The Constitution of Basic Open - Hearth Steel Furnace Slags.

A

Thesis.

Presented by

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I hereby declare that the composition of the thesis entitled " The Constitution of Basic Open-Hearth Steel Furnace Slags" is my own work.

The Constitution of Basic Open - Hearth Steel Furnace Slags.

It is well known that the constitution of Basic Open - Hearth steel furnace slags varies with the type of material charged into the furnace, and also, that the constitution of the slag must necessarily be different at different stages of the steel-making process. It is known that the ultimate constitution of the slag determines the type of steel produced, but the effect of the slag constitution on the purity of the finished steel is still imperfectly understood. The research recorded here was undertaken with the object of identifying the fundamental chemical compounds occurring in slags, and of applying the information obtained to the identification of non-metallic particles in steel, and the possible correlation of these with the composition of the finishing slag.

The work was divided, broadly, into four separate parts;

a. The microscopical examination of the crystalline compounds occurring in various binary equilibrium diagrams of slag components.

b. The application of the data obtained from Section a. to various typical furnace slags.

c. The qualitative effect of the various components of a typical slag on steel, at elevated temperatures, but below the melting point of these components.

d. The application of the information obtained, towards the identification of non-metallic particles in steel.

SECTION a.

Since the fundamental components of slags are iron oxides, manganese oxide, silica and lime, the compounds forming when these react together at elevated temperatures, were assumed always to go through the same phase changes on cooling; so that, while the crystalline compounds seen at room temperature might possibly vary slightly from those existing at freezing point, nevertheless, the characteristics found would always indicate a certain condition of the materials reacting. The materials examined were melted in a series of equilibrium diagram determinations and were as follow,

a. Ferrous oxide and Manganous oxide.
b. Ferrous oxide and Silica.
c. Manganous oxide and Silica.
d. Ferrous oxide, Manganous oxide, and Silica.
e. Manganous oxide and Alumina.
f. Lime and Ferric oxide.

In addition to these, a few mixtures of Ferrous oxide, Manganous oxide, Silica and Alumina, were also melted and examined. The section of the quaternary diagram was chosen, as representing, fairly closely, that which might occur in actual practice.

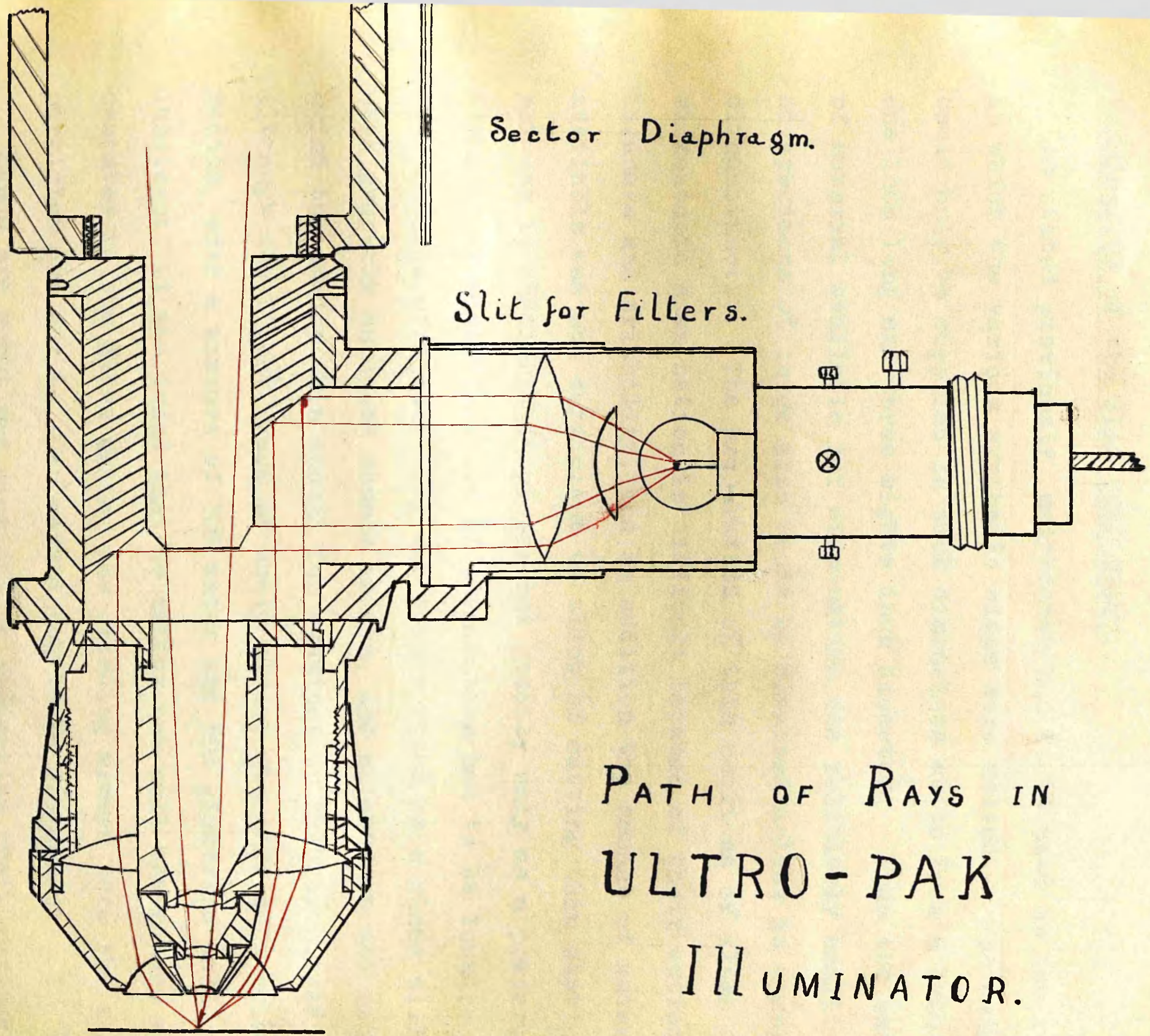
As stated above, the materials examined were obtained from equilibrium diagram determinations. It was very essential that the various synthetic slags should be prepared free from impurity. Accordingly, the refractory material of the crucible in which the slags were melted had to be non-reactive towards the synthetic slags. Fireclay was found to be of no use, since the silicates and other materials of which it is composed reacted with the material which was to be melted. Platinum extracts iron, although in very small quantity, from iron oxides, unless the partial pressure of oxygen in the furnace atmosphere exceeds a certain value. Therefore a platinum crucible could not be used to hold the material to be melted, since most of the fusions were done in vacuo. Molybdenum was found to be resistant to all the synthetic slags made and examined, with the exception of the lime - ferric oxide

oxide ones. Accordingly, crucibles were prepared from molybdenum rod, and the synthetic slags made in these crucibles were rigorously examined, chemically and spectroscopically, for traces of metal; in every case the tests were negative.

APPARATUS.

The furnace used for melting the mixtures is described in a later page (no. 40.). The microscope employed was capable of being used either as a metallurgical one or as a petrographical one. It was equipped with a polariser and a convergent lens system, underneath a rotating stage. This stage could be rotated by a tangent screw, and the degree of rotation could be read to the nearest minute. In the tube of the instrument was a slot into which could be placed either a half-wave plate or a quartz prism, and the analysing Nicol's prism was mounted in a rotating ocular. The instrument was also fitted with a small Bertrand's lens for magnifying interference figures. The objectives used with the microscope ranged from a 16 mm. to an oil-immersion 4mm, and the oculars ranged in magnifying power from 4 to 12, according to the magnification required. With such a fittings on the microscope, it was possible to find the extinction angle, crystal character and birefringence of any transparent material. As a metallurgical microscope, the instrument was capable of casting a beam of polarised light perpendicularly on a polished specimen, so that it was possible from examination of such a specimen to state whether a certain constituent were isotropic or not.

As the work proceeded, it was found desirable to supplement this instrument with others fitted with different types of illumination. For thin section and transparent crystal work a microscope fitted to give dark field illumination by transmitted light was used. For dark field illumination by reflected light an " Ultro-pak "illuminator was used. A diagram of this fitting is given on page 4. For very large specimens to be examined under low magnifications, a parabolic mirror, fitting on the side of the objective, was used, giving fairly good dark



PATH OF RAYS IN
ULTRO-PAK
Illuminator.

dark field conditions. The " Ultro-pak " fitting was used for higher magnifications.

EXAMINATION of the SLAG COMPONENTS.

As stated previously, molybdenum had to be used as the refractory in which the various synthetic slags were melted. The molybdenum could only be supplied in such dimensions as to form a crucible one inch long and three-eights inch diameter. Thus the amount of material available for examination was relatively small, and no specimens of large size could be obtained unless in exceptional circumstances. The preparation of thin sections of slags for microscopic examination is difficult because of their extreme hardness and friability, and in addition the amount of material available was not sufficient to allow of cutting thin sections, nor was it available in pieces but usually only as a powder. Accordingly another method of examination had to be found.
The powdered synthetic slag was firmly fixed on a glass slide with properly hardened canada balsam, and an attempt was made to grind the powder thin enough for examination by transmitted light. Although the finest grade of emery powder was used as a grinding medium, with a mixture of 50% water and 50% glycerine as a lubricant, it was found that no matter how well the powder was cemented to the glass slide, the grinding always tore the slag particles out and so this method had to be abandoned.

Sands are sometimes examined by separating their various constituents by flotation. A series of liquids are chosen, such that each component of the sand will float off in some particular liquid while those of higher specific gravity will sink. this method, while of advantage when the sand is of fairly large particle size, is of no value for slags, where the crystals of the various components are of so small size that grinding to 240 meshI.M.M. sieve size is not sufficient to separate the intergrown crystals. In addition, the amount of slag constituent in some cases is only a fraction of one per cent of the whole; so this method had also to be abandoned.

The relative refractive index of a transparent material, immersed in a liquid, may be determined under the microscope by Beck's method.[1] If a series of liquids of different refractive indices be obtained, it is possible, within narrow limits, to determine the refractive index of the substance. Use was made of this fact in the examination of the slag components. A series of liquids of different refractive indices were obtained and the slags were immersed in each in turn. By a process of elimination it was found possible to state how many compounds of different refractive index were present. The following table gives a list of the different liquids used.

LIQUID.	REFRACTIVE INDEX.	LIQUID.	REFRACTIVE INDEX.
Water................	1.33.	Chlorobenzene...........	1.53.
Absolute Alcohol.....	1.36.	Nitrobenzene............	1.55.
Chloroform...........	1.44.	Monobromobenzene........	1.56.
Glycerine............	1.47.	Bromoform...............	1.59.
Castor Oil...........	1.48.	Monoiodobenzene.........	1.62.
Xylene...............	1.49.	Monobromonaphthalene....	1.66.
Benzene..............	1.50.	Methylene Iodide........	1.74.
Methylene Iodide saturated with		Sulphur................	1.78.

The refractive index of all these liquids was carefully checked by means of an Abbe Refractometer before they were used. The Abbe Refractometer cannot measure refractive indices greater than 1.66, so, for methylene iodide, by itself, and also when saturated with sulphur, it is necessary to use a Pulfrich Refractometer which will measure refractive indices up to 2.00.

Very many slag constituents have refractive indices greater than the range covered by the above liquids; so another modification of the method of determination had to be adopted. It has been found that sulphur and selenium when mixed in different proportions and melted give glasses of different refractive indices, ranging in value from approximately 2.00 to 2.93. [2]

(The figures 1, 2, etc. refer to references to be found at the end)

Accordingly, glasses were prepared, containing these two substances, in the proportions shown in the table below.

SULPHUR.	SELENIUM.	REFRACTIVE INDEX.	
		For Lithium Light.	For Sodium Light.
100%	00%	1.978.	1.998.
91%	9.0%	2.000.	2.022.
82.4%	17.6%	2.025.	2.050.
75.0%	25.0%	2.050.	2.078.
68.2%	31.8%	2.075.	2.107.
62.5%	37.5%	2.100.	2.134.
56.8%	43.2%	2.125.	2.163.
51.8%	48.2%	2.150.	2.193.
47.0%	53.0%	2.175.	2.220.
43.0%	57.0%	2.200.	2.248.
36.0%	64.0%	2.250.	2.307.
30.0%	70.0%	2.300.	2.365.
25.0%	75.0%	2.350.	2.423.
20.0%	80.0%	2.400.	2.490.
12.3%	87.7%	2.500.	2.524.
6.2%	93.8%	2.600.	2.755.
0.8%	99.2%	2.700.	2.90.
0.0%	100.0%	2.716.	2.92.

The sulphur - selenium glasses were prepared by carefully weighing out the required amounts of the two substances, and then melting the selenium in a small glass tube, care being taken to just melt the material and avoid any overheating and danger of volatilisation. The sulphur was then added to the molten selenium and the mixture became homogeneous almost at once. The melt was cooled very quickly to prevent any sublimation of the sulphur and the glass was preserved for use.

The glasses were standardised against pure minerals, whose refractive indices had been determined by other methods, and the values adopted were taken from the International Critical Tables.

A few examples of the minerals used are;

Mineral.	Refractive Index.
Zircon.	1.95.
Cerussite.	1.99.
Cassiterite.	2.00.
Phosgenite.	2.13.
Calomel.	2.31.
Zinc Blende.	2.35.
Diamond.	2.42.

For examination of the specimens in Lithium light, use was made of the fact that a very thin section of selenium glass of pure selenium allows light to pass which corresponds nearly exactly to the wave-length of Lithium light. So a thin section of pure Selenium was placed in the path of the incident light, thus giving the required condition.

The method of using the glasses was as follows; the slag for examination was first powdered, but not too finely. A coarse crushing was found to be quite satisfactory, although some of the crystals obtained were rather thick when compared with standard thin geological sections, and were also, in some cases fragmentary. In a large number of cases, however, complete crystals were obtained. The crushed slag was placed on a slide, together with a small piece of the glass to be used. A cover glass was placed over all and the slide was gently heated over a micro-burner; the sulphur-selenium glass melted and the cover glass was pressed gently but firmly and uniformly, down on the material. The refractive indices of the slag components and that of the glass were then compared. (v.s.) [1.] The purpose of the cover glass is to prevent volatilisation of the sulphur. In the case of glasses high in sulphur the slide had to be cooled as quickly as possible since these glasses showed a great tendency to crystallise.

When the liquids were being used, the procedure was practically the same. The crushed slag was placed on the slide and a drop of the liquid being used was placed on top; the whole was then covered with a cover glass and the relative refractive indices of of the slag minerals and that of the liquid compared. By varying the liquid, the refractive indices of the different crystals were found. In addition, it was found to be fairly easy to determine the extinction angles of the different components. The birefringence of anisotropic crystals was also determined, at least qualitatively, and their crystal character was in several instances also determined. In several cases crystals were so oriented that it was possible to obtain interference figures; and so the crystal could be stated to be either uniaxial or else biaxial. All this data was compiled, and knowing, in the case of synthetic slags, the materials present, the names of the minerals present could be obtained from books of reference.

This then was the method of examining the slags made from pure materials to find the compounds formed when these pure components reacted at elevated temperatures.

THE PREPARATION of FERROUS OXIDE.

