting and freezing temperatures of these mixtures was used. It was considered advisable owing to the lower melting points of these silicate mixtures to use a platinum - platinum/10% Rhodium thermo-couple. Since the usefulness of the molybdenum-tungsten thermo-couple only extends down to approximately 1200°C. with any degree of accuracy, the use of the platinum thermo-couple was essential for temperatures below 1200°C. Except for this small difference the method was exactly as has been previously described. The heating was done in a molybdenum wire-wound furnace and the silicates melted under nitrogen.

A fireclay crucible was again used and except for slight surface effects was found to be quite satisfactory.

The heating curves for this system are given in Figs. 51 to 53, and the cooling curves in Figs. 54 to 56. The melting temperatures obtained from the heating curves are plotted in diagram form in Fig. 57. As can be seen the diagram again shows a eutectic which occurs at 58% of 2 FeO. SiO<sub>2</sub> and at a temperature of 1170°C. From the thermal data it can be deduced that approximately 8% of 2 FeO. SiO<sub>2</sub> is soluble in MnO. SiO<sub>2</sub> in the solid state. The 2 FeO. SiO<sub>2</sub>-rich side of the diagram takes a peculiar form and suggests the existence of a compound. Owing to the uncertain nature of the extent of the liquidus and solidus lines as obtained by purely thermal measurements this part of the diagram has been inserted as a dotted line. There can be no doubt, however, that the mixture having a composition of 90% of 2 FeO. SiO<sub>2</sub> and 10% of MnO. SiO<sub>2</sub> exhibits some peculiarity which can be best interpreted as a compound having that composition. The mixtures containing more than 90% of 2 FeO. SiO<sub>2</sub> up to the pure iron silicate form a series of solid solutions. The deductions made here are substantially correct and have been confirmed by

Heating Curves.

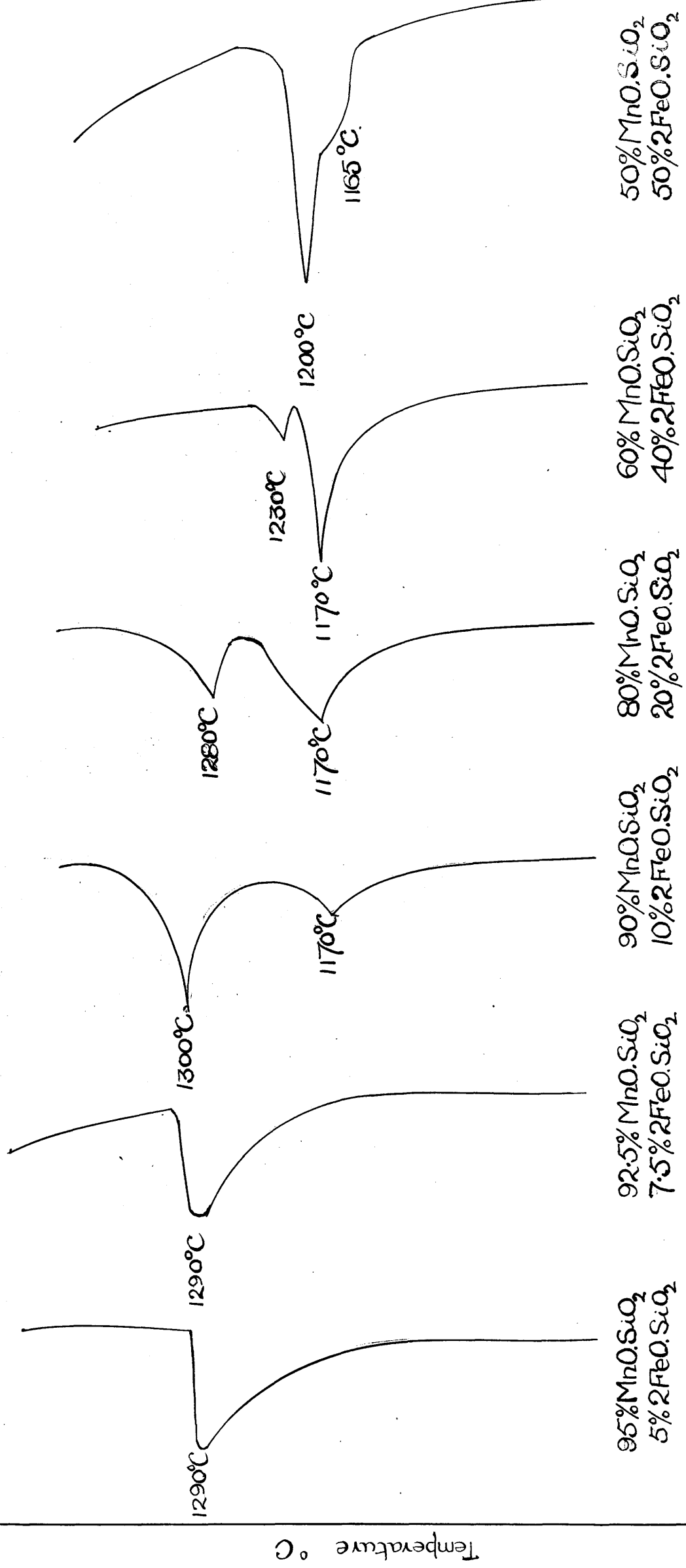


Fig. 51

Heating Curves.

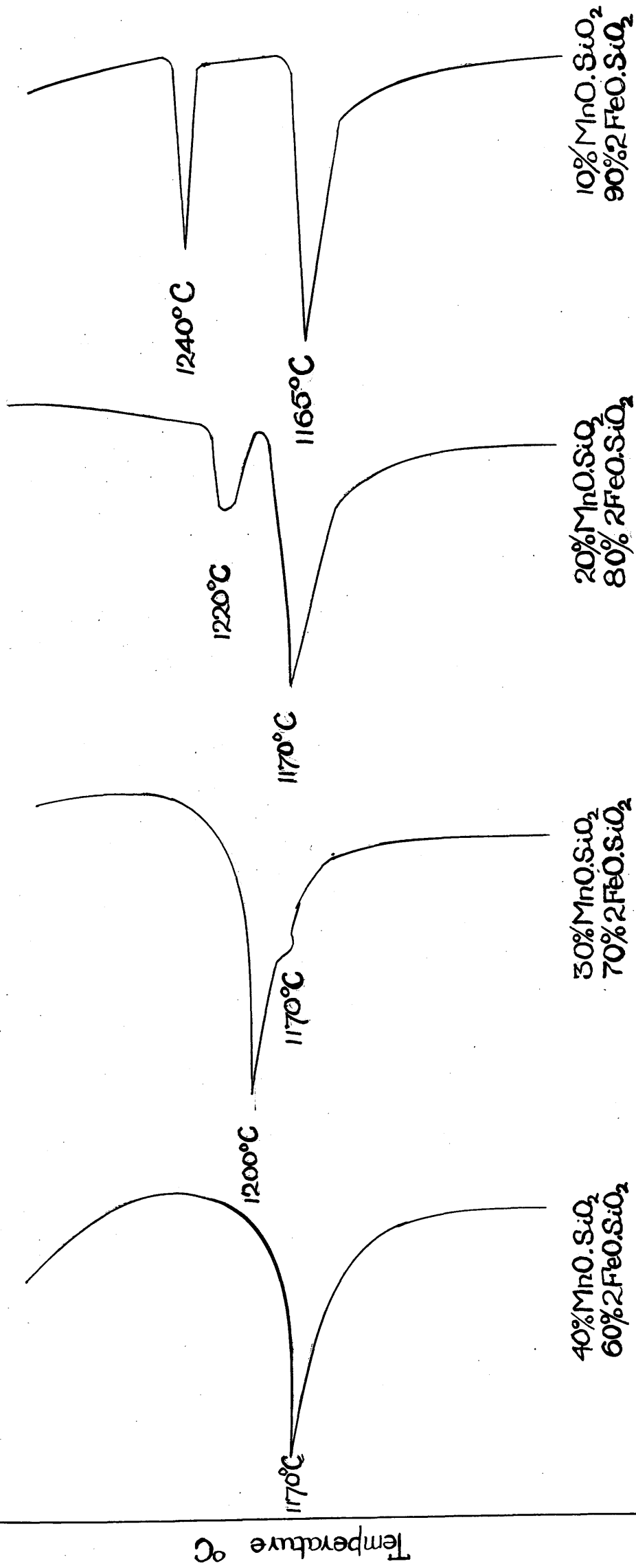


Fig. 52

Heating Curves.

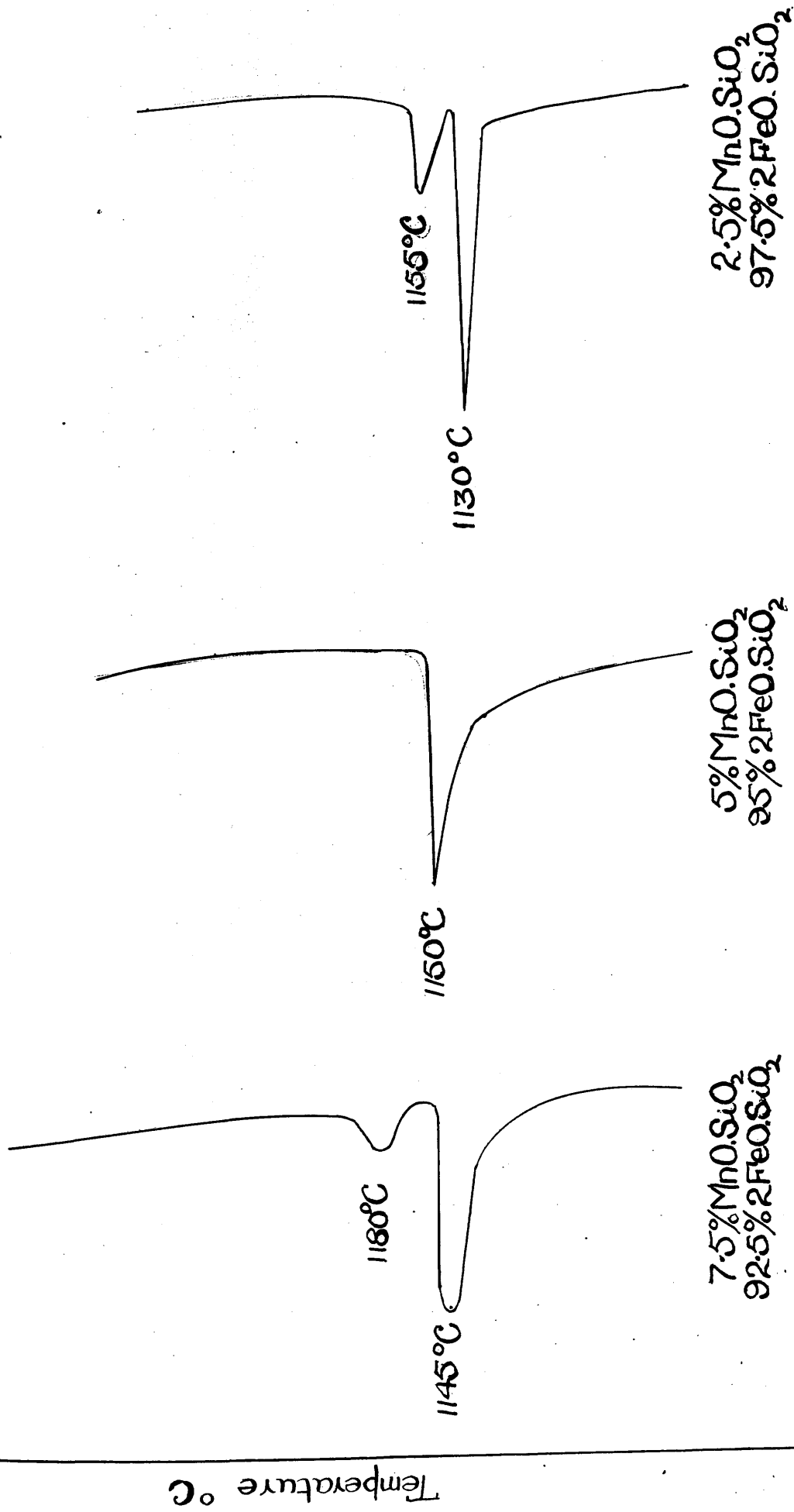


Fig. 53

Cooling Curves

Temperature °C

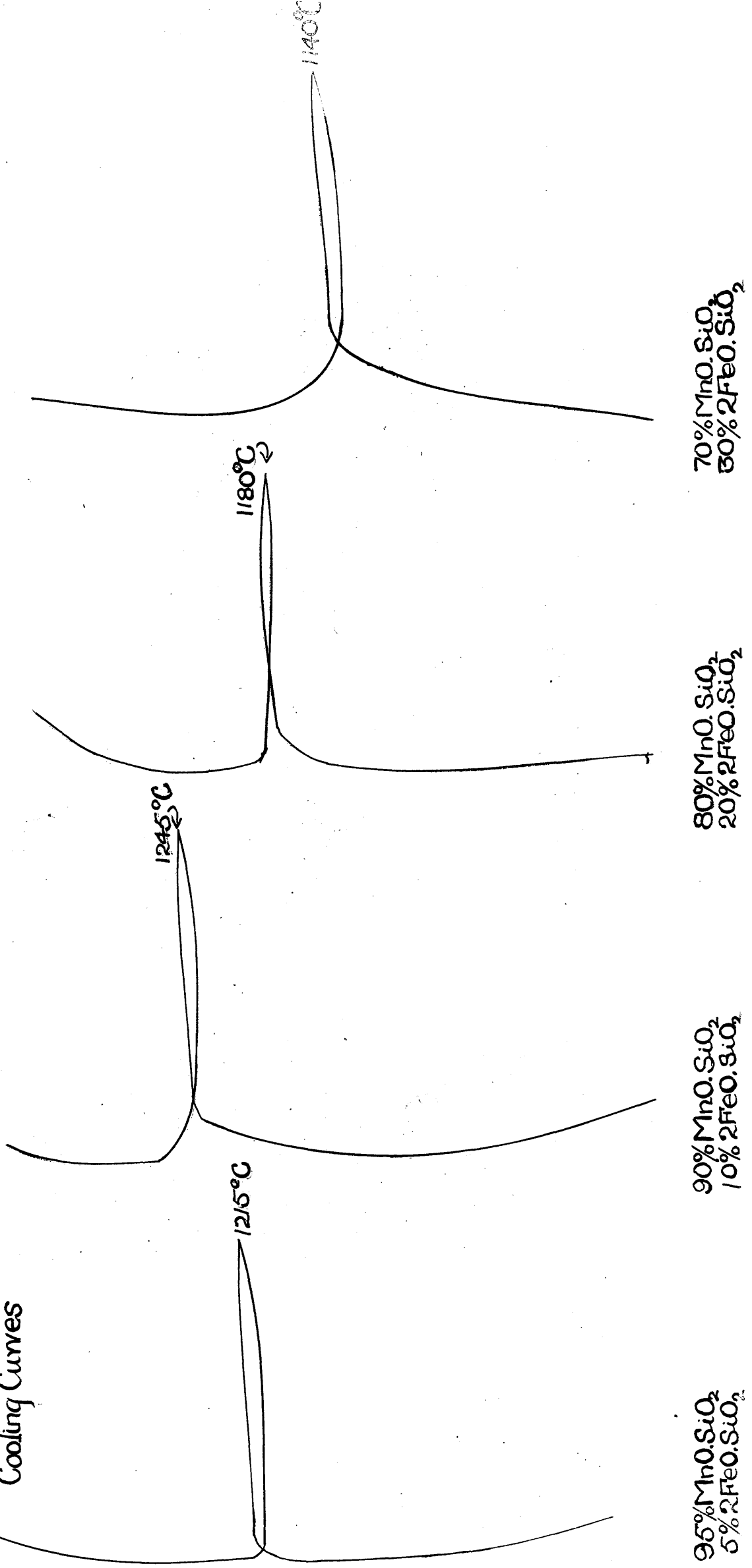


Fig. 54

Cooling Curves

1145°C  
1130°C

60% MnO. SiO<sub>2</sub>  
40% 2FeO. SiO<sub>2</sub>

1120°C

50% MnO. SiO<sub>2</sub>  
50% 2FeO. SiO<sub>2</sub>

1107°C

40% MnO. SiO<sub>2</sub>  
60% 2FeO. SiO<sub>2</sub>

1110°C

30% MnO. SiO<sub>2</sub>  
70% 2FeO. SiO<sub>2</sub>

1070°C

Temperature °C

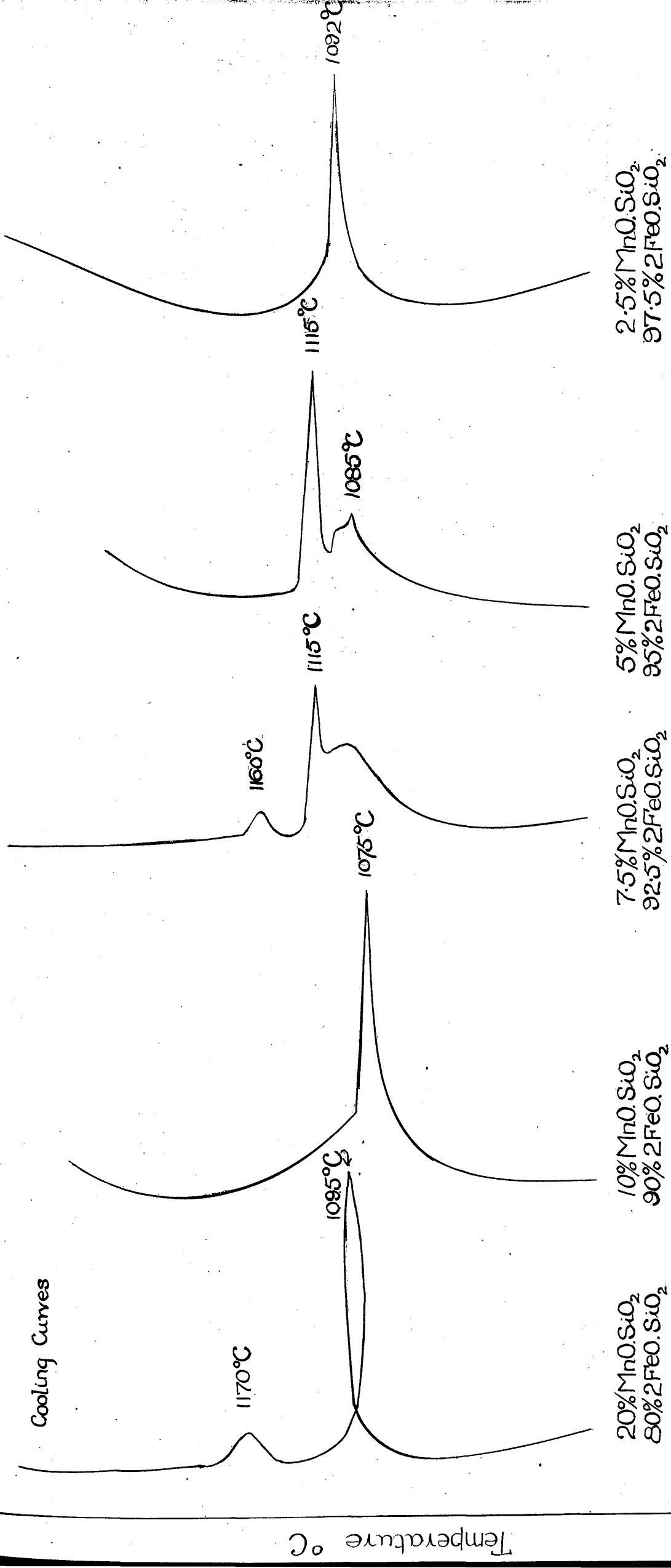


Fig. 56.



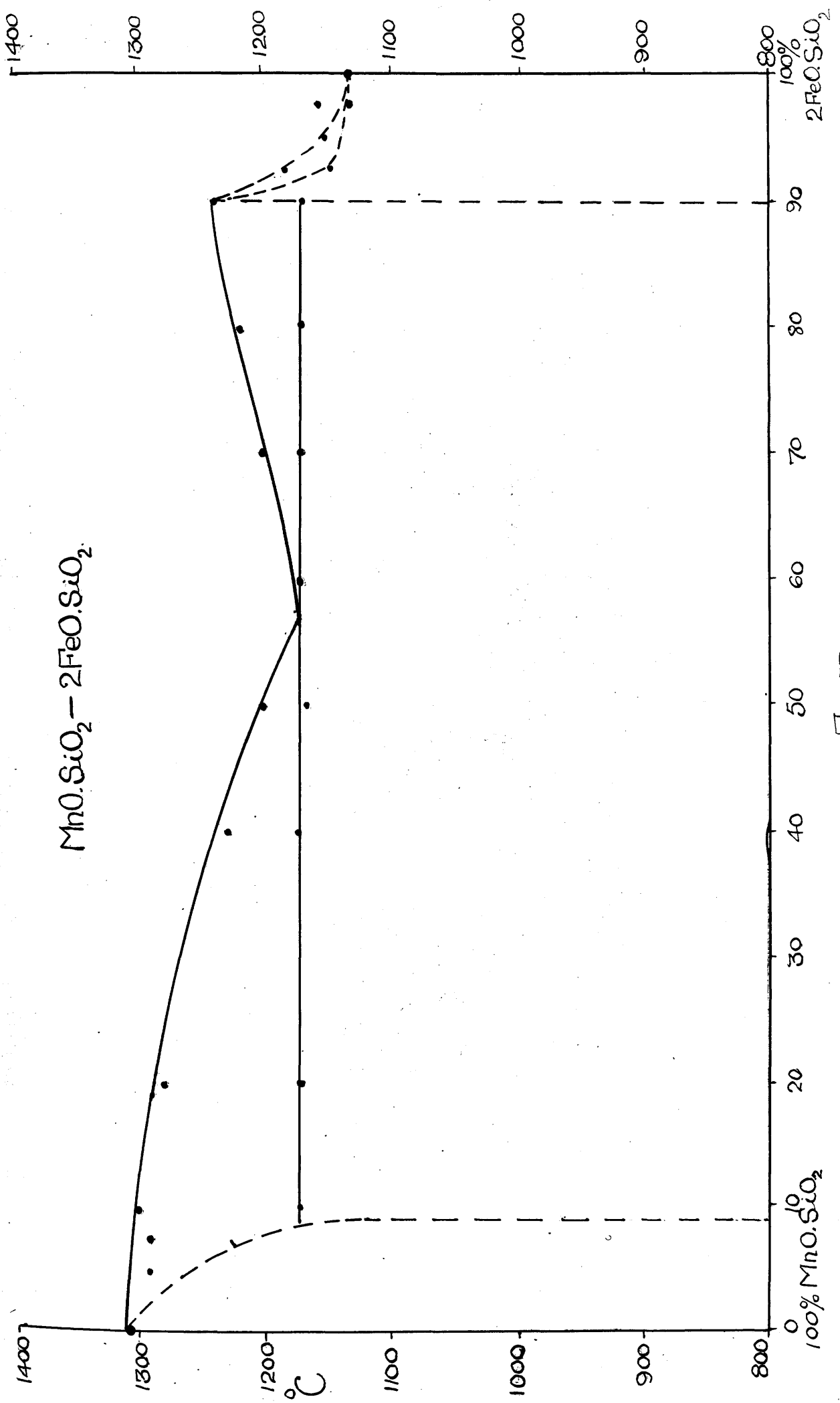


Fig. 57

the density determinations for this diagram which are described below. Another significant fact is that the cooling curves obtained for this 90% 2 FeO. SiO<sub>2</sub> mixture all show a single definite evolution of heat at 1075°C. The other mixtures having compositions varying from 80% to 98% of 2 FeO. SiO<sub>2</sub> all show more than one heat evolution on cooling (Fig.56). Again, the 90% 2 FeO. SiO<sub>2</sub> mixture freezes at a lower temperature than the other melts which points to the fact that this mixture shows peculiarities which can only be explained by the formation of a definite compound.