The ferrous oxide used was prepared from chemically pure ferrous oxalate. The ferrous oxalate was placed in an alundum container, which was found not to contaminate the finished product. The alundum container was placed in a refractory " Pythagoras " tube and this was placed in a resistance wire electric furnace. The "Pythagoras" tube was then evacuated by a "Cenco" hyvac pump. The refractory tube was closed by a rubber bung through which passed a glass tube for evacuating the refractory tube and another for allowing of admission of thermo--couple wires. These glass tubes were closed by pieces of pressure rubber tubing which could be clipped and were further sealed by means of celluloid dissolved in amyl acetate. The "Pythagoras"tube having been evacuated, then the vacuum was tested and adjustments made to make the tube absolutely air-tight if necessary. When a perfectly gas-tight condition was obtained, the pump was restarted and the tube was heated. It was essential that there were no gas leaks in the tube or else the ferrous oxide would have been oxidised at high temperature yielding

yielding a mixture of all three oxides of iron. The evacuating pump was kept going all the time the tube was heating, in order to draw off any gases that might be formed. It is necessary to heat fairly slowly, for ferrous oxalate decomposes giving off carbon dioxide which at the temperature of evolution dissociates sufficiently far to carbon monoxide and oxygen to oxidise the ferrous oxide formed and if the gases come off in large volume due to rapid heating, then the pump is unable to cope with the volume of gas, and the oxygen is left in contact with the ferrous oxide sufficiently long to oxidise it. Decomposition of the oxalate commences at 330°C. but to complete the decomposition it is necessary to heat the material to 750°C. . Ferrous oxide can exist in two modifications, a low temperature pyrophoric form and a more stable high temperature form.[3.] To obtain the more stable form, the material, after decomposition had ceased, was heated to just over 1000°C. and maintained there for two hours. The product, opened in an atmosphere of carbon dioxide, was a bluish-black, friable, non-magnetic powder. If any magnetic properties were shown, then the material had to be rejected, as it would contain magnetic oxide. Analysis of the powder proved it to have a total iron content of 77.6%--77.7% . If the final heating to 1000°C. were omitted, the material was spontaneously oxidised in air to Fe_3O_4 and became rapidly magnetic. The low temperature modification of ferrous oxide, when heated with nitric acid produces nitrous fumes, but the high temperature modification does not.

THE PREPARATION of MANGANOUS OXIDE.

Manganous oxide was also prepared from its corresponding oxalate, which can be obtained chemically pure. The same technique as that employed in the manufacture of ferrous oxide is followed. Manganous oxide also occurs in two modifications,

the

the low temperature modification again being pyrophoric. The high temperature modification, produced by heating to 1000°C. is olive green in colour and stable in air. The high temperature modification under the microscope in thin section, is of a deep green colour and transparent; the pyrophoric modification seen under the microscope, is translucent and seems to be composed of a very great number of crystallites producing a cross-hatched effect. This would account for its very reactive nature since very finely divided material is always more reactive than the same material in massive form.

The mixtures of ferrous oxide and manganous oxide were made by weighing out the necessary materials to give the desired composition and thoroughly mixing them by grinding them in an agate mortar. The mixture was then transferred to the molybdenum crucible and melted, about three grammes of material being used.

The various melts were examined and the results were tabulated, see Table 1. page 12.

In view of the easy oxidisability of ferrous oxide it was feared that the oxide might be oxidised in air while weighing and grinding. To prove whether this was the case some of the oxide was weighed and left exposed to the atmosphere inside the balance case for forty eight hours and the weight of 0.2112 grms. increased to only 0.2113 grm. so that no contamination was to be expected by exposing the oxide to the atmosphere during grinding and weighing. Nevertheless, the oxide was preserved in stock in an atmosphere of carbon dioxide. In case the melts were changing during melting, analysis were made on the melted material, and the mixture of composition ferrous oxide, 60%, manganous oxide 40% gave on analysis after melting a total iron content, ferrous iron, of 46.5% as compared with a theoretical value of 46.6%. The analysis of this mixture is typical of all those that were performed when enough material was available. The method of analysis was to place the tared powder in a flask in an atmosphere of carbon dioxide, and to dissolve the ferrous iron in concentrated hydrochloric acid. No reducing agent was added to the solution which was titrated with standard potassium dichromate in an

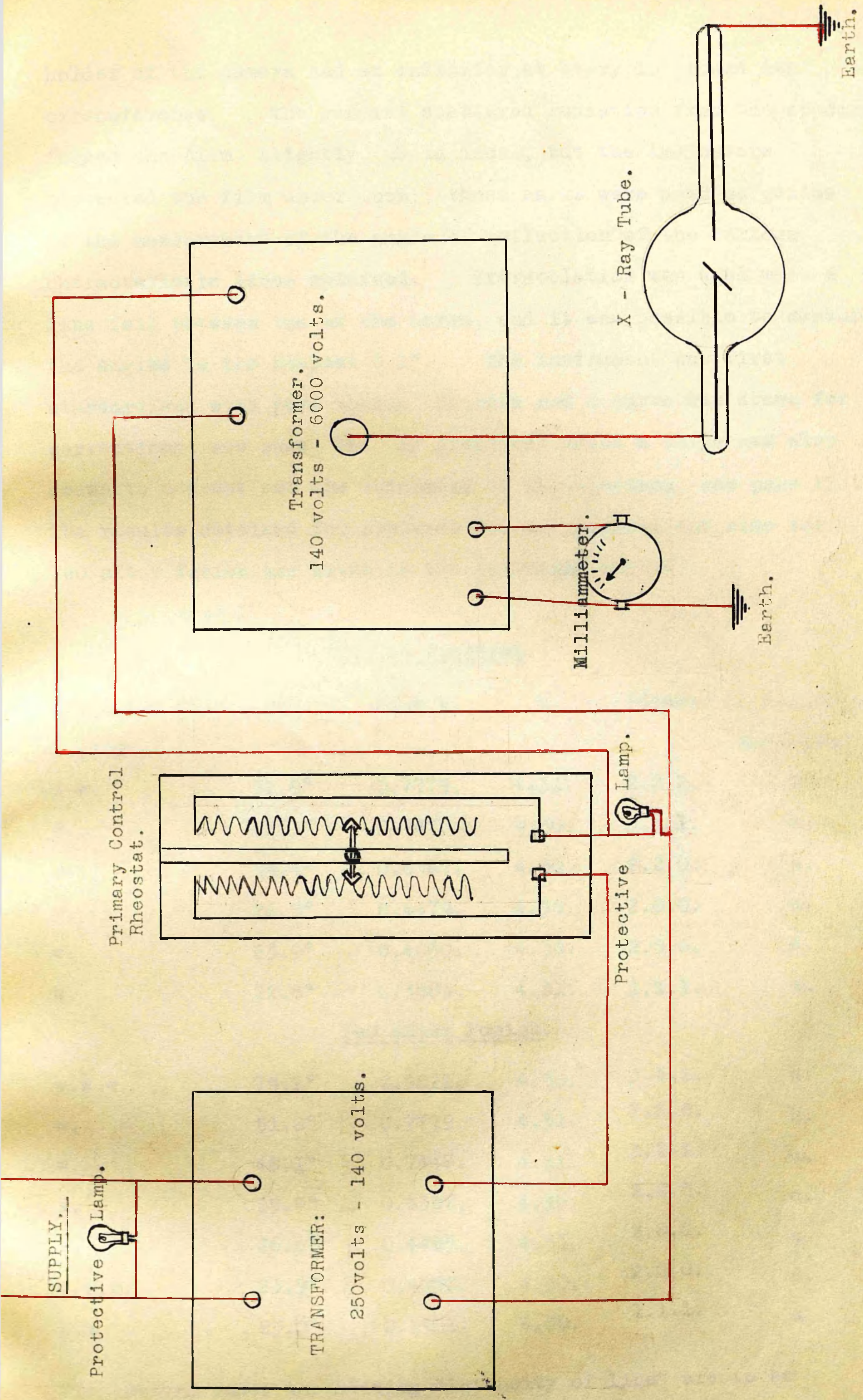
TABLE 1.

COMPOSITION of SYNTHETIC SLAG.		COLOUR of PHASES.	REFRACTIVE INDEX.	PLEOCHROISM.	BIREFRINGENCE.	EXTINCTION ANGLE.
FeO.	MnO.					
100%.	0%.	Dull grey.	2.00.	Nil.	Nil.	Isotropic.
90%.	10%.	Dull grey.	2.00.	Nil.	Nil.	Isotropic.
80%.	20%.	Dull grey.	2.02.	Nil.	Nil.	Isotropic.
		Red -Brown.	2.08.	Nil.	Nil.	Isotropic.
70%.	30%.	Dull grey.	2.05.	Nil.	Nil.	Isotropic.
		Red-Brown.	2.08.	Nil.	Nil.	Isotropic.
60%.	40%.	Red-Brown.	2.08.	Nil.	Nil.	Isotropic.
		Light Green.	2.13.	Nil.	Nil.	Isotropic.
50%.	50%.	Red-Brown.	2.11.	Nil.	Nil.	Isotropic.
		Light Green.	2.14.	Nil.	Nil.	Isotropic.
0%.	100%.	Deep Green.	2.16.	Nil.	Nil.	Isotropic.

The fused FeO was Dull grey in transmitted light, and Steel blue in reflected light.

atmosphere of carbon dioxide, using diphenylamine as an indicator, internally. During the period of solution the atmosphere in the flask was kept neutral by having the flask sealed with a delivery tube passing from it to a water seal; the solution was also cooled in an atmosphere of carbon dioxide before titration.

The ferrous oxide, fused, was, as stated, dull grey in thin section. Ferrous oxide is opaque, but by grinding exceedingly thin it can be made translucent enough to allow of refractive index determination. The value found agrees well with that found by other investigators; one other method of determination, by the interference of light on small slag inclusions, giving a value of 2.1 ± .1[4]; the inclusion cannot, however, be expected to contain only ferrous oxide, possibly containing some higher oxide of iron in solution. It has been stated[5] that ferrous oxide does not exist as such but as a mixture of iron and oxygen with more O than is required to satisfy the formula FeO. This statement is based on data obtained by the quenching of mixtures of Fe_2O_3 Fe_3O_4 and Armco iron, and analysing the product by X-rays and chemical analysis. The highest homogeneous alloy of iron and oxygen found by these workers is reported to be one containing 77.4% iron, and the size of the space lattice was taken as the determining factor of homogeneity. However, it has since been shown that a space lattice can show a break before any precipitation takes place, due to strain, and this is common in aluminium alloys. Further it is known that if ferrous oxide does exist as such, the further increase of oxygen in the alloy produces a mixture of FeO and Fe_3O_4, so it is possible that FeO does ? exist as a homogeneous alloy. Figure 1. a photomicrograph of pure melted FeO shows that the phase is homogeneous, at least, microscopically. The space lattice of FeO was examined by X-rays, both for the powder as prepared from ferrous oxalate, and for the material after melting. The diagram of the X-ray apparatus employed is given on page 14 . The target or anti-cathode used was of iron and gave a characteristic X-radiation of 1.934A° for the α-ray and 1.946A° for the β-ray. The film holder



Sketch of the apparatus used in connection with X - Ray equipment.

holder of the camera had an indicator at every 10° round its circumference. The general scattered radiation from the specimen fogged the film slightly, as is usual, but the indicators protected the film under them; these marks were used as guides in the measurement of the angle of reflection of the various characteristic lines obtained. Extrapolation was used when a line fell between two of the marks, and it was possible to measure the angles to the nearest 0.1°. The instrument was first standardised with pure sodium chloride and a curve was drawn for corrections; see page 16. By graphical means a curve was also drawn to correct for the thickness of the specimen, see page 17 . The results obtained for powdered FeO as prepared and also for FeO after fusion are given in the following tables.

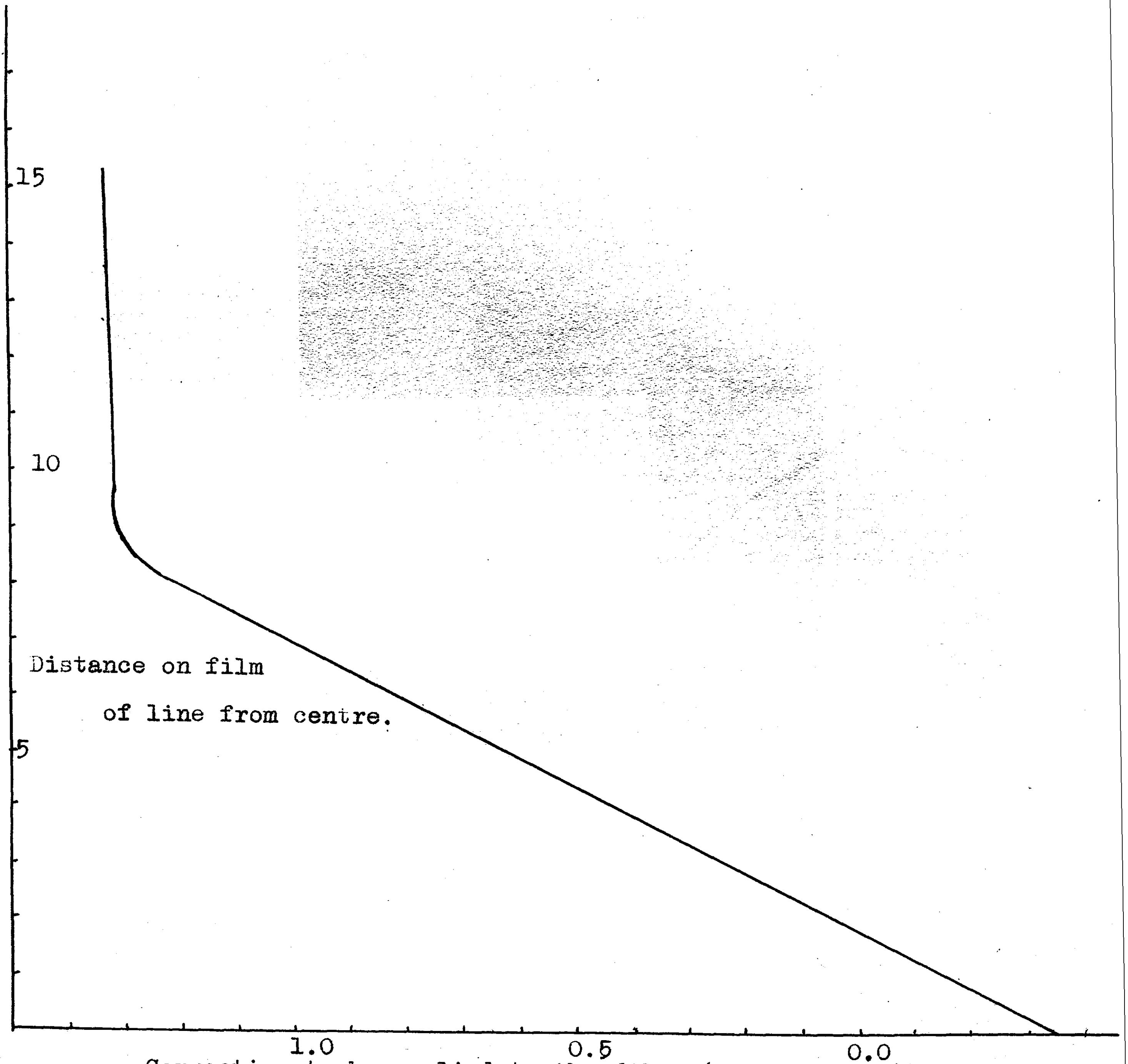
FeO as Prepared.