It has been known (13) for some considerable time that fayalite can dissolve 10% of Rhodonite in solid solution and with this maximum amount of rhodonite it exhibits definite characteristic properties. For this reason fayalite containing approximately 10% of rhodonite is known as a separate mineral and is called 'Knebelite'. McCance (14) has also referred to this compound.

The cooling curves for this diagram are extremely irregular and cannot be plotted satisfactorily in diagrammatic form. They are of interest in that they show that silicates of these compositions have very definite crystallisation temperatures, and do not, as is often assumed, pass through a temperature range on freezing.

The microphotographs in Figs.58 to 61 show the type of structures that are obtained with the mixed silicates. It has already been pointed out that owing to the supercooling of the melts it is extremely difficult to interpret correctly the microstructures obtained. Fig.61 shows the structure of the compound.

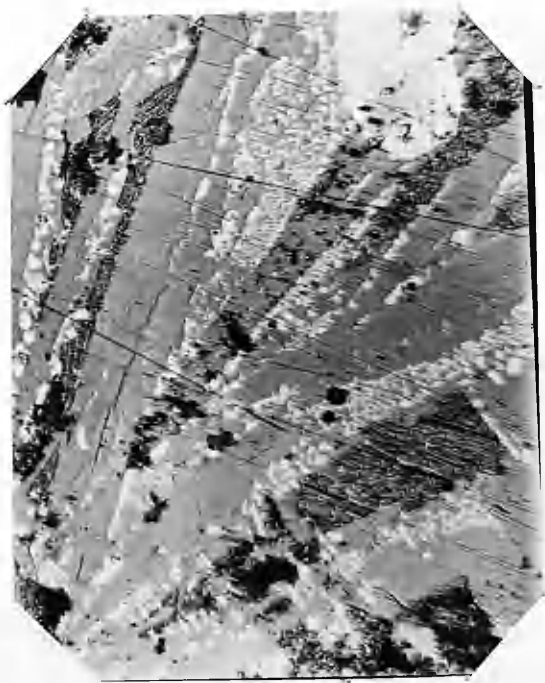


Fig. 58. 50%  $\text{MnO.SiO}_2$   
50%  $2\text{FeO.SiO}_2$   
× 250.