Intensity of line.	θ.	Sine θ.	a.	Planes.	Radiation Wave-length.
w w.	51.0°	0.7779.	4.31.	2.2.2.	α.
w.	48.3°	0.7470.	4.30.	3.1.1.	α.
s.	39.5°	0.6367.	4.30.	2.2.0.	α.
s.	26.5°	0.4479.	4.30.	2.0.0.	α.
w.	23.9°	0.4050.	4.30.	2.0.0.	β.
s.	22.8°	0.3883.	4.31.	1.1.1.	α.

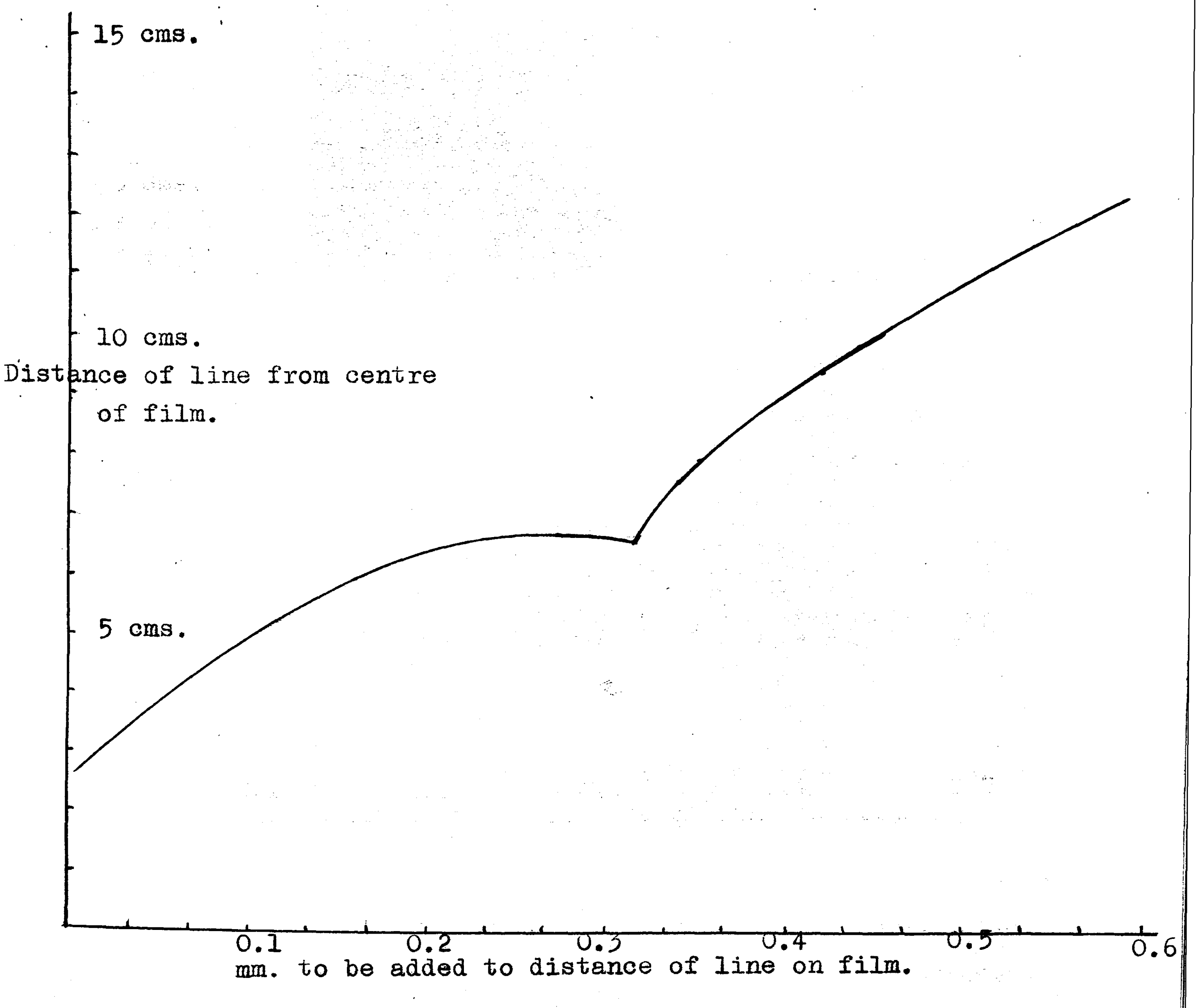
FeO after Fusion.

Intensity of line.	θ.	Sine θ.	a.	Planes.	Radiation Wave-length.
w.w.w.	79.1°	0.9821.	4.30.	3.3.1.	α.
w,	51.0°	0.7779.	4.31.	2.2.2.	α.
w.	48.1°	0.7447.	4.31.	3.1.1.	α.
s.	39.5°	0.6367.	4.30.	2.2.0.	α.
s.	26.6°	0.4485.	4.31.	2.0.0.	α.
w.w.w.	23.9°	0.4050.	4.30.	2.0.0.	β.
w.w.	23.0°	0.3901.	4.30.	1.1.1.	α.

The letters under the heading "Intensity of line" are to be interpreted , w.w.w, extremely weak; w.w, very weak; w, weak; and s, strong.



Curve showing the correction to be made, obtained from a pure sodium chloride film.



Curve used to correct for the thickness of the specimen in X - Ray examination.

The method of calculating space lattices was as follows;

For a cubic crystal, $$n\lambda = \frac{\sin.\ \theta_1}{\sqrt{(h_1^2 + k_1^2 + l_1^2)}}$$

and $$n\lambda = \frac{\sin.\ \theta_2}{\sqrt{(h_2^2 + k_2^2 + l_2^2)}}$$

Therefore, $$\frac{n\sqrt{(h_1^2 + k_1^2 + l_1^2)}}{n\sqrt{(h_2^2 + k_2^2 + l_2^2)}} = \frac{\sin.\theta_1}{\sin.\theta_2}$$

Therefore, $$\frac{h_1^2 + k_1^2 + l_1^2}{h_2^2 + k_2^2 + l_2^2} = \frac{\sin.^2\ \theta_1}{\sin.^2\theta_2}$$

So the ratio of the planes can be obtained from the ratio of the square of the sines of " θ ". By trial and error a series of integral values can be found for these ratios, and so the value of " a ", the space lattice can be calculated.

It can be seen from the figures that there is no appreciable change in the value of the lattice constant after the FeO has been fused. No lines were found in the various films taken that had values of " θ " that did not fit into the values found and for which a set of "h,k,l," planes could not be found. Thus it is stated that the ferrous oxide used was pure. In addition, since the X-ray examination proves the ferrous oxide to be cubic in structure, this bears out the statement that it is isotropic.

The method employed in finding the space lattices necessitated the preparation of a tube in which to place the powder. It was found that while celluloid could be used, allowances had to be made for the lines from this material. Collodion did not give any lines so the tubes to hold the powders were made of this material. A polished steel pin was coated with the collodion

collodion and allowed to harden slightly. The small tube thus formed was then slipped off the pin and allowed to dry thoroughly for twenty four hours before filling. The tubes when finished had a diameter of one millimeter and were rigid enough to allow of packing with the powder to be examined. The more finely the material being examined was ground the sharper were the lines obtained in the film. A fluorescent zinc sulphide screen was used to ensure accurate centring of the collodion tube in the camera, and while the exposure was being made, the tube was continually rotated at a slow uniform speed by a clock-work mechanism. In the film, all measurements were made to the centre of the lines and then the corrections, previously mentioned, were applied to the angles of reflection.

The manganous oxide used was also examined by X-ray analysis. The results are tabulated below.

MnO after Fusion.

Intensity of line.	θ.	Sine θ.	α.	Planes.	Radiation Wave-length.
s.	77.3°	0.9754.	4.44.	4.2.0.	α.
w.w.	71.8°	0.9500.	4.44.	3.3.1.	α.
w.w.	60.4°	0.8693.	4.45.	4.2.0.	β.
s.	48.8°	0.7523.	4.45.	2.2.2.	α.
w.	46.1°	0.7206.	4.45.	3.1.1.	α.
s.	38.0°	0.6155.	4.45.	2.2.0.	α.
s.	25.8°	0.4359.	4.44.	2.0.0.	α.
w.w.	22.1°	0.3765.	4.45.	1.1.1.	α.

The microscopic examination yielded results which did not entirely agree with what should have been obtained, had the equilibrium diagram possessed the shape postulated by previous investigators.[6.] It is claimed that the equilibrium diagram shows a complete solubility in the solid state, but this claim cannot be substantiated by the results listed above. It can be seen from these results that a break is to be expected somewhere in the solubility curve, such as that postulated by other

other investigators.4. The purity of the ferrous oxide in mixtures containing a fair amount of manganous oxide might be questioned from the rise in refractive index, but arguing from the same phenomenon occurring in the soda-lime felspars, it can be stated that this is due to the solution of some material, in this case, manganous oxide, of higher refractive index in the ferrous oxide.

THE EXAMINATION of THE BINARY SYSTEM FERROUS OXIDE - SILICA.

The ferrous oxide employed in the mixtures was obtained as described previously on page 9. The silica used was a very pure sand containing 99.9+% of SiO_2 which had been ground very finely. The mixtures were weighed out, ground together, and melted in the same manner as the mixtures of ferrous oxide and manganous oxide. The melted mixtures were examined in the same manner as those of ferrous oxide and manganous oxide, and the results are tabulated on page 21. As before the molybdenum refractory was found not to react with either of the components of the mixture and this was proved by chemical and spectroscopic analysis. In the table, fayalite is reported as being white in colour but if the fayalite were seen in thick section then the compound assumed a yellowish brown tinge. The birefringence of the fayalite was measured by preparing a slide of definite thickness, approximately 0.03 m.m. , and then balancing the polarisation colour of this slide against the colours developed by different thicknesses of a quartz wedge. When the colours were balanced, the relative retardation of the portion of the quartz wedge used could be found from tables, then, knowing the thickness of the fayalite the birefringence could be calculated. The birefringence was found to be 0.05 except in the case of the mixture consisting only of fayalite, when the value was 0.046. This was probably due to none of the pieces of material examined lying in the proper plane to give maximum birefringence.

THE OPTICAL PROPERTIES of THE BINARY SYSTEM FERROUS OXIDE + SILICA.

Composition of Mixture.		Phases Present.	Colour of Phases.	Refractive Index.	Pleochroism.	Extinction Angle.	Polarisation Colours.	Birefringence and Crystal Character.
Ferrous Oxide.	Silica.							
90%	10%	Ferrous oxide. Fayalite.	Dull grey. White.	2.0 1.78-2.0	Nil. Fair.	Nil. Straight.	Nil. Very strong.	Isotropic. 0.05 and neg.
85%	15%	Ferrous oxide. Fayalite.	Dull grey. White.	2.0 1.78-2.0	Nil. Fair.	Nil. Straight.	Nil. Very strong.	Isotropic. 0.05. and neg.
80%	20%	Ferrous oxide. Fayalite.	Dull grey. White.	2.0 1.78-2.0	Nil. Fair.	Nil. Straight.	Nil. Very strong.	Isotropic. 0.05 and neg.
75%	25%	Ferrous oxide. Fayalite.	Dull grey. White.	2.0. 1.78-2:0	Nil. Fair.	Nil. Straight.	Nil. Very strong.	Isotropic. 0.05 and neg.
70.6%	29.4%	Fayalite.	White.	1.78-2.0	Fair.	Straight.	Very strong.	0.046 neg.
65%	35%	Fayalite. Grunerite.	White. Light brown.	1.78-2.0 1.74	Fair. Faint.	Straight. 10$_0$	Very strong. Low.	Uniaxial. Biaxial.
60%	40%	Fayalite. Grunerite.	White. Light brown.	1.78-2.0 1.74.	Fair. Faint.	Straight. 10	Very strong. Low.	Uniaxial. Biaxial.
55%	45%	Grunerite.	Light brown.	1.74.	Faint.	10	Low.	Biaxial.
50%	50%	Grunerite(little) Fayalite. Tridymite.	Light brown White. Colourless.	1.74. 1.78-2.0 1.49.	Faint. Fair. Nil.	10 Straight. Straight.	Low. Very strong.	
40%	60%	Grunerite. Fayalite. Tridymite.	Light brown. White. Colourless.	1.74. 1.78-2.0 1.49.	Faint. Fair. Nil.	10 Straight. Straight.	Low.	Not Determined.

The optical character of the fayalite crystal was also obtained by comparing its behaviour in polarised light with the quartz prism; partial interference figures were all that could be obtained when determining whether the crystal were uniaxial or biaxial, but the movement of the isogyrs was sufficiently developed to allow of determination.

The results obtained from examination of the various mixtures are in good agreement with those found by others.[6.] Some, however dispute the existence of grunerite as a separate phase. In this case, mixtures containing more than 42% SiO_2 were not examined, nor was the temperature of 1500°C. exceeded; and it is definite that the solubility line in the FeO - SiO_2 equilibrium diagram rises sharply to very high temperatures as the composition of grunerite is approached. Moreover, it was found that unless the temperature of the molten mixture had been raised to over 1600°C. then no grunerite was to be found in the solid material afterwards, and in several cases, when the temperature had just exceeded 1600°C., it was found that the grunerite in the solid state appeared to be only partially formed. The rate of cooling of the melt also seemed to have a definite bearing on the formation of grunerite; slow cooling producing well defined grunerite crystals, and very fast cooling producing only very little grunerite. Grunerite is found as a natural mineral and has been examined by several investigators.[7.8.9.] It has been found in the country rock in the Champion mine in America, and also in a metamorphic schist occurring in the Department du Var, in France. In the natural state it has about 1% of impurity, consisting almost entirely of alumina and ferric oxide, but its extinction angle is given as between 10° and 20° by all those who have examined it. Silicate melts are sluggish to crystallise and grunerite occurs where the percentage of silica is relatively high, about 45%; also just above this proportion the equilibrium diagram consists of two immiscible liquids in the liquid state, so that by fast cooling of a mixture which should normally contain grunerite, one might be able to reach a metastable freezing point at which fayalite and

and not grunerite would be formed, in a manner analogous to the metastable point in the sulphur equilibrium diagram. On this postulation, fayalite would be a metastable phase between 45% and 50% of silica and if the mixtures were cooled slowly enough to allow of complete equilibrium to be established, the grunerite would be the phase formed.

Fayalite, as stated, is yellowish brown in thick section, but ground to thinner section becomes white in colour, and the pleochroism easily seen in thick sections disappears. Grunerite, on the other hand is of a light brown to greenish brown colour and in thick sections the pleochroism is not any more marked than in thin sections. The two compounds can be differentiated by their interference figures in convergent light, for grunerite shows a biaxial figure, whereas fayalite shows a uniaxial figure.