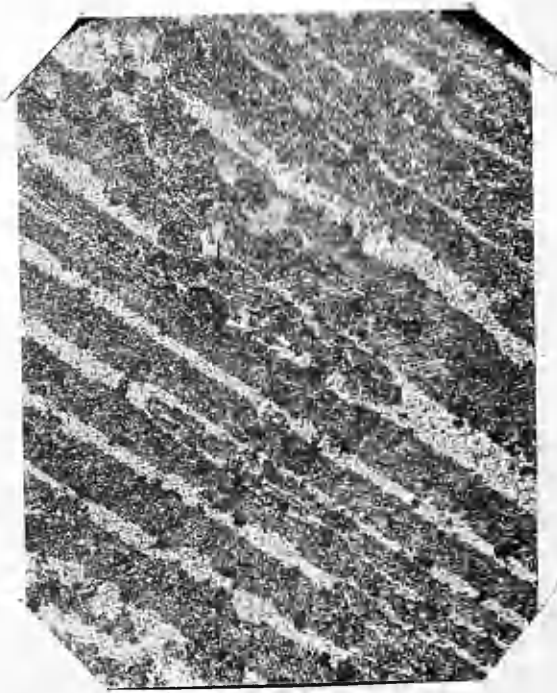


Fig. 59. 40%  $\text{MnO.SiO}_2$   
60%  $2\text{FeO.SiO}_2$   
× 160.



Fig. 60. 20%  $\text{MnO.SiO}_2$   
80%  $2\text{FeO.SiO}_2$   
× 200.

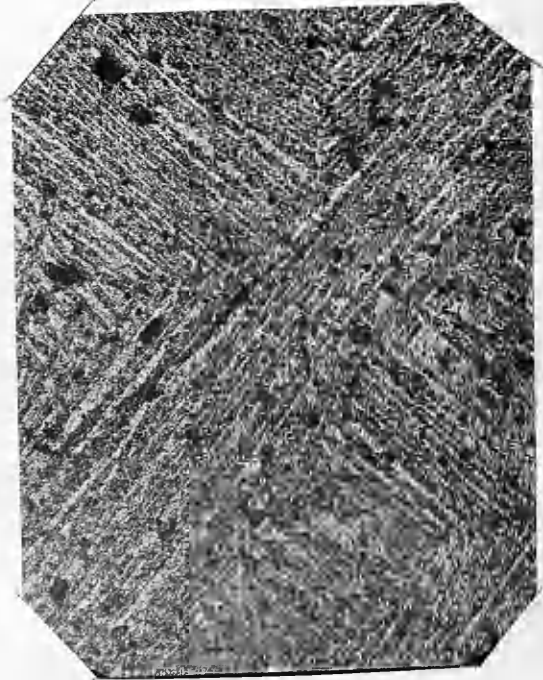


Fig. 61. 10%  $\text{MnO.SiO}_2$   
90%  $2\text{FeO.SiO}_2$   
× 160.

FeS - 2 FeO. SiO<sub>2</sub>.

Pure ferrous sulphide was prepared by a method very similar to that adopted for manganese sulphide. The commercial product was heated to 900°C. in a current of H<sub>2</sub>S for two to three hours and then cooled. As soon as the sulphide had cooled to 500°C. the H<sub>2</sub>S was displaced by hydrogen and the furnace maintained at that temperature for a short period. The product was finally cooled in hydrogen. The sulphide thus produced was golden in colour, markedly crystalline but very brittle.

Melting was carried out as before, using a fireclay crucible and a platinum - platinum/rhodium couple.

The melting curves are given in Figs.62 to 63, and the freezing curves in Figs.64 to 66. The equilibrium diagram obtained from the melting temperatures is plotted in Fig.67.

The most noticeable feature of these determinations is the reversibility of melting and freezing in the FeS-rich mixture and the greater amount of supercooling in the 2 FeO. SiO<sub>2</sub>-rich melts. The diagram is eutectiferous; the eutectic occurring at 47% of FeS and at 990°C. The solid solubility of the silicate in FeS is extremely small, the maximum limit being in the order of 0.5% to 1.00%. The silicate, on the other hand, is capable of dissolving approximately 10% of FeS.

Heating Curves

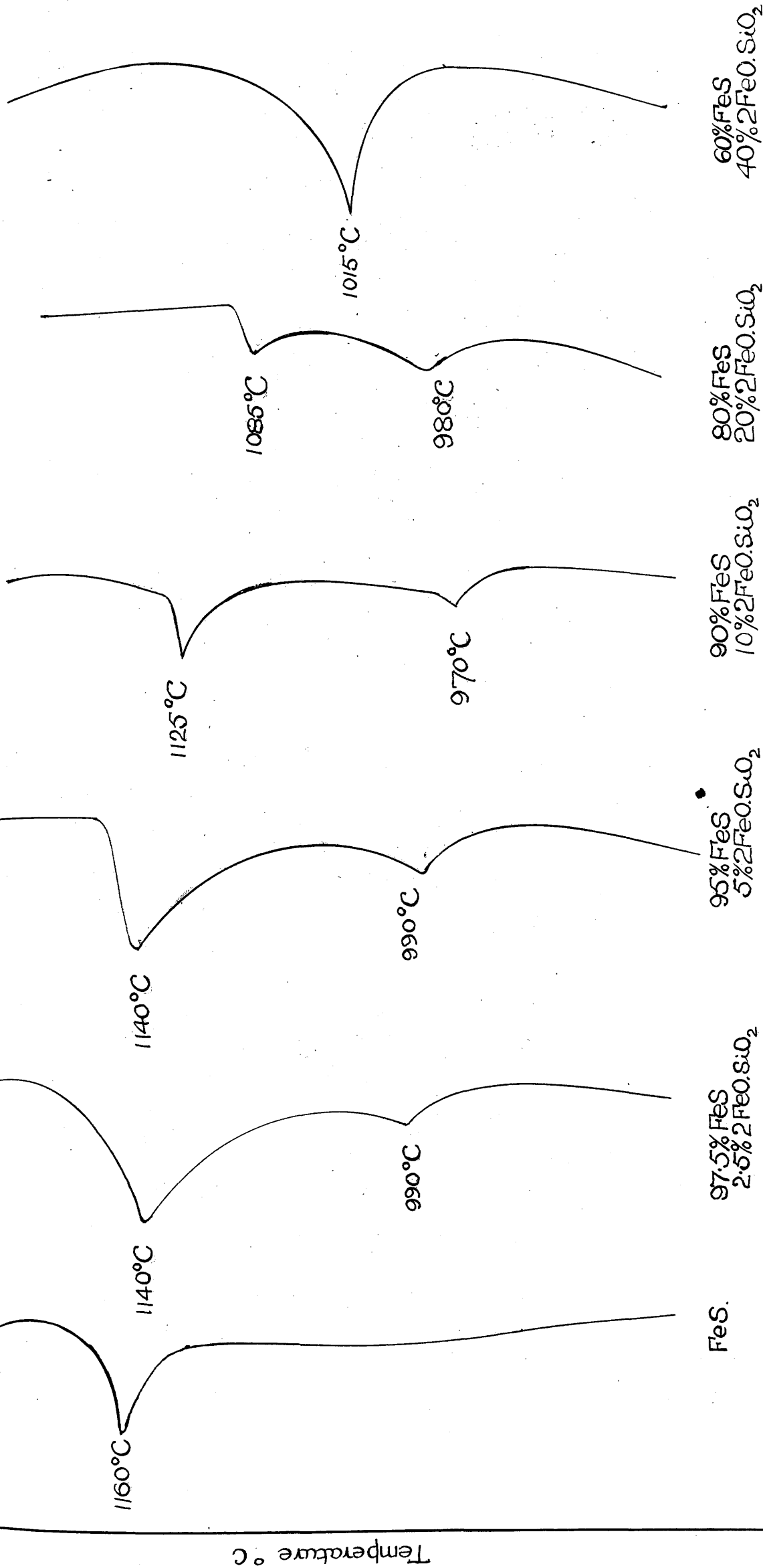


Fig. 62

Heating Curves

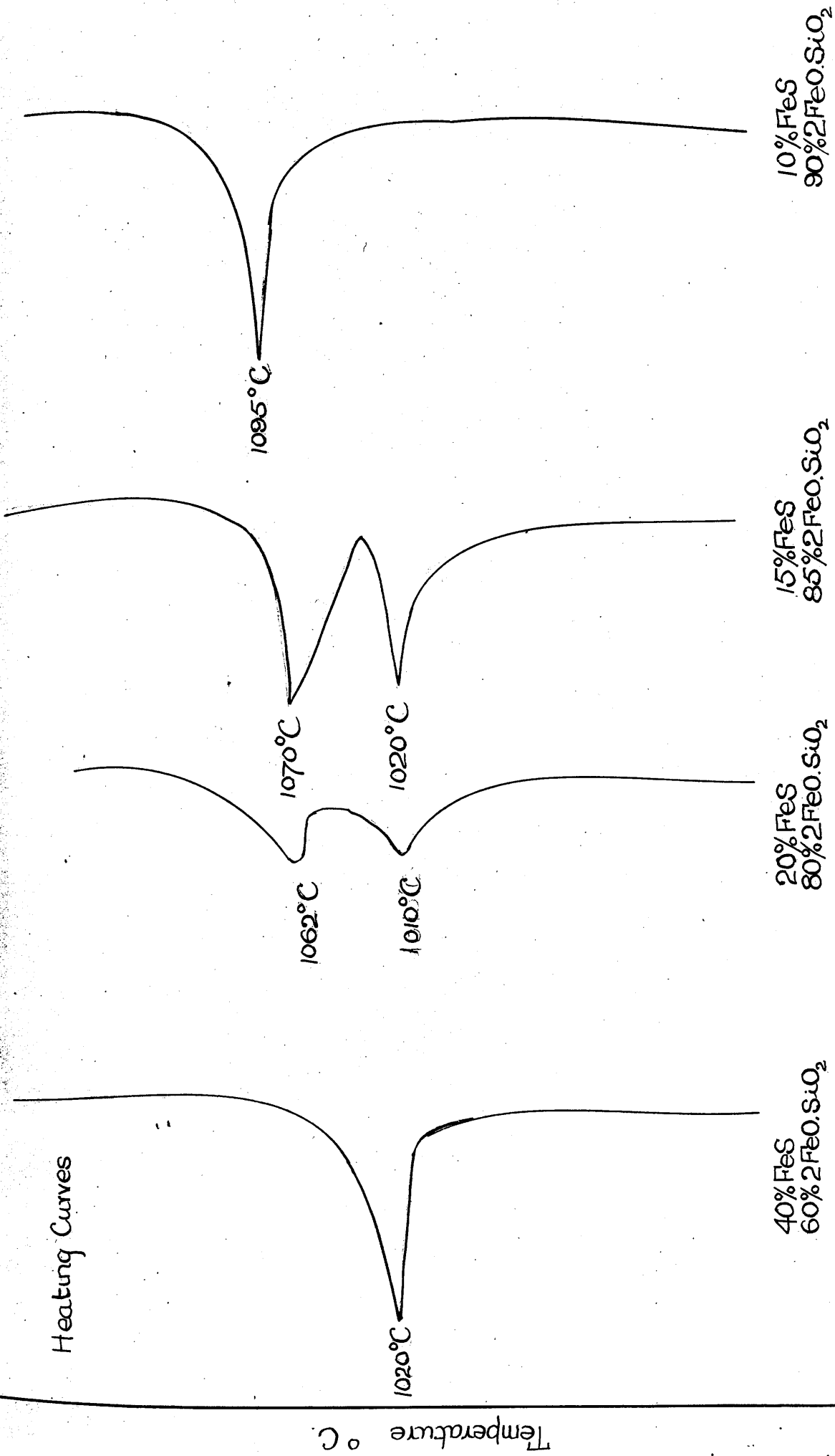


Fig. 63

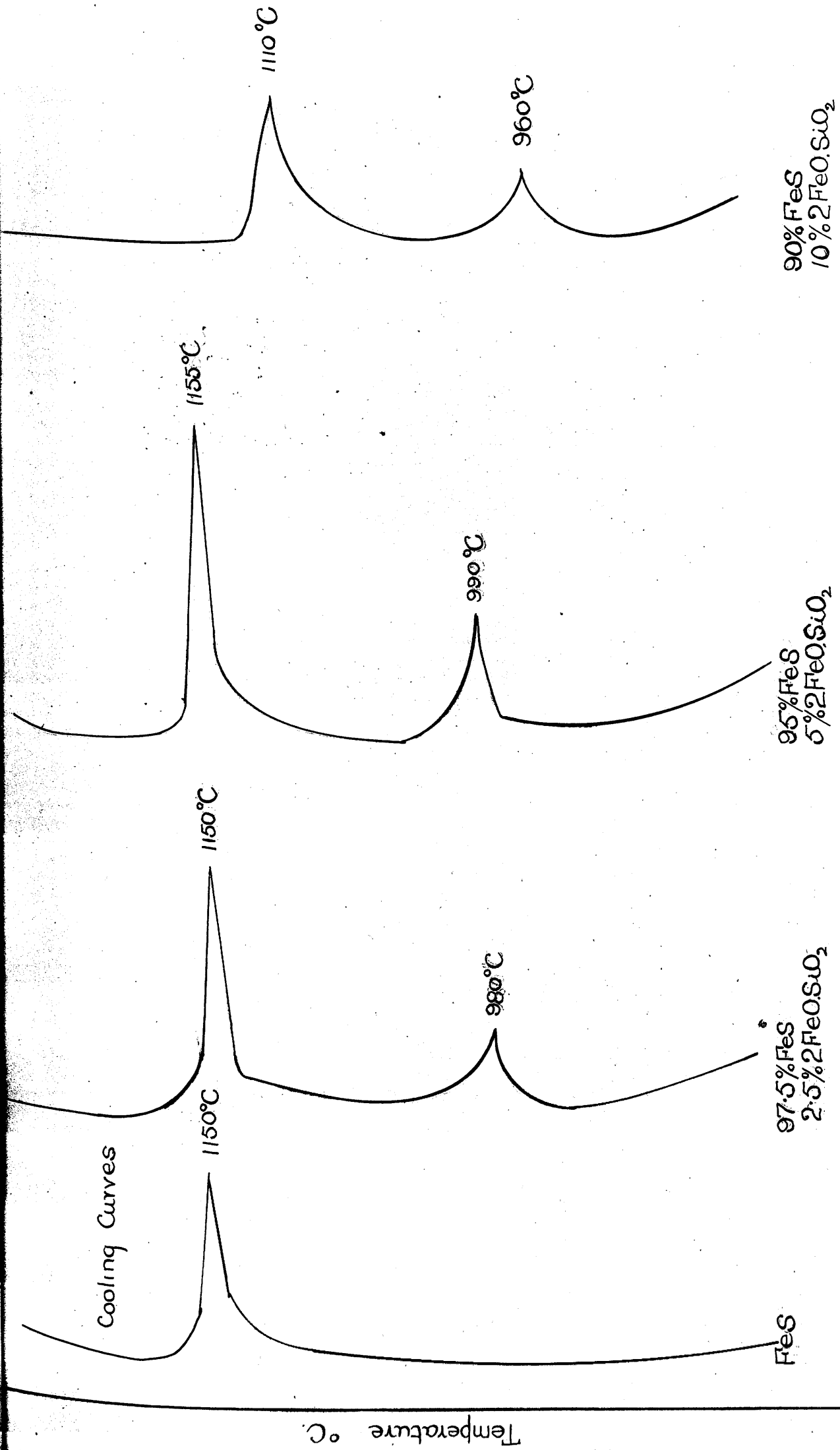


Fig. 64