The refractive index of the material identified as tridymite is higher than that usually assigned to this material, 1.49 as compared with 1.47. The rise may be accounted for by postulating a small solubility of grunerite in the tridymite. That the phase is undoubtedly tridymite is proved by the fact that the lath shaped crystals are soluble in fused sodium and potassium carbonates and the solution will give a precipitate of gelatinous silicic acid on being acidified with hydrochloric acid. No such precipitate is obtainable with the silica from which the mixture was prepared. In addition, the lath shaped crystals have straight extinction as compared with the slightly oblique extinction of ordinary quartz.

THE EXAMINATION ofTHE BINARY SYSTEM MANGANOUS OXIDE-SILICA.

The manganous oxide used in the preparation of the various mixtures examined in this binary system, was prepared from chemically pure manganous oxalate, in the manner described on page 10. The silica was the same as that used in the examination of the binary system FeO - SiO_2. The components were weighed out in the proportions required, ground together in an agate mortar and melted in a molybdenum crucible. The first few mixtures were examined, as in all the binary systems examined, after melting, for traces of melybdenum in the fused mass. No trace was found either chemically or spectroscopically. The various mixtures were examined, after melting, in the usual manner and the results are tabulated on pages 25 and 26.

In this system, as in the system ferrous oxide - silica, the tridymite which appears in the silica-rich mixtures, shows an abnormally high refractive index, 1.49 as compared with 1.47, given in tables. In this case the thermal curves showed definitely that the higher figure was due to the small solution of rhodonite in the tridymite. The numerical values of the birefringence and the optical characters of the crystals were not examined, in this case, since the decided differences in the other properties of the phases that occur in this system were deemed sufficient to enable identification to be made. There is no solution of the tephroite in the manganous oxide as can be predicted from the constancy of the refractive index of the manganous oxide occurring in the mixtures which have manganous oxide and tephroite as phases. The amount of rhodonite which dissolves in the tridymite

THE OPTICAL PROPERTIES of THE BINARY SYSYEM MANGANOUS OXIDE + SILICA.

Composition of Mixture. Manganous Oxide.	Silica.	Phases.	Colour of Phases.	Refractive Index.	Pleochroism.	Birefringence.	Angle of Extinction.
100%.	0%.	Manganosite.	Green.	2.16.	Nil.	Nil.	Isotropic.
95%.	5%.	Tephroite. Manganosite.	Colourless. Green.	1.78-2.00. 2.16.	Nil. Nil.	Very strong. Nil.	Straight. Isotropic.
82%.	18%.	Tephroite. Manganosite.	Colourless. Green.	1.78-2.00. 2.16.	Nil. Nil.	Very strong. Nil.	Straight. Isotropic.
70.4%.	29.6%.	Tephroite.	Colourless.	1.78-2.00.	Nil.	Very strong.	Straight.
68%.	32%.	Rhodonite. Tephroite.	Brown. Colourless.	1.76. 1.78-2.00.	Faint. Nil.	Medium. Very strong.	45°. Straight.
64%.	36%.	Rhodonite. Tephroite.	Brown. Colourless.	1.76. 1.78-2.00.	Faint. Nil.	Medium. Very strong.	45°. Straight.
60%.	40%.	Tephroite. Rhodonite.	Colourless. Brown.	1.78-2.00. 1.76.	Nil. Faint.	Very strong. Medium.	Straight. 45°

THE OPTICAL PROPERTIES of THE BINARY SYSTEM MANGANOUS OXIDE - SILICA. Contd.

Composition of Mixture. Manganous Oxide.	Silica.	Phases.	Colour of Phases.	Refractive Index.	Pleochroism.	Birefringence.	Angle of Extinction.
57.5%.	42.5%.	Rhodonite.	Brown.	1.76.	Faint.	Medium.	45°.
54.2%.	45.8%.	Rhodonite.	Brown.	1.76.	Faint.	Medium.	45°.
50%.	50%.	Rhodonite. Tridymite.	Brown. Colourless.	1.76. 1.49.	Faint. Nil.	Medium. Low grey.	45°. Straight.
40%.	60%.	Rhodonite. Tridymite.	Brown. Colourless.	1.76. 1.49.	Faint. Nil.	Medium. Low.	45°. Straight.
30%.	70%.	Rhodonite. Tridymite.	Brown. Colourless.	1.76. 1.49.	Faint. Nil.	Medium. Low.	45° Straight,
3%	97%.	Rhodonite. Tridymite.	Brown. Colourless.	1.76. 1.49.	Faint. Nil.	Medium. Low.	45°. Straight.
1%.	99%.	Rhodonite. Tridymite.	Brown. Colourless.	1.76. 1.49.	Faint. Nil.	Medium. Low.	45°. Straight.

tridymite must not be very large because the refractive index is raised only 0.02.

In the mixtures containing over 50% SiO_2, a very interesting phenomenon was noticed. When the material from the top of the crucible was examined, it proved to contain tridymite and rhodonite but the proportions, even though qualitative, seemed to be wrong, the tridymite appearing in too great an excess. On examining the material from the bottom of the crucible, however, this material was found to consist almost entirely of rhodonite. This is in itself an indication that two immiscible liquids are formed at elevated temperatures, and this is found to be so on examining thermally.

One difficulty to the identification of mixtures of FeO - MnO- - SiO_2 was also noted and later found to be practically insurmountable The colour, crystal form, birefringence, and optical character of crystals of tephroite, ($2 MnO.SiO_2$), and fayalite, ($2FeO.SiO_2$), are identical, and microscopically, they cannot be distinguished.

The phases found for the different mixtures of MnO and SiO_2 are in complete agreement with those found by other investigators for the same proportions.

THE EXAMINATION of THE TERNARY SYSTEM FERROUS OXIDE, MANGANOUS OXIDE AND SILICA.

The three binary systems, FeO - MnO, FeO - SiO_2, and MnO - SiO_2, having been examined, it was then decided to combine all three equilibrium diagrams into one ternary, and to find what phases were obtained when all three components were present in varying amounts. Since a ternary diagram has three components it can only properly be represented by a solid figure, and then even, one of the degrees of freedom, usually the pressure, has to be neglected. However, since neither FeO, MnO, nor SiO_2, tend to decompose at high temperatures, it is quite permissible to neglect the pressure, and in any case, the pressure is constant all through the determinations.

The FeO, and MnO used were prepared in the manner described on pages 9 and 10. The silica used was the same type as that used previously, and is described on page 20; the synthetic slags were melted in molybdenum crucibles as in the case of the previous ones. There was no contamination of the slags from the crucibles, this being tested for as before.

Only such mixtures as were likely to be encountered in actual slags were examined. Accordingly, all the slags examined were relatively high in ferrous oxide content, and the others were examined mainly to indicate the shape of the complete ternary diagram. The melted slags were examined in the usual manner and the results are tabulated on pages 29 and 30. The shape of the diagram has been deduced and the plan and approximately isometric views are on pages 31 and 32.

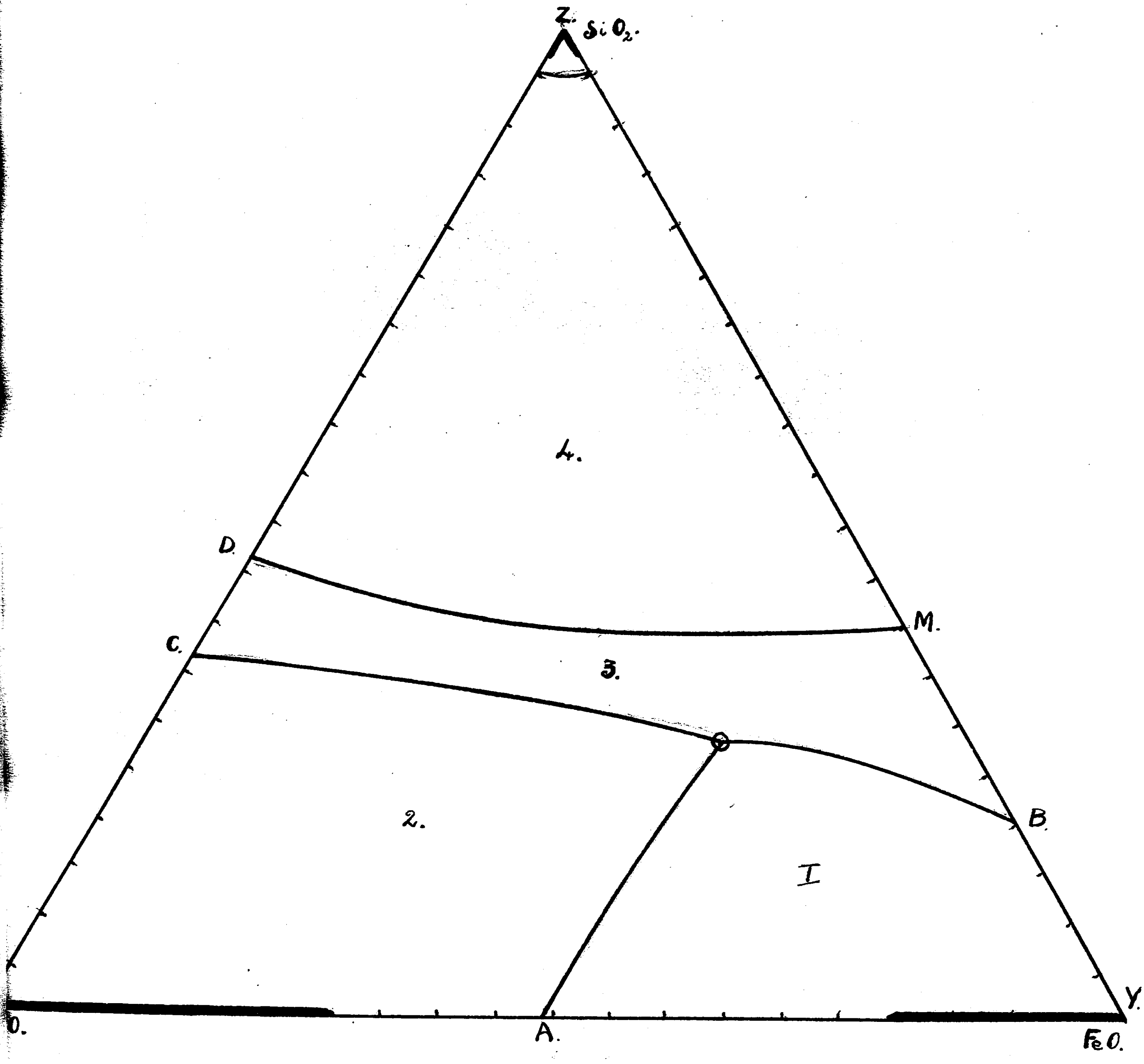
As can be seen from the diagrams, slags high in silica are to be avoided in actual practice, because of their extreme refractoriness and lack of fluidity. A slag high in silica content would, in addition, not be of great use for deoxidising purposes as can be seen from the phases which occur in them; fayalite, tephroite, and tridymite, for example, being very stable compounds and compounds which do not easily lose the

THE OPTICAL PROPERTIES OF THE VARIOUS MIXTURES OF FERROUS OXIDE - MANGANOUS OXIDE - and SILICA.

Composition of Mixture. FeO.	MnO.	SiO_2	Phases.	Colour.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Freezing point of Mixture.
80%.	10%.	10%.	Ferrous oxide.	Dull grey.	2.60.	Nil.	Nil.	Isotropic.	
			Knebelite.	Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	1350
			Fayalite-Tephroite.	Colourless.	1:78-2.0.	Nil.	Very strong.	Straight.	1350°C.
70%.	20%.	10%.	FeO.	Dull grey.	2.00.	Nil.	Nil.	Isotropic.	
			Knebelite.	Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	1450
			FeO-MnO.	Brown.	2.1.	Nil.	Nil.	Isotropic.	1450°C.
70%.	10%.	20%.	FeO.	Dull grey.	2.00.	Nil.	Nil.	Isotrppic.	
			Knebelite.	Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	
			Fayalite-tephroite.	Colourless.	1.78-2.0.	Nil.	Very strong.	Straight.	1310. 1310°C.
60%.	20%.	20%.	FeO.	Dull grey.	2.00.	Nil.	Nil.	Isotropic.	
			Knebelite.	Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	
50%.	30%.	20%.	Fayalite-tephroite	Colourless.	1.78-2.0	Nil.	Very strong.	Straight.	1390 1390°C.
			FeO.	Dull grey.	2.00.	Nil.	Nil.	Isotropic.	
			Knebelite.	Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	
30%.	40%.	30%.	Fayalite-tephroite.	Colourless.	1.78-2.0.	Nil.	Very strong.	Straight.	1290°C.
			Knebelite.	Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	
			Fayalite-tephroite.	Colourless.	1.78-2.0.	Nil.	Very strong.	Straight.	
			FeO-MnO.	Brown.	2.1.	Nil.	Nil.	Isotropic.	1337°C. 1337
40%.	30%.	30%.	Knebelite.	Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	
			Fayalite-tephroite.	Colourless.	1.78-2.0.	Nil.	Very strong.	Straight.	
			FeO-MnO.	Brown.	2,1.	Nil.	Nil.	Isotropic.	1208°C.

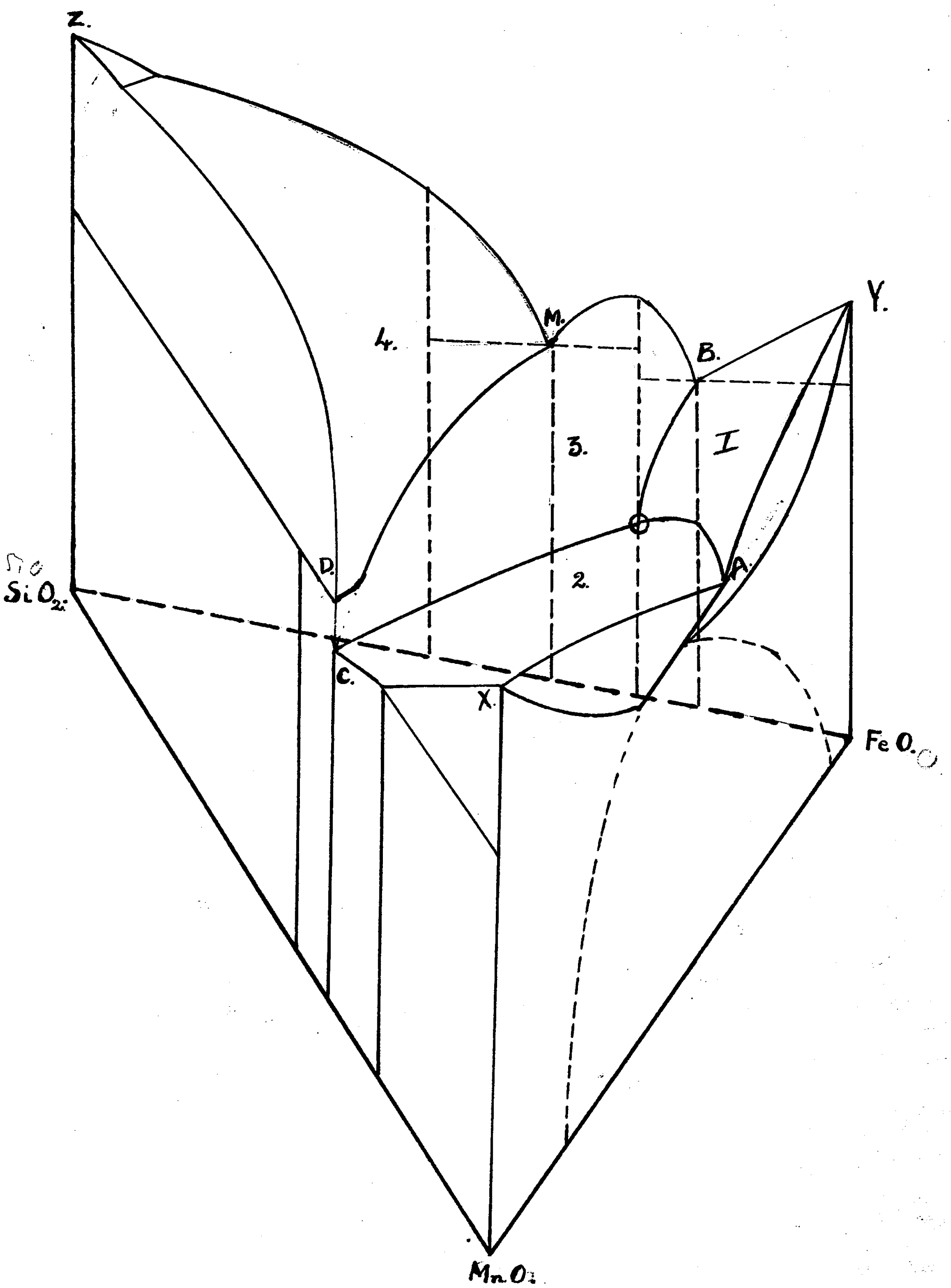
THE OPTICAL PROPERTIES OF THE VARIOUS MIXTURES OF FERROUS OXIDE - MANGANOUS OXIDE - and SILICA.

Composition of Mixture. FeO. MnO. SiO_2.	Phases.	Colour.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Freezing point of Mixture.
60%. 10%. 30%.	Knebelite.	Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	
	Fayalite-tephroite.	Colourless.	1.78-2.0.	Nil.	Very strong.	Straight.	1290°C.
	FeO.	Dull grey.	2.0.	Nil.	Nil.	Isotropic.	
50%. 20%. 30%.	Knebelite.	Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	
	Fayalite-tephroite	Colourless.	1.78-2.0.	Nil.	Very strong.	Straight.	1170°C.
	FeO.	Dull grey.	2.0.	Nil.	Nil.	Isotropic.	
10%. 50%. 40%.	Fayalite-tephroite.	Colourless.	1.78-2.0.	Nil.	Very strong.	Straight.	
	Rhodonite.	Brown.	1.76.	Faint.	Medium.	45°.	
20%. 40%. 40%.	Rhodonite.	Brown.	1.76.	Faint.	Medium.	45°.	
	Fayalite-tephroite.	Colourless	1.78-2.0.	Nil.	Very strong.	Straight.	
	Grunerite.	Light brown.	1.74.	Faint.	Weak.	10°.	1222°C.
40%. 20%. 40%.	Rhodonite.	Brown.	1.76.	Faint.	Medium.	45°.	
	Grunerite.	Light brown.	1.74.	Faint.	Weak.	10°.	1222°C.
	Also a trace of free silica.						
50%. 10%. 40%.	Rhodonite.	Brown.	1.76.	Faint.	Medium.	45°.	
	Grunerite.	Light brown.	1.74.	Faint.	Weak.	10°.	
	Also a trace of free silica.						1220°C.
30%. 20%. 50%.	Grunerite.	Light brownl	1.74.	Faint.	Weak	10°.	
	Rhodonite.	Brown.	1.76.	Faint.	Medium.	45°.	
	Tridymite.	Colourless with green tinge.	1.49.	Nil.	Low.	Straight.	1430°C.



Plan view of the liquidus face of the ternary diagram

The black shaded areas indicate regions of solubilities. The figures on the various areas are referred to in the text.



Elevation of the ternary diagram. The points X Y andZ are indicating the melting points of MnO, FeO, and SiO_2. The figures on the various faces are referred to in the text.

oxygen in their composition. Manganous oxide, on the other hand, if in excess, would tend also, but not to the same extent, to make the slag rather difficult to melt; but, in addition, such an excess would produce a slag which would be very corrosive on the furnace lining, very slow in working the carbon down to the required degree and would probably tend to give a steel with a rather high manganese content. Accordingly furnace slags should be relatively high in ferrous oxide and this is what is found in actual practice.

The shape of the ternary diagram was deduced in the following manner. In area "1" the phases found vary from ferrous oxide, fayalite and knebelite, to ferrous oxide, knebelite, and the material found due to the peritectic reaction in the FeO - MnO diagram. It might be explained that the term, knebelite, is applied to an alloy of FeO - MnO - SiO_2, of variable composition but always found as a solid solution, giving it the appearance of a real chemical compound. The change in the phases found in area "1" is explained by stating that depending whether the slag solidifies into trough OB, or into trough OA, then either the one or the other set of phases will make their appearance. Thus the surface of the area O A Y B, must be curved, with a line of maximum temperatures running, roughly from O to Y. According as the composition of the slag lies on one side or the other of this line then fayalite or the FeO - MnO peritectic material will be found in the fused slag along with knebelite and ferrous oxide.

In area "2", only two synthetic slags were examined, and these lie close to the trough running from the eutectic of tephroite - rhodonite to the ternary point O. This field has been represented as a solubility face. In connection with this field, a difficulty previously mentioned was encountered; it is impossible to state, petrographically, whether the white crystals found near the ternary point are tephroite or fayalite, since these are petrographically identical. These crystals have therefore been called fayalite - tephroite, since there is every reason to believe

believe that these compounds are isomorphous.

Field "3" presented some difficulty of interpretation. The fusion temperatures of the mixtures containing about 40% of silica are not much higher than the fusion temperature of the slag occurring at the ternary point, but the phases found here are different from those found in mixtures containing about 35% of silica, whose melting points are about the same. So a ridge must be assumed to exist between mixtures of these compositions. (The values 40% silica and 35% silica mentioned are only very approximate.) Thus another ternary point must be assumed to exist at " M " since this eutectic point between grunerite and fayalite has the lowest melting point of the range.

Area " 4 " is assumed to be a region of immiscibility of silica, rhodonite and grunerite, since such a region occurs in both of the binary systems, FeO - SiO_2 and MnO - SiO_2; and also since the melting point temperatures rise very rapidly for very small increases in the percentage of silica. Since FeO and MnO are both soluble to a very small amount in silica, about 2%- 3%, a small solubility face can be expected to occur at about 98% of silica, as shown.

The diagram deduced, while laying no claims to absolute accuracy, since only a limited number of mixtures were examined, is, nevertheless, borne out by actual slag investigations in the main essentials. A series of three slags, taken from a properly run acid steel furnace, showed the components to be present approximately in the ratio, FeO, 45%, MnO, 20% -25%, and SiO_2, 30%, the rest being made up of lime, ferric oxide, alumina and magnesia. A slag which tended to be rather viscous in the furnace, proved on analysis to have a rather higher silica percentage, approximately 45%.

THE EXAMINATION of THE BINARY SYSTEM MANGANOUS OXIDE - ALUMINA.

The manganous oxide used in the mixtures examined in this system was the same as that used in the systems previously described, and was prepared in the same manner from manganous oxalate, see page 10. The alumina used was a very fine powder which had been carefully washed free from impurities, and was of the order of purity, Al_2O_3 99.9+%. The various mixtures were prepared in the same manner as the previous ones and, like them, were melted in molybdenum crucibles. These melts were also tested for contamination by the molybdenum but none was found. The melted mixtures were examined in the usual petrographic manner, and the results are tabulated on page 36.

The fused mixtures of manganous oxide and alumina were extremely hard and it was very difficult to obtain sufficient material for examination. It seems puzzling as to why nearly all the mixtures are composed of only one white phase. However it is to be noted that when the golden-brown material disappears from the mixtures, then the refractive index of the green isotropic phase, manganous oxide, falls from 2.16 to 2.13. Had it been possible to examine material from the bottom layers of the fused mixtures, perhaps it would have been found, since alumina is lighter than manganous oxide, that liquation was taking place in the molten state. This has already been found to take place in the binary system, MnO - SiO_2; so it is just possible that alumina is soluble to some extent in the manganous oxide and manganous oxide in the alumina. The manganous oxide might be forcing its crystal habit on the alumina, causing this to assume a pseudo-cubic structure, instead of its usual hexagonal one. This is borne out by the birefringence of the white phase being very weak, and in some cases seeming to be isotropic, although this latter phenomenon might be due to the section of a hexagonal crystal being basal. The equilibrium diagram of the system MnO - Al_2O_3, if the liquation theory is correct, would therefore present

THE EXAMINATION OF THE BIMARY SYSTEM MANGANOUS OXIDE-- ALUMINA.

Composition of Mixture.		Colour of Phases.	Refractive Index.	Birefringence.	Pleochroism.	Extinction Angle.
MnO.	Al_2O_3.					
90%.	10%.	Green.	2.16.	Nil.	Nil.	Isotropic.
		Golden brown.	1.76+.	Nil.	Nil.	Isotropic.
		White.	1.57.	Very weak.	Nil.	Straight.
85%.	15%.	Green.	2.16.	Nil.	Nil.	Isotropic.
		Golden brown.	1.76+.	Nil.	Nil.	Isotropic.
		White.	1.57.	Very weak.	Nil.	Straight.
75%.	25%.	Green.	To small for determinations.			
		Golden brown.	1.76+.	Nil.	Nil.	Isotropic.
70%.	30%.	Green.	2.13.	Nil.	Nil.	Isotropic.
		White	1.76+.	Very weak.	Nil.	Straight.
65%.	35%.	White.	1.76+.	Very weak.	Nil.	Straight.
60%.	40%.	White.	1.76+.	Very weak.	Nil.	Straight.
57.75%	42.25%.	White.	1.76+.	Very weak.	Nil.	Straight.
50%.	50%.	White.	1.76+.	Very weak.	Nil.	Straight.
40%.	60%.	White.	1.76+.	Very weak.	Nil.	Straight.

present the form of two substances, soluble in the solid and liquid states to a certain extent, and forming two layers after the manner of ether and water, However, the data obtained is sufficient to allow of recognition of aluminate combinations when met with in actual slags.

THE EXAMINATION of THE BINARY SYSTEM LIME - FERRIC OXIDE.

In the literature, data concerning the equilibrium diagram of the binary system Fe_2O_3 - CaO, is very contradictory. Some have postulated only two compounds of CaO and Fe_2O_3 , while others have postulated four or five compounds of these two substances. So it was decided to investigate the equilibrium diagram of $Fe_2O_3$and CaO both thermally and microscopically.

The lime used was prepared from chemically pure calcium oxalate; this material being first examined microchemically for sodium and potassium, neither of which were found, however. The oxalate was decomposed by heating in a furnace to 1000°C, and the quick - lime produced was preserved in a dessicator. The lime was tested for carbonate before using and was also heated to about 900°C. before being weighed out to form part of a mixture.

Pure ferric oxide is difficult to prepare by ordinary methods, since, if ferric hydroxide is ignited, ferric oxide is not obtained, but the resultant material is a mixture of Fe_2O_3 and Fe_3O_4. An attempt was made, at first, to prepare ferric oxide in a similar manner to ferrous oxide. The ferric oxalate, which could be obtained pure, was decomposed in vacuo, at a fairly high temperature, about 700°C., but the product was a mixture of the three oxides of iron, FeO, Fe_2O_3 and Fe_3O_4.

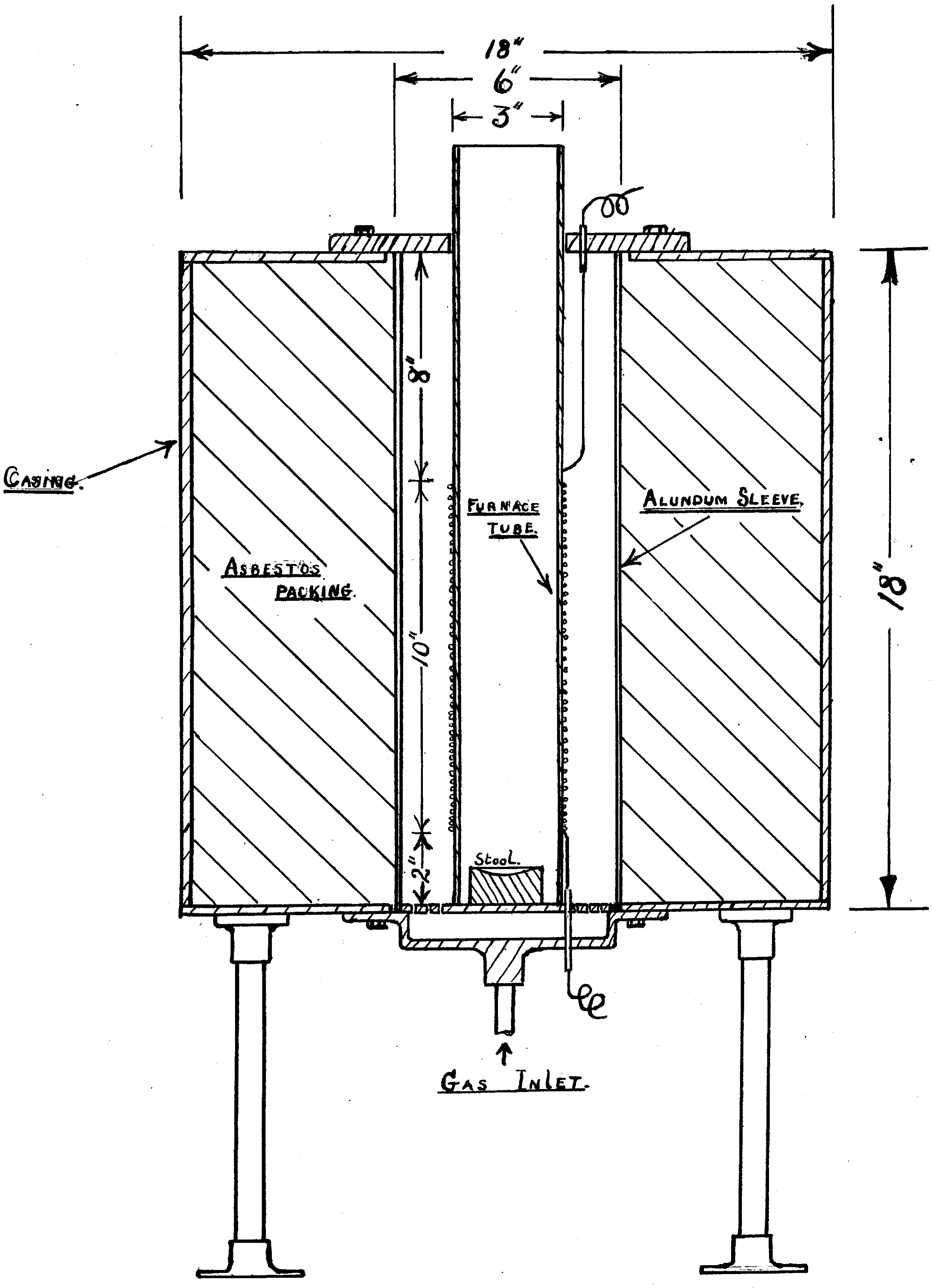
After this it was evident that the formation of ferric oxide

oxide was dependent on the oxidising conditions which exist in the atmosphere of the furnace. Therefore it was decided to try to prepare ferric oxide by totally oxidising ferrous oxide. Ferrous oxide was first to be prepared from the ferrous oxalate, and then oxygen was to be admitted to oxidise it. Therefore it was desirable to expose as big a surface of the ferrous oxide as possible to the gas; so the ferrous oxalate was put, not in the alumina container used to prepare ferrous oxide, but in very shallow " morganite " refractory boats such as are used in estimating the carbon in steels by the combustion method. These boats were placed in the " Pythagoras " tube and the tube was closed by a rubber bung and sealed gas-tight with celluloid dissolved in amyl acetate. When absolutely gas tight, the " Pythagoras " tube was placed in a resistance wire electric furnace and the ferrous oxalate was decomposed as previously described, the only difference being that the decomposition was carried out at the lowest possible temperature. Also, after decomposition had been completed, the temperature was not raised to 1000°C., but on the contrary, was allowed to fall to 300°C.. The reason for this step is, the pyrophoric form of ferrous oxide is very reactive with oxygen, and it was found that when the oxygen was admitted to the tube, the temperature of the material, in the boats, measured by a base metal thermo - couple rose as much as 200°C.. This figure indicates the general rise and the rise in some spots must have been greater than this. It was found if oxygen were admitted too rapidly to the tube, or if the temperature were too high, then a semi - fritted mass of Fe_3O_4 and FeO was obtained instead of Fe_2O_3. So, the temperature of the material having been allowed to fall to 300°C., the oxygen was admitted a little at a time, to the tube until there was an atmosphere of oxygen in the tube; the pressure of oxygen was then allowed to rise to one and a half atmospheres and the system was then held static for half an hour before allowing the tube to cool. After the tube had cooled to room temperature it was opened and the material inside was examined.