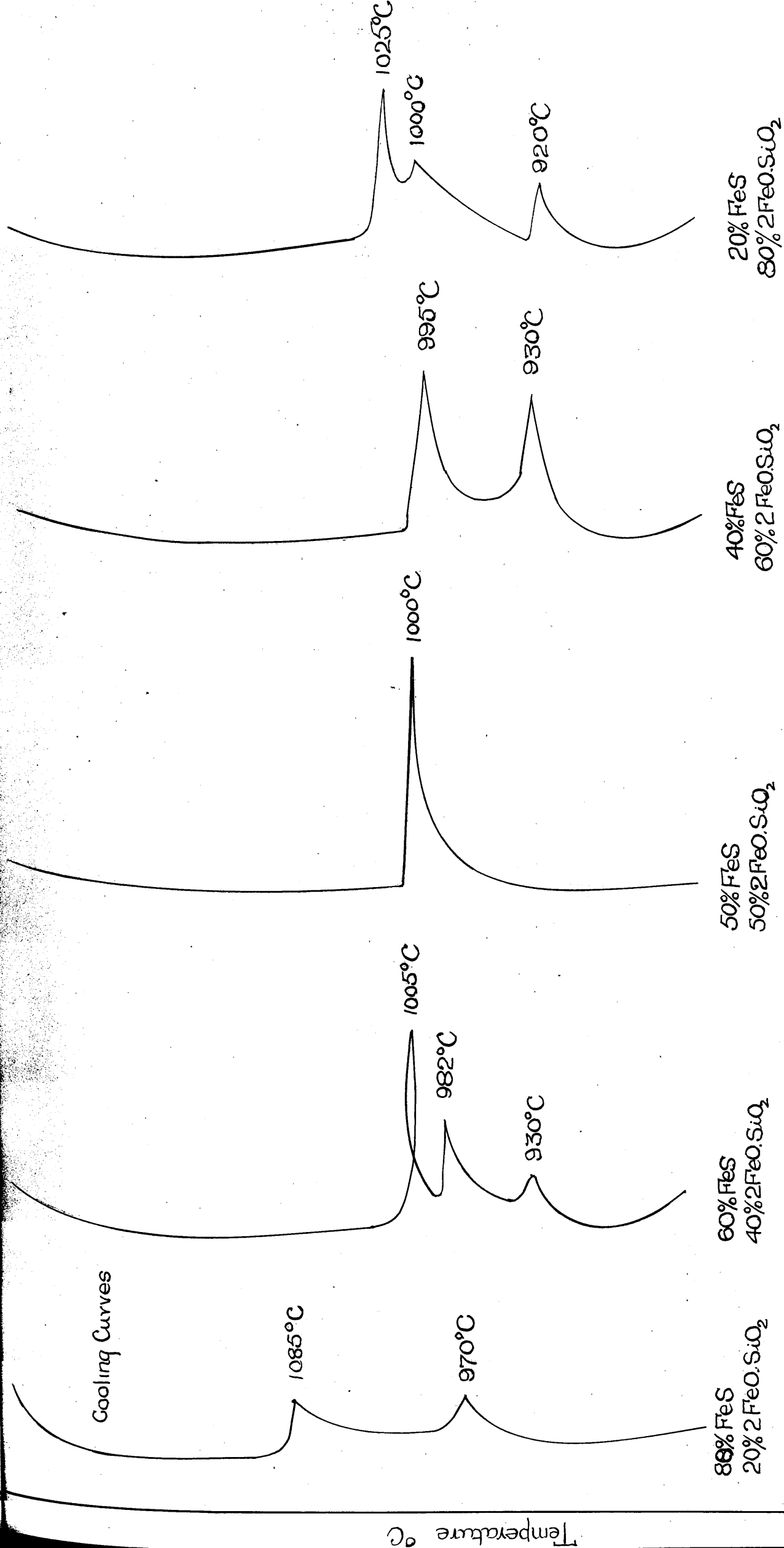


Fig. 65



Cooling Curves.

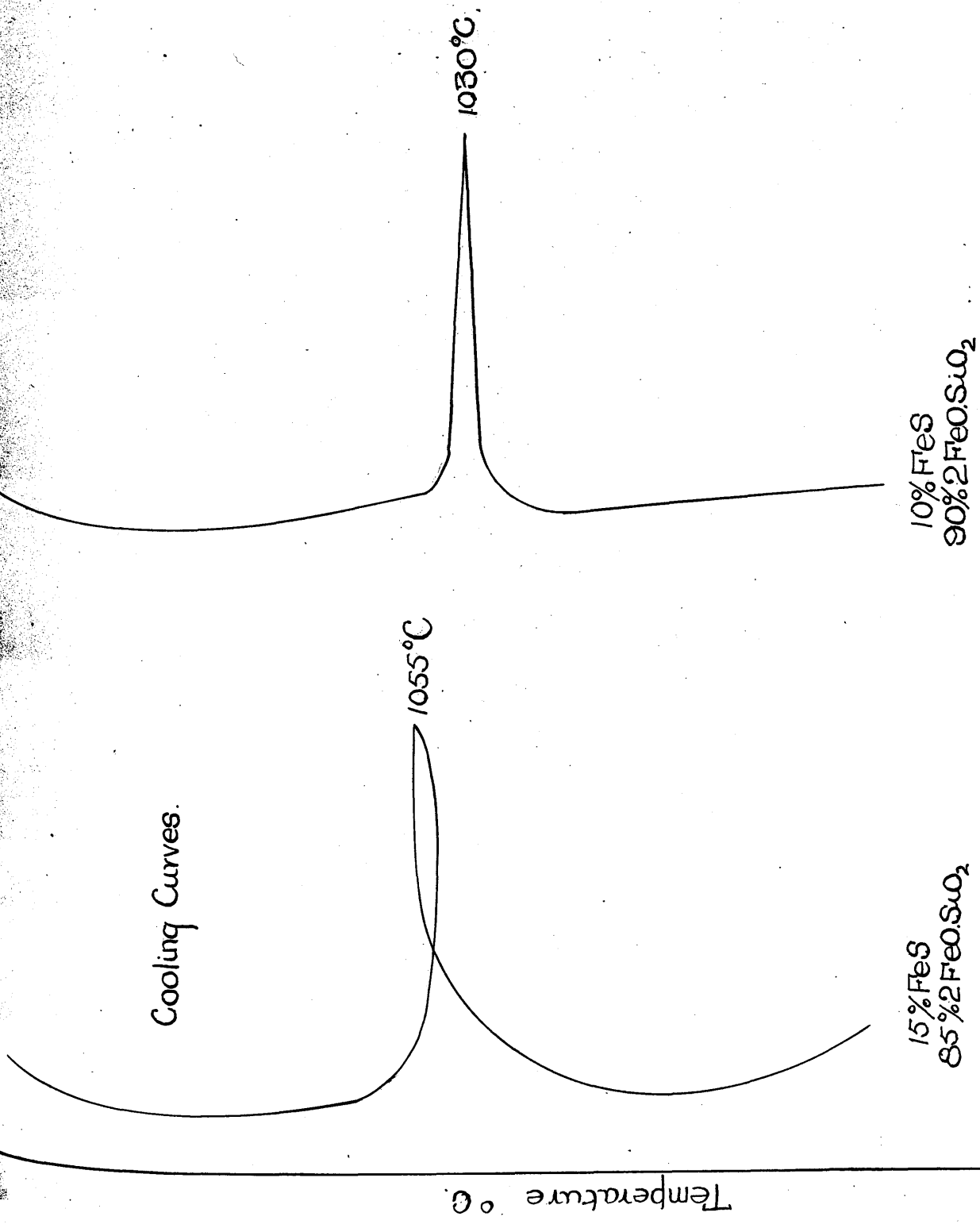


Fig. 66

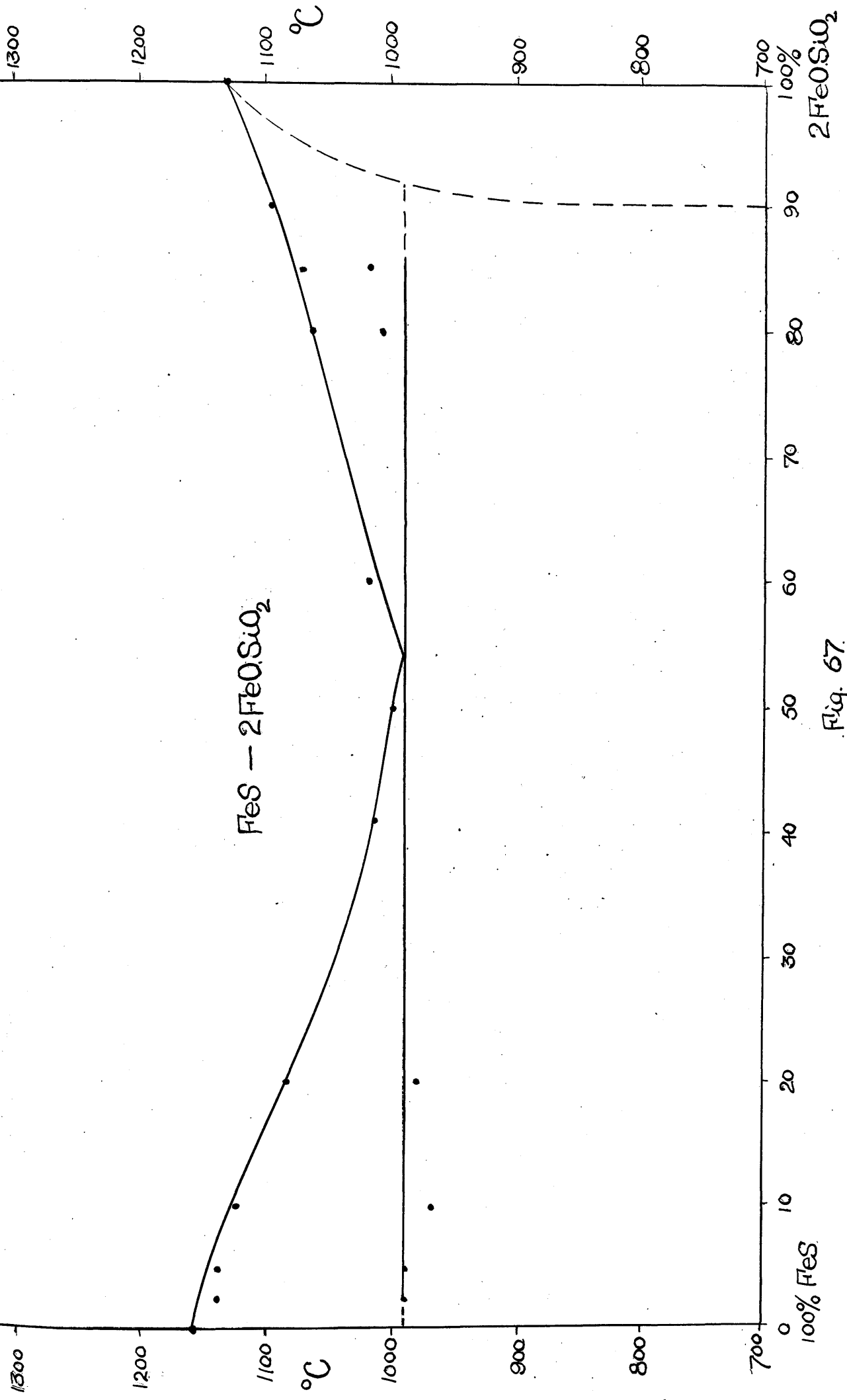


Fig. 67

DENSITY DETERMINATIONS.