The ferric oxide produced by this method varied in colour according to small variations in temperature and pressure. This was shown by the colour of the oxide varying even in the same boat; the ferric oxide coming from the cooler end of the boat being of a redder colour than the material from the hotter end, which was of a slate blue colour. The ferric oxide was always examined for ferrous iron by the dimethylglyoxime test. This substance, in alkaline solution, gives with very slight traces of ferrous iron, a crimson colour, but does not give any colour with ferric iron. So some of the ferric oxide was dissolved in hydrochloric acid and added, when cold, to an ammoniacal solution of the dimethylglyoxime. The solution was protected from oxidation by dissolving and cooling in an atmosphere of carbon dioxide. Magnetism could not be used as a test for the presence of oxides other than the ferric one, for on one occasion the ferric oxide was obtained a bright vermilion colour and although no trace of ferrous iron could be obtained, the oxide was strongly magnetic.

Later it was found that if ferrous oxalate is decomposed in air by gentle heating and is constantly stirred, then red ferric oxide is obtained. So ferric oxide could also be obtained in this way.

The furnace used in the determination of the equilibrium diagram is an electric resistance one, and a drawing of the furnace appears on page 40. The actual heating unit is made of a grooved alundum tube, with molybdenum wire of 0.5m.m. diameter, wound in the grooves. Forty one feet of wire are normally used. The current passing through the wire was controlled by a large rheostat, capable of passing currents from 5 amps. to 40 amps.. The furnace tube, 2¼ inches in diameter, admits a "Pythagoras" tube and this sits vertically in a cup shaped alundum stool placed at the bottom of the furnace tube, the stool being so shaped as to fit the rounded, closed end of the "Pythagoras" tube.



Section showing the construction of the furnace used in determining the thermal change points for the various mixtures of Fe_2O_3, and CaO, examined.

The open top of the tube, reaching at least two feet above the furnace casing, was closed with a large rubber bung, through which passed tubes to carry the thermo - couple wires, and also a glass tube to permit of evacuation. Since the furnace was sitting vertically, the hottest part of the winding occurred about one third the length from the bottom, so it was arranged that the material to be melted should be in this region. Molybdenum wire oxidises to a volatile oxide at very low temperatures, although the melting point of molybdenum, itself, is about 2200°C., so the winding had to be protected from oxidation. This was done by "cracking" ammonia gas by passing the dry gas over iron filings at 900°C., inside a suitable tube. The resultant hydrogen and nitrogen, after drying and washing, were passed continuously over the surface of the winding and then allowed to escape.

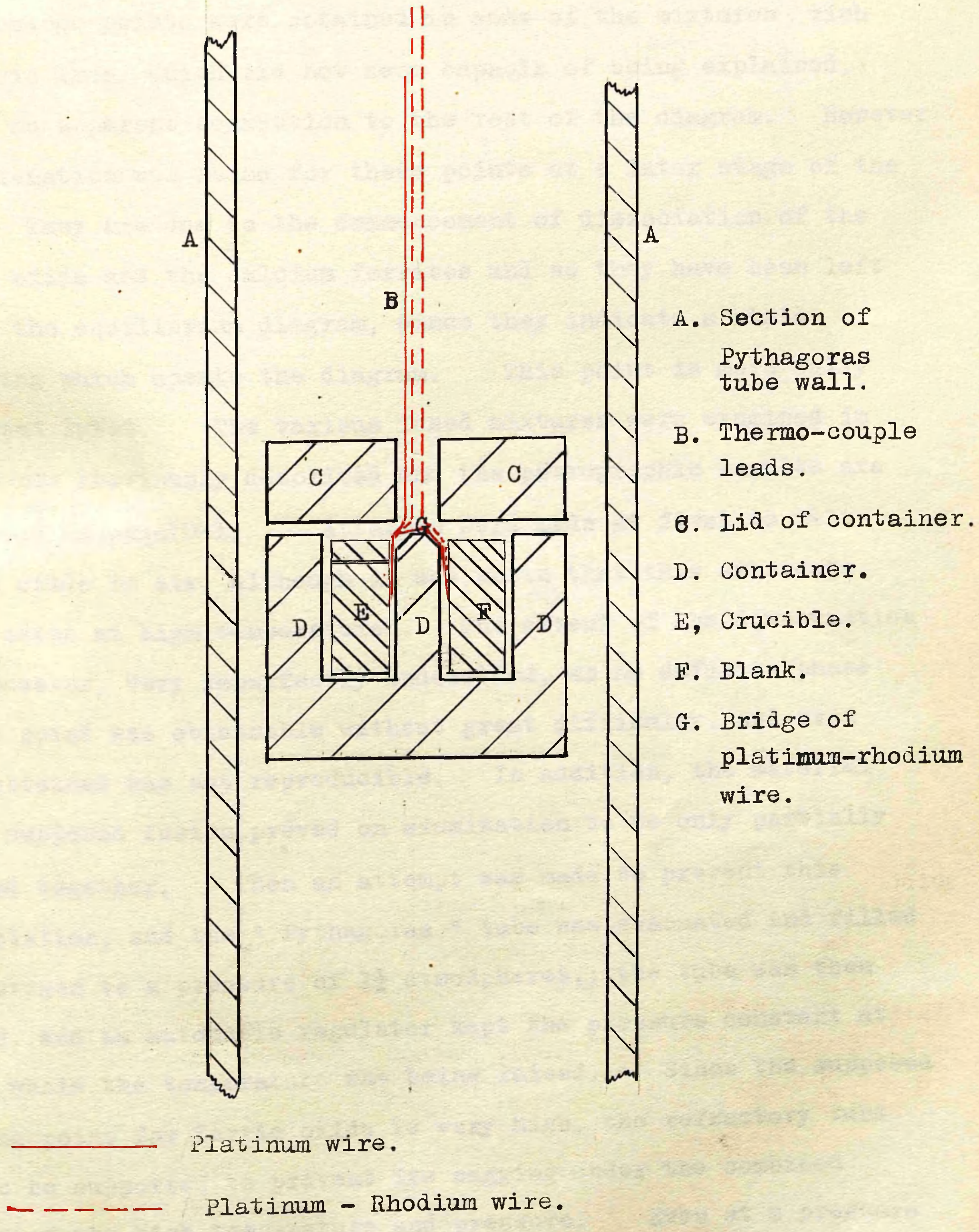
Molybdenum crucibles could not be used to hold the mixtures of ferric oxide and lime since it oxidises so easily, and also since the materials were melted in an oxygen atmosphere. As has been stated previously, platinum extracts iron from iron oxides unless a certain pressure of oxygen is present in the atmosphere around the platinum. This pressure was always exceeded in the melting of the various mixtures of lime and ferric oxide, so that ~~the~~ a platinum crucible could be used with safety.

A platinum - platinum-rhodium thermo - couple was used to measure the temperatures. This couple was standardised, in the first instance, against pure metals of known melting temperature, and latterly, against another platinum - platinum-rhodium thermo -couple which had been standardised against a gas thermometer.

The melting points of the various mixtures were found by both the inverse rate, time-temperature curves and by the differential heating curves. These latter curves are derived in the following way. If two thermo-couples are used to measure the rate of heating of two equal masses of the same specific heat, and the wires composing these two thermo-couples have the same electrical characteristics, then, if one of the masses heat at a greater rate than the other a potential difference will exist between the

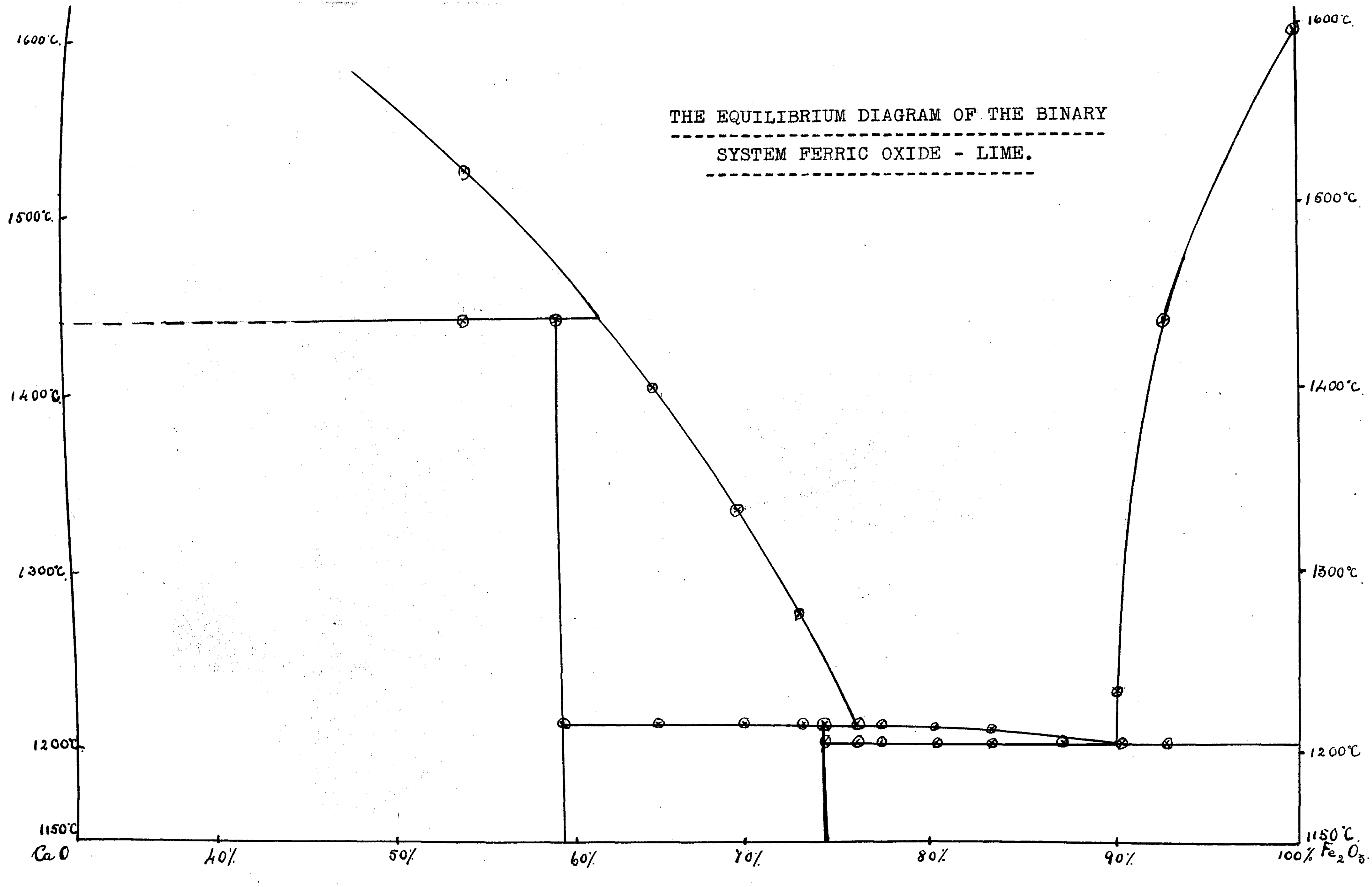
the thermo-couples, and if these be connected to a sensitive galvanometer, the difference in potential will cause a deflection. This difference in potential was obtained by having a piece of pure platinum, of mass equal to that of the crucible and melt, placed alongside the crucible. The arrangement was as in the sketch on page 43. A piece of platinum- platinum-rhodium wire was used as a "bridge" between the crucible and the blank. If A the blank, had the same temperature as the crucible B, no potential difference existed between the platinum leads and no deflection of the galvanometer was recorded; if on the other hand, A becomes warmer than B, due to phase changes in the material in B, then the potential difference in the leads will cause a deflection of the galvanometer. Thus, theoretically, no deflection should be observed unless a phase change is taking place in the crucible, but due to the impossibility of obtaining an exact balance in the specific heats in the blank and the crucible, and also to a slight difference in the heating of the two, there is always a small drift of the galvanometer spot. To keep this in check and also to keep the spot on the scale, a small back potential was put on the differential leads; this was checked to ensure that it was not interfering with the proper readings of the thermo-couple but it was found that it did not. The points of the thermo-couple were attached to the outside of the crucible, because of the tendency of ferrite mixtures to climb up the wires by surface tension, which they did when the points were immersed in the crucible, sometimes an inch or more. No appreciable difference could be detected in the temperature recorded as that of the melting point of a mixture, whether the thermo-couple points were inside or outside the crucible, probably because of the good heat conducting properties of platinum.

The millivolts generated by the thermo-couple were measured by a vernier potentiometer capable of reading tenths of milli--volts. The accumulator used with this instrument was standardised frequently against a standard cell of 1.0183 volts.