All the density determinations were done in a specific gravity bottle. The method adopted, and adhered to throughout the investigation, was as follows:-

The melted mixtures were crushed as fine as possible and then placed in the dried and weighed specific gravity bottle. The bottle and contents were then placed under a bell jar which was evacuated to remove any air that had become absorbed by the mixture. After this treatment the bottle was weighed. Distilled water that had been boiled in vacuo was always used.

Unfortunately, on account of the whole of the melts from the FeO - MnO system having been used for analysis, density determinations on this system had to be omitted. The density results were plotted against composition and are shown in Fig. 68. Densities of mixtures of the following systems were determined:-

MnO - MnS

MnS - MnO. SiO<sub>2</sub>

MnS - 2 FeO. SiO<sub>2</sub>

MnO. SiO<sub>2</sub> - 2 FeO. SiO<sub>2</sub>

2 FeO. SiO<sub>2</sub> - FeS.

SYSTEM MnO - MnS:

The density diagram (Fig.68) of the MnO - MnS system confirms the data obtained in the thermal diagram remarkably well. The sharp change in direction of the curve at its extremities shows the extent of the solid solubility of each constituent in the other. 10% of MnS is soluble in MnO and 18% of MnO is soluble in MnS, in the solid state. This gives ample corroboration of the solubilities deduced from the thermal diagram.

SYSTEM MnS - MnO. SiO<sub>2</sub>:

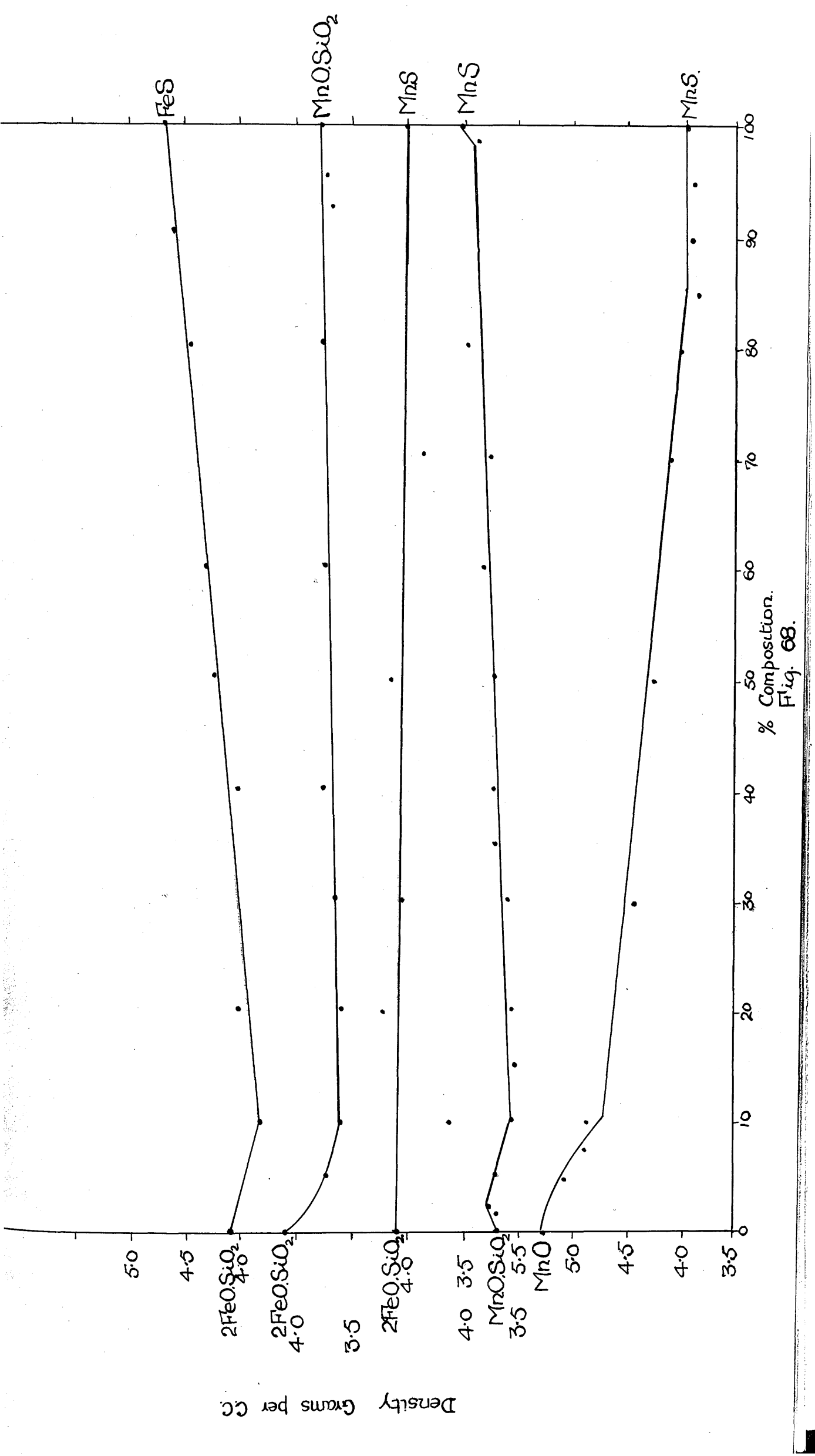
The solid solubilities obtained by the density determinations for this system agree very well with those obtained for the thermal equilibrium diagram.

SYSTEM 2 FeO. SiO<sub>2</sub> - MnO. SiO<sub>2</sub>:

The density diagram for this system proves very definitely the solution of 10% of MnO. SiO<sub>2</sub> in 2 FeO. SiO<sub>2</sub>. The density falls on the addition of 10% of MnO. SiO<sub>2</sub> from 4.12 (2 FeO. SiO<sub>2</sub>) to 3.6 at which point the curve shows a sharp change in direction. From that point, with increasing percentages of MnO. SiO<sub>2</sub>, the curve takes the form of a straight line which is typical of the density diagram of a simple eutectiferous series.

SYSTEM 2 FeO. SiO<sub>2</sub> - FeS:

The diagram clearly shows the almost complete insolubility of 2 FeO. SiO<sub>2</sub> in FeS, and the extent of the solution of FeS in 2 FeO. SiO<sub>2</sub>.



% Composition.  
Fig. 68.

CONCLUSIONS:

It is realised that from the binary systems investigated no final deductions can be drawn as to the behaviour of inclusions in general in steel but certain types of inclusions can be studied in more detail.

A few facts of interest and importance, however, have been elucidated. The first of these is that the micro-constituent commonly known as oxide is in all probability a solid solution of FeO and MnO which has a melting point varying between  $1410^{\circ}\text{C}$ . and  $1585^{\circ}\text{C}$ . according to the composition. Since the rate at which the inclusions rise depends to a great extent on the size of those inclusions, all factors which promote coalescence are important. And again, since coalescence is only possible with liquid inclusions it is problematical whether oxide inclusions rich in MnO will ever form particles large enough to rise rapidly to the surface of an ingot and thus be eliminated. It is probably for this reason that oxide inclusions are always present in steels in the form of very small particles which are fairly evenly disseminated throughout the mass.

Another feature of considerable interest is that MnS was found to be soluble in manganese oxide and in the silicates of iron and manganese. It is also very probable that MnS is soluble in ferrous oxide and in the mixtures of the two silicates.

The solubility of MnS in steel has been proved to be extremely small so that any sulphur present in the steel must exist either as free MnS or as MnS dissolved in the oxides or silicates. These oxide and silicate inclusions will then be able to act as scavengers for MnS, dissolving it in small quantities wherever contact between the two inclusions is brought about.

This solution of MnS by the oxides and silicates has a profound effect upon the interpretation of sulphur printing.