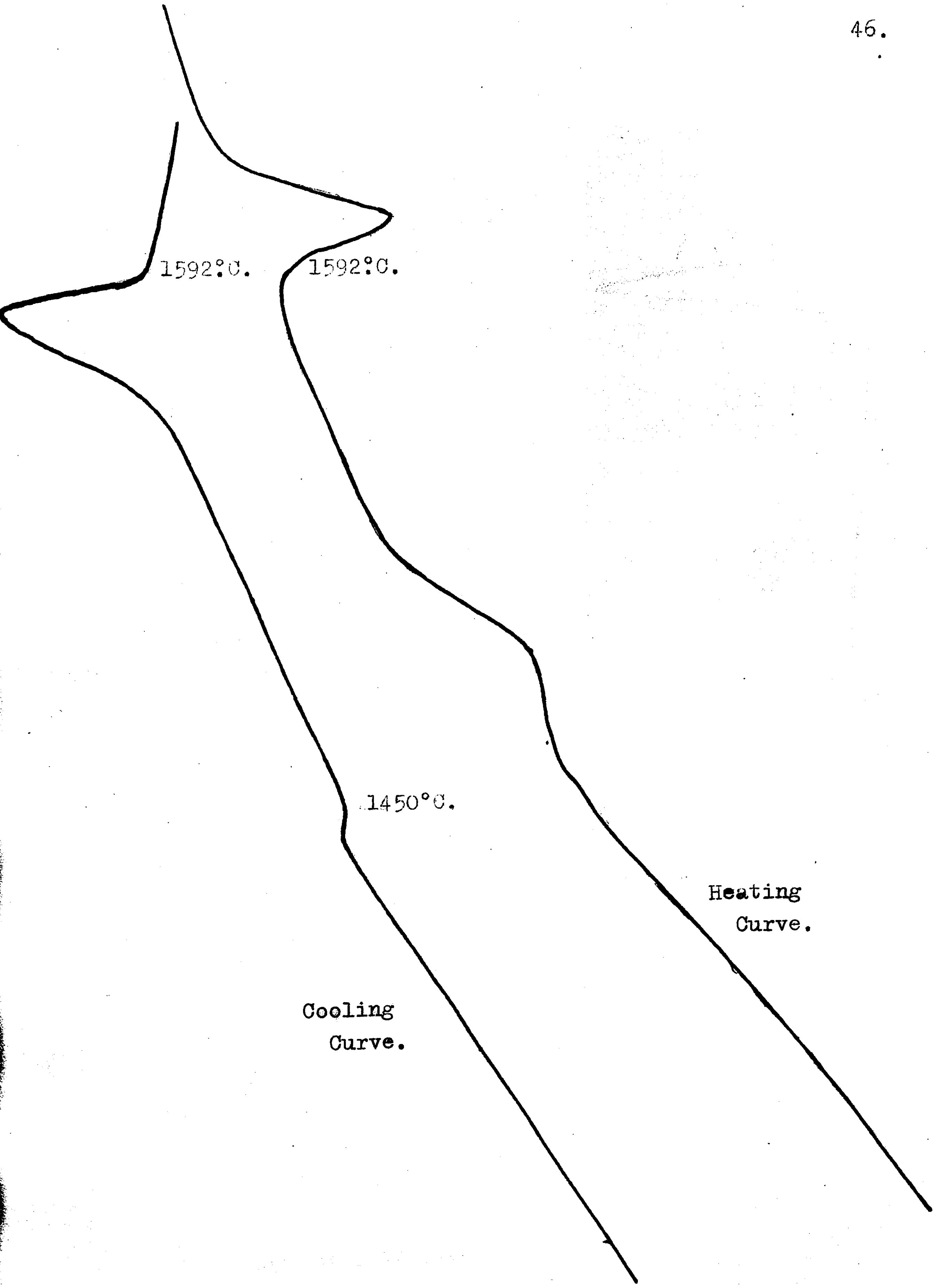


Sketch showing the arrangement of the crucible and blank inside the " Pythagoras " tube, and also the method of connecting the thermo-couple and differential wires.

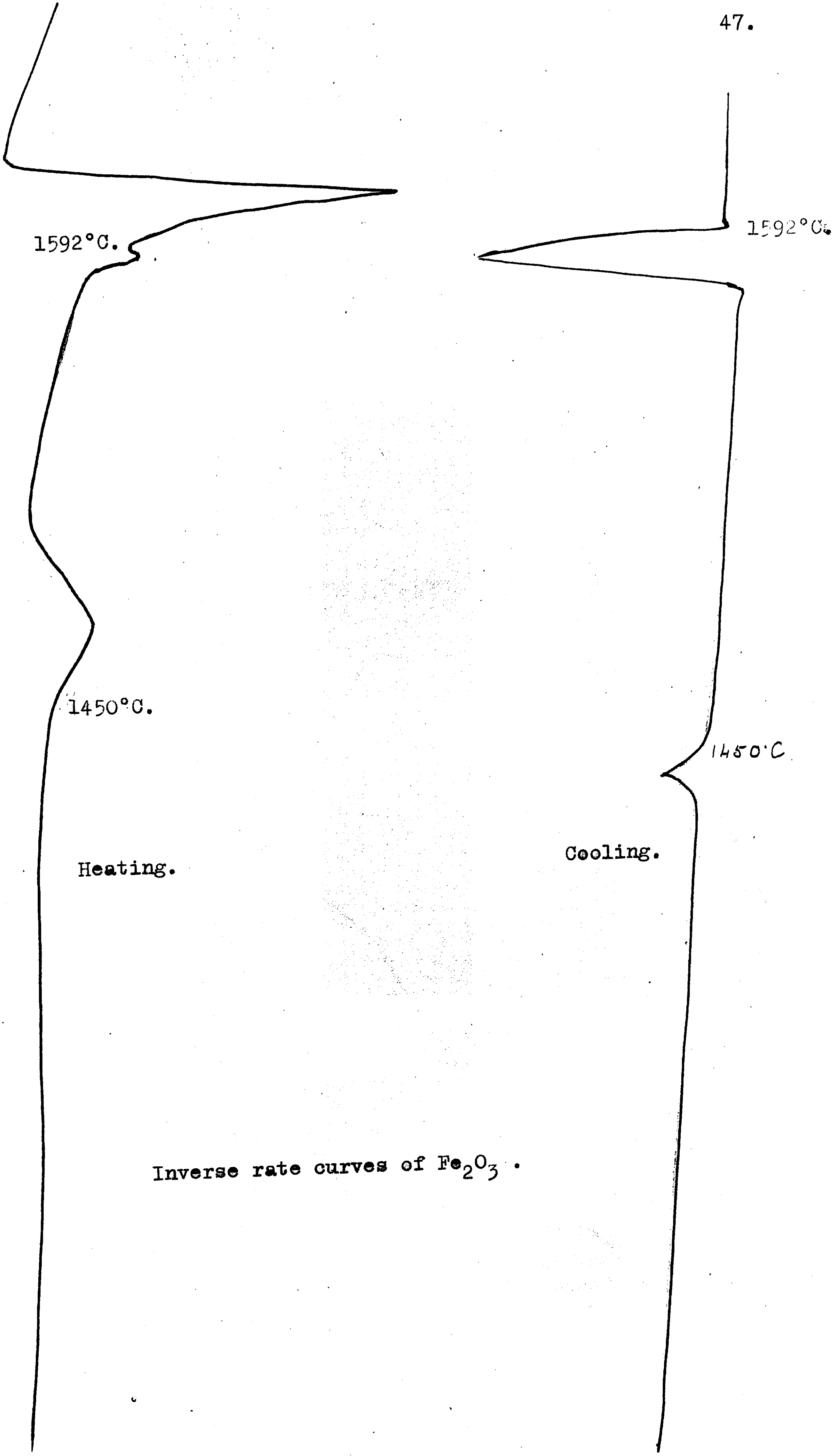
The agreement between the inverse rate curves and the differential curves is very good as can be seen from the curves, page 46, et seq. The melting points obtained from the curves were plotted on a diagram, and the equilibrium diagram of the binary system, CaO - Fe_2O_3, was drawn, page 45. Seeming phase change points were obtained in some of the mixtures rich in ferric iron, which did not seem capable of being explained, having no apparent connection to the rest of the diagram. However an explanation was found for these points at a later stage of the work. They are due to the commencement of dissociation of the ferric oxide and the calcium ferrites and so they have been left out of the equilibrium diagram, since they indicate a state occurring which upsets the diagram. This point is more fully discussed later. The various fused mixtures were examined in the manner previously described and the petrographic results are tabulated on page70-1. Attempts were made at first to melt ferric oxide in air, although it was known that this substance dissociates at high temperatures. The extent of the dissociation was, however, very imperfectly understood, as no definite phase change point was obtainable without great difficulty, and even when obtained was not reproducible. In addition, the material after supposed fusion, proved on examination to be only partially fritted together. Then an attempt was made to prevent this dissociation, and the " Pythagoras " tube was evacuated and filled with oxygen to a pressure of 1¼ atmospheres,; the tube was then heated, and an automatic regulator kept the pressure constant at least while the temperature was being raised. Since the supposed melting point for ferric oxide is very high, the refractory tube had to be supported to prevent its sagging under the combined effect of the high temperature and pressure. Even at a pressure of 1¼ atmospheres of oxygen, ferric oxide dissociated a little, and from work done later, it was calculated, that to completely stop the dissociation of ferric oxide at its melting point, a pressure of approximately 5×10^5 atmospheres of oxygen would be necessary.



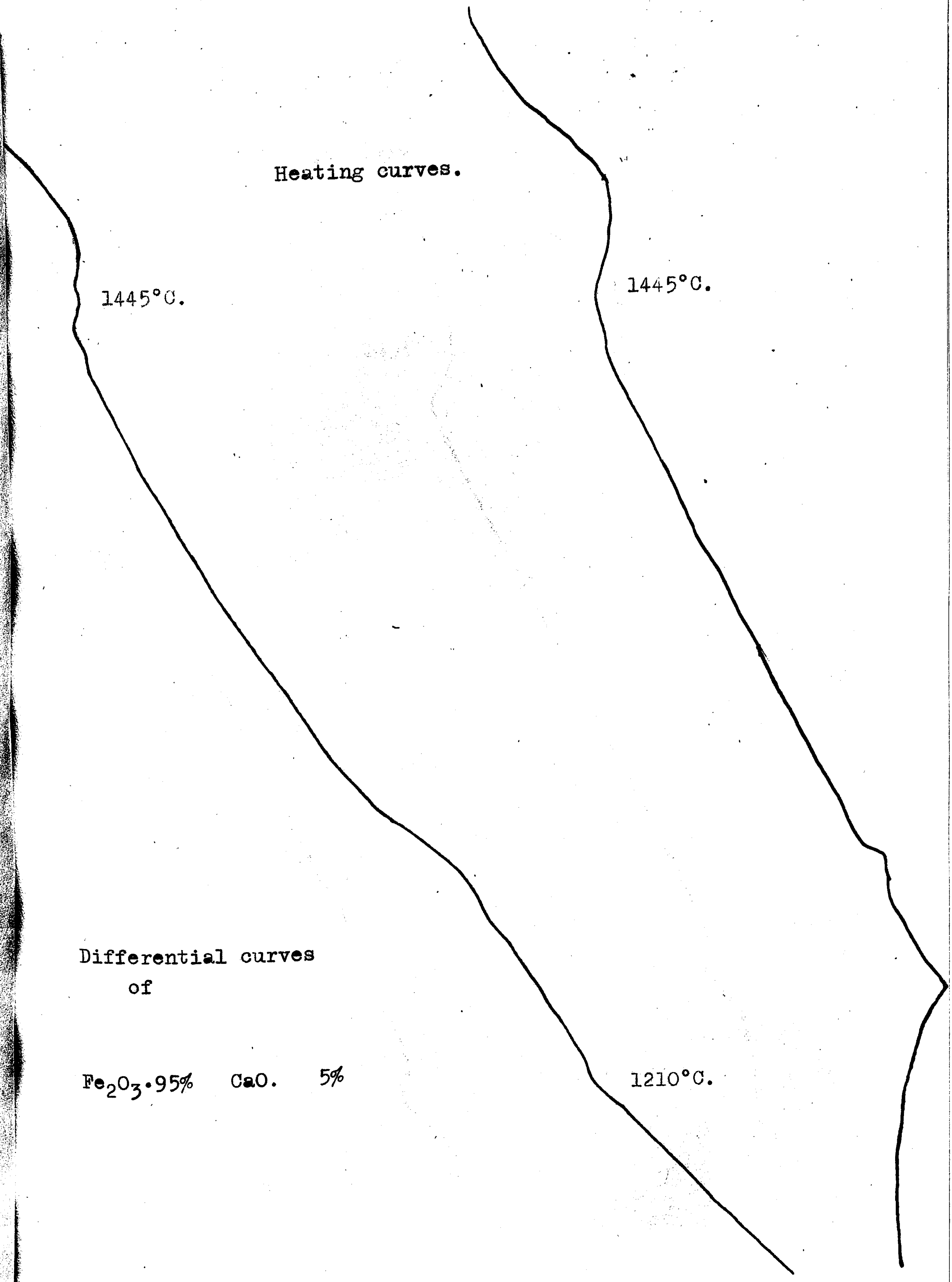
THE EQUILIBRIUM DIAGRAM OF THE BINARY SYSTEM FERRIC OXIDE - LIME.



Differential curves of Fe_2O_3.



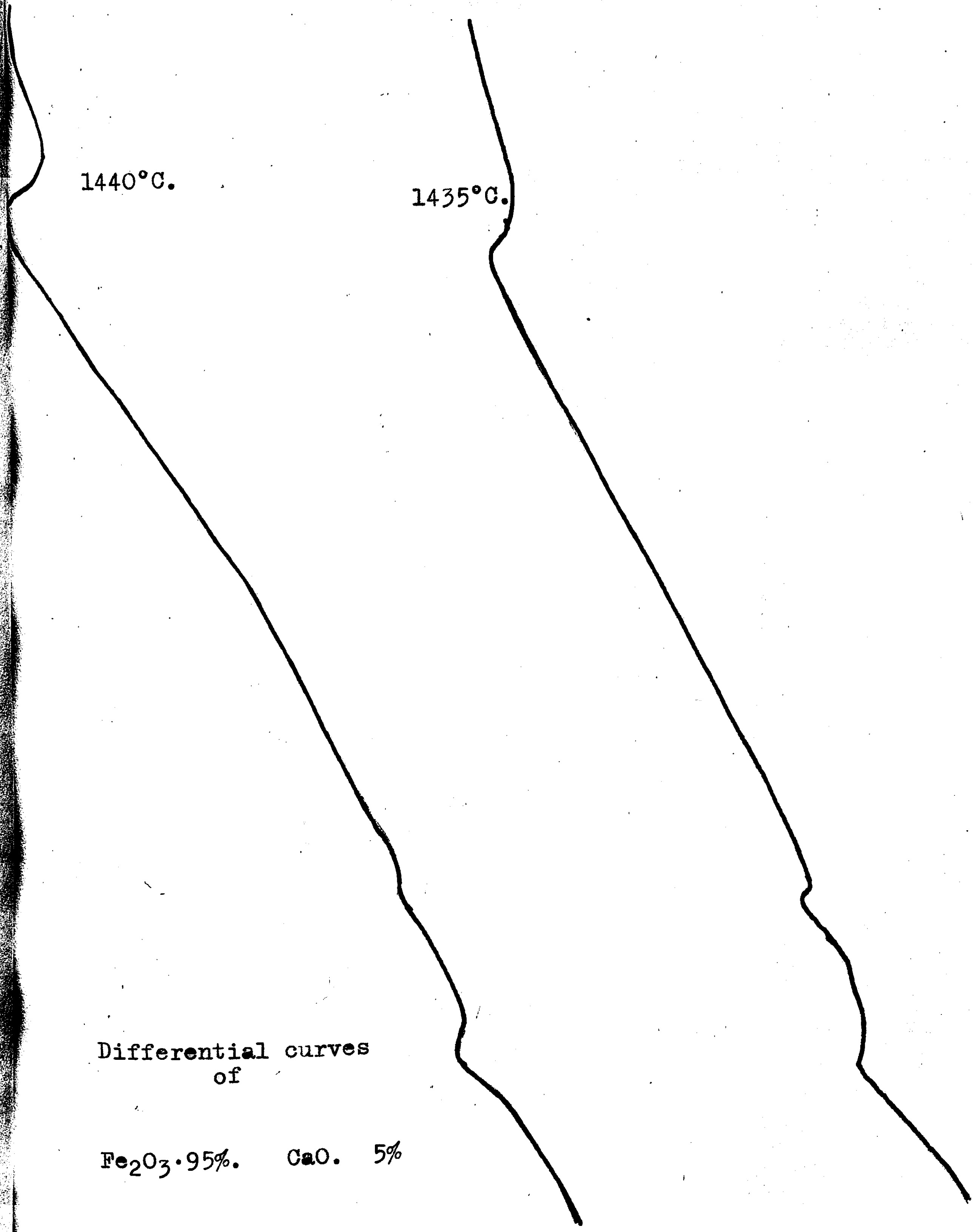
Inverse rate curves of Fe_2O_3.