Since a sulphur-print gives a dark impression where there is sulphur, it stands to reason that however small may be the amount of sulphur in an inclusion it will leave its mark on a sulphur-print. It follows, then, that a sulphur-print does not merely represent the distribution of free sulphide but must be representations of all inclusions that are sulphur-bearing. In other words, a sulphur-print is virtually a print showing completely all non-metallic inclusions, the sulphur dissolved in these merely serving as a means of bringing about their detection. It becomes obvious, then, the large brown markings on a sulphur-print do not necessarily mean high sulphur segregation but might represent segregation of other inclusions which contain dissolved MnS.

In Table I. are given the densities of the various non-metallics studied, together with the densities of steel for the sake of comparison.

TABLE I.

Substance.	density gm./cc.	Steel <sup>(10)</sup>			
			.03%C.	.21%C.	1.04%C.
MnO. SiO <sub>2</sub>	3.710				
MnS	3.980	1700°C.	7.01	6.89	6.74
2 FeO. SiO <sub>2</sub>	4.120	1600°C.	7.13	7.00	6.84
FeS	4.68	M.Pt.	7.21	7.10	7.02
MnO	5.26				
FeO	(5.90)	M.Pts.	1521°C.	1502°C.	1452°C.

From Table I. it can be seen that these inclusions and mixtures of these, should tend to rise in the liquid metal if their size is such that they are affected by gravity. The rate at which they rise in the liquid steel is of vital importance to the final distribution of these slag grains in the

solid ingot.

The rate of rising of spherical particles in a liquid can be calculated from the formula deduced by Stokes, namely:-

$$u = \frac{2g}{9n} r^2 (d^1 - d)$$

where u = final rising velocity

r = radius of grain

d = density of grain

d<sup>1</sup> = density of medium

n = coefficient of viscosity of medium.

If it is assumed that the steel is quiescent and that the particles are spherical, an impression of the rate at which non-metallic substances would tend to rise in the steel can be obtained by applying the above formula. For a given particle size the rate of rising is directly proportional to the difference in density between the particle and the liquid steel. In Table II. are given the calculated rates of rising for the pure substances and for the MnO - MnS eutectic assuming a particle size of .001 cm. in diameter.

TABLE II.

Substance.	Density gms. per c.c.	Rate of rising (Particles .001 cm. dia.). cm. per min.	Melting Point °C.
MnO	5.26	0.36	1585
FeS	4.68	0.49	1160
MnO - MnS (eutectic)	4.29	0.57	1280
2 FeO. SiO <sub>2</sub>	4.12	0.60	1130
MnS	3.98	0.63	1620
MnO. SiO <sub>2</sub>	3.71	0.69	1305

The rate of rising of any inclusion must fall between .3 and .7 cm. per minute if the particle size is .001 cm. in



diameter. This slow rate of rising will only become apparent in large ingots where the solidification takes several hours. However, a particle having a diameter of 0.1 cm. will rise ten thousand times as quickly as a particle having a diameter of 0.001 cm. The size of the slag particle can thus be shown to have an enormous effect upon its elimination from the steel by rising to the head of the ingot. All influences, then, which promote the formation of large particles, coalescence and coagulation, increase the rising velocity and contribute to their final removal.

The object of deoxidation then becomes not only a question of removing the dissolved ferrous oxide by the addition of suitable reducing agents, but also the production of deoxidation products that are liquid at the temperature of the steel and are thus capable of coalescing into larger particles. The viscosity of the non-metallic particles in question would seem to have a profound effect on the size of the grain produced. The lower the viscosity the greater the rate of coalescence of given particles. Since viscosity decreases with increasing temperature it is evident that the greater the degree of superheat of the non-metallic matter above its melting point, the less will be its viscosity, and the greater its opportunity of forming larger particles by coalescence. For all practical purposes the temperature of the more common classes of steel can be taken as constant at tapping, and is generally considered to be in the region of 1600 - 1650°C. This temperature will then be the maximum temperature to which non-metallic matter can be heated and hence, constitutes the maximum amount of superheat that can be imparted to a slag particle, having a given melting point. In order to obtain the maximum amount of coalescence between the inclusions, the melting temperature of these inclusions must be reduced so that their degree of superheat can

be increased, the temperature to which they can be heated being limited. To produce a steel that is relatively free from inclusions, then, it is not merely necessary to produce liquid products of deoxidation, but products which have the lowest melting temperature under a given set of conditions.

It is for this reason that the silico-spiegel alloys have met with so great a success in practice. Instead of producing inclusions either rich in  $MnO$  or in  $SiO_2$  when either manganese or silicon alloys were used alone, the silico-manganese type of deoxidising agent produces  $MnO$  and  $SiO_2$  in intimate contact with one another. At the temperature of the steel they immediately combine to form  $MnO \cdot SiO_2$  which has a melting temperature at least  $300^\circ C.$  below that of  $MnO$ . The  $SiO_2$  will also flux some of the  $FeO$  which has not already been reduced and the  $MnO \cdot SiO_2$  and  $2 FeO \cdot SiO_2$  dissolve in one another to form mixtures with melting temperatures between  $1305^\circ C.$  and  $1130^\circ C.$  and having densities between 3.7 and 4.1. Such inclusions would have every opportunity of coalescing and rising rapidly to the surface of the metal. On their way upwards these silicate inclusions could dissolve any sulphide particles that they come into contact with and in this capacity act as scavengers of  $MnS$ . Various methods of aiding coalescence have been suggested since the problem of non-metallic inclusions became of real importance. Such extreme measures as the addition of some type of fluid slag have been advocated as well as the vigorous stirring of the metal in the ladle. These methods have seldom, if ever, been put to the test of practice so that it is only in a tentative way that the mechanism by which they are expected to clean the steel can be studied. The methods themselves are different; the addition of slag merely acting as a solvent for the sulphides and oxides of iron and manganese whereas the process of stirring would obviously aid coalescence by bringing slag particles

together more frequently.

Although artificial stirring of steel in the ladle has never been developed, an action similar to such treatment must be present in an 'effervescing' steel. It is particularly interesting, then, to know that 'effervescing' steel has been proved on numerous occasions to contain fewer but very much larger inclusions. There can only be one reason for such a phenomenon - the stirring action of the rising gases on the ingot has enabled coalescence to proceed to a greater extent than in a 'dead killed' steel, with the consequent formation of larger particles.

Although it is not always appreciated, a very violent circulation of the metal is set up by the most recent steel producing units - the high-frequency induction furnace. The circulation of the metal, which is in a vertical plane, is under accurate electrical control. With a covering slag that is fairly viscous, and the slags in high-frequency furnaces cannot be other than viscous because they are not directly heated, the slag particles that are brought to the surface by the circulation, are held in the slag and are permanently removed from the metal. The degree of circulation in the metal can be controlled so that no slag is taken down with the metal. This reason also favours the production of high class steel in high-frequency furnaces.

The time does not seem far distant when the large capacity high-frequency furnace will be installed in all modern steel works not as a refining unit but as a supplementary ladle in which the steel is freed from slag particles by the circulation of the metal. The open hearth furnace could then be worked at a very rapid rate with no worry of the oxygen content of the steel or deoxidation products.

From what has already been said, the production of

fluid particles during deoxidation is obviously best, and the deoxidisers should be used in such a way that the products of deoxidation should melt at as low a temperature as possible so that the maximum amount of coalescence can be obtained. It is here that the greatest progress can be made in the production of cleaner steel and it is only by further research on more complicated systems of non-metallics that the necessary data can be obtained.

REFERENCES :

1. A.McCance: Trans.For.Soc.XIII. 309, 1918.
2. C.H.Herty: Trans.American Society for Steel Treating, Vol.XIX., 1931-32.
3. F.S.<sup>u</sup>Taitton and D.Hanson: Journal of the Iron and Steel Inst. No.II., 1924.
4. C.H.Herty: *ibid.*
5. J.H.S.Dickenson: Journ.Iron and Steel Inst., 1926, No.I. 177.
6. Fitterer: A.I.M.E., 1929.
7. Oberhoffer and Vonkiel: Stahl und Eisen, 1921, Vol.41.
8. C.H.Herty: Metals and Alloys, 1929-1930, Vol.I.
9. L.B.Pfeil: Journ.Iron and Steel Inst., 1931, No.I.
10. C.Benedicks and Lofquist: 'Non-metallic inclusions in iron and Steel', London, 1930, Chapman & Hall, Ltd.
11. Woloskow: Annales de l'Institut Polytechnique de St. Petersburg, 1911, Vol.15.
12. Levy: Journ.Iron and Steel Inst., Carnegie Schol. Memoirs, 1911, Vol.3.
13. Mellor: Comprehensive Treatise on Inorganic Chem., Vol.VI. Part II.
14. A.McCance: Journ.Iron and Steel Inst., 1918, No.1.