Differential curves
of

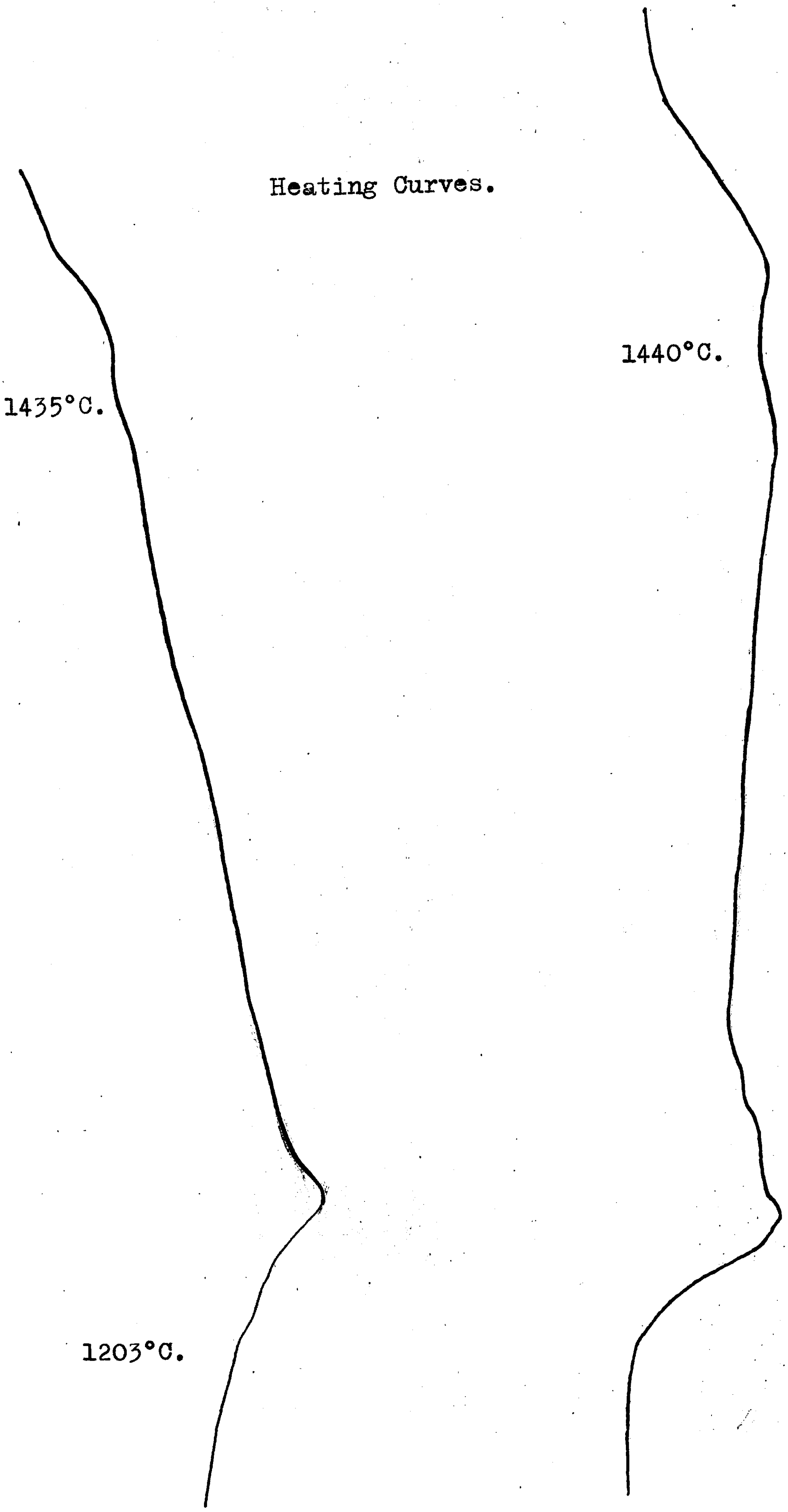
Fe_2O_3·95%   CaO.   5%

Cooling Curves.



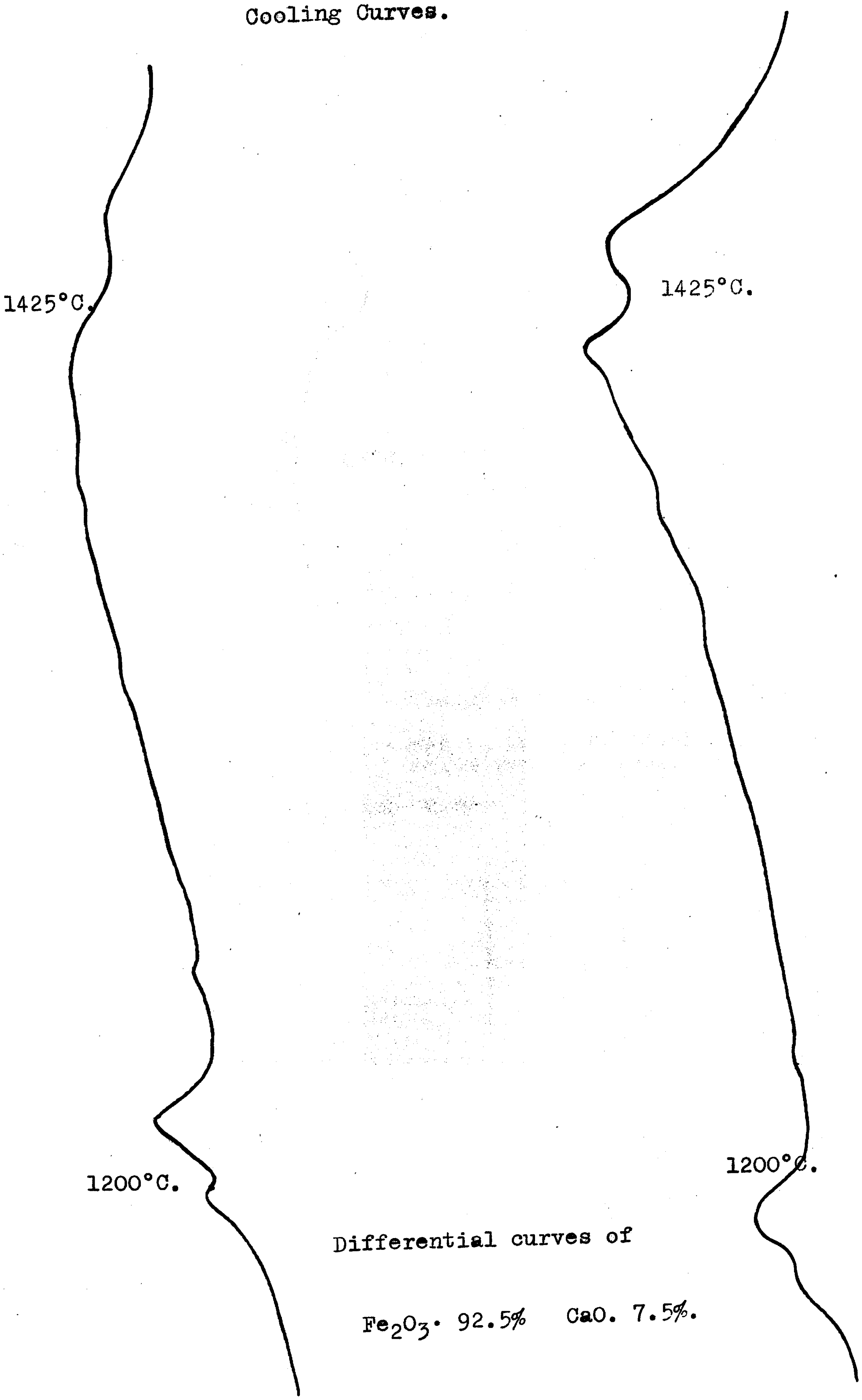
Differential curves
of

$Fe_2O_3 \cdot 95\%$. CaO. 5%



Differential Curves of Fe_2O_3. 92.5% CaO. 7.5%

Cooling Curves.

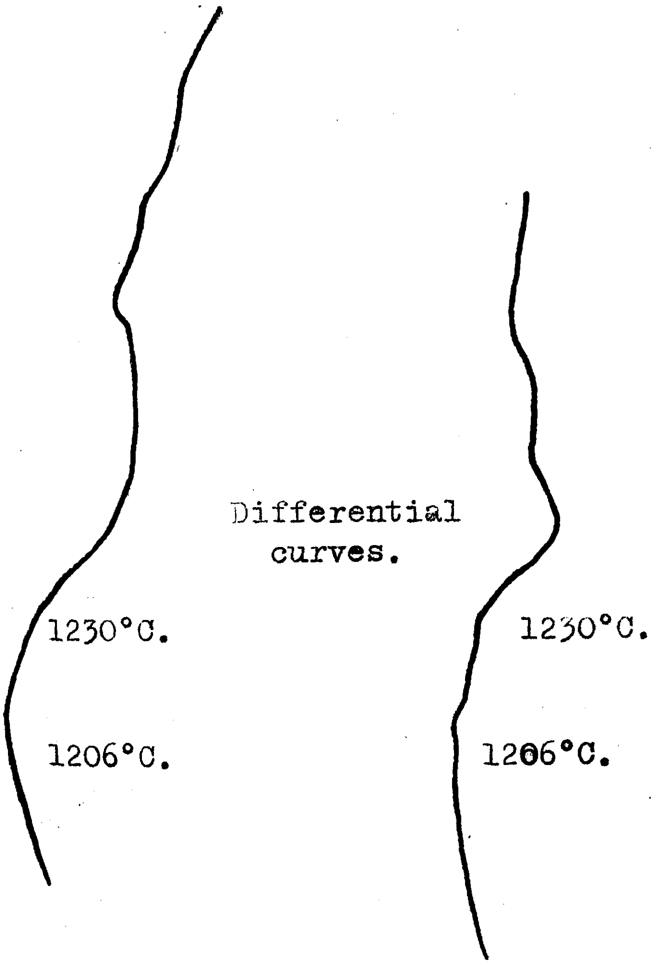


Differential curves of

Fe_2O_3. 92.5% CaO. 7.5%.

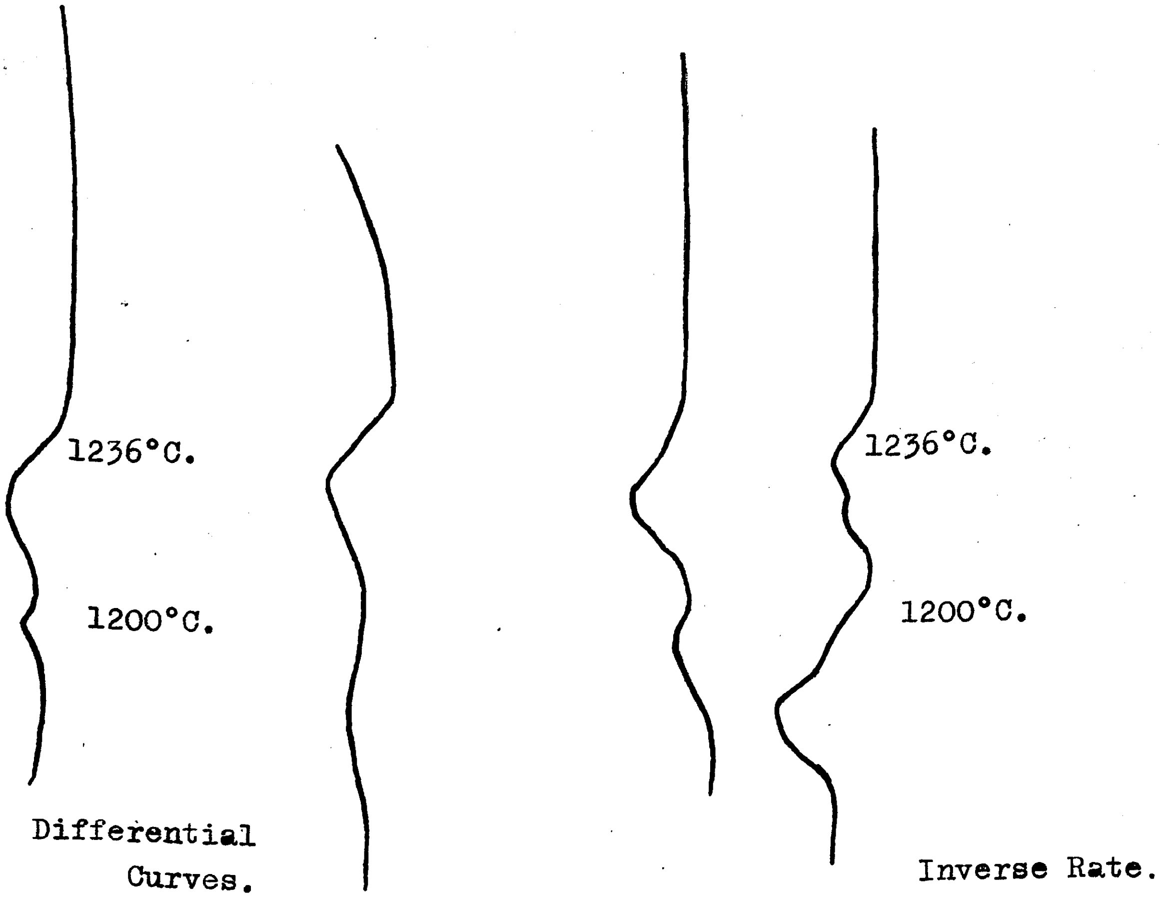
Fe_2O_3. 90%. CaO. 10%.

Heating curves.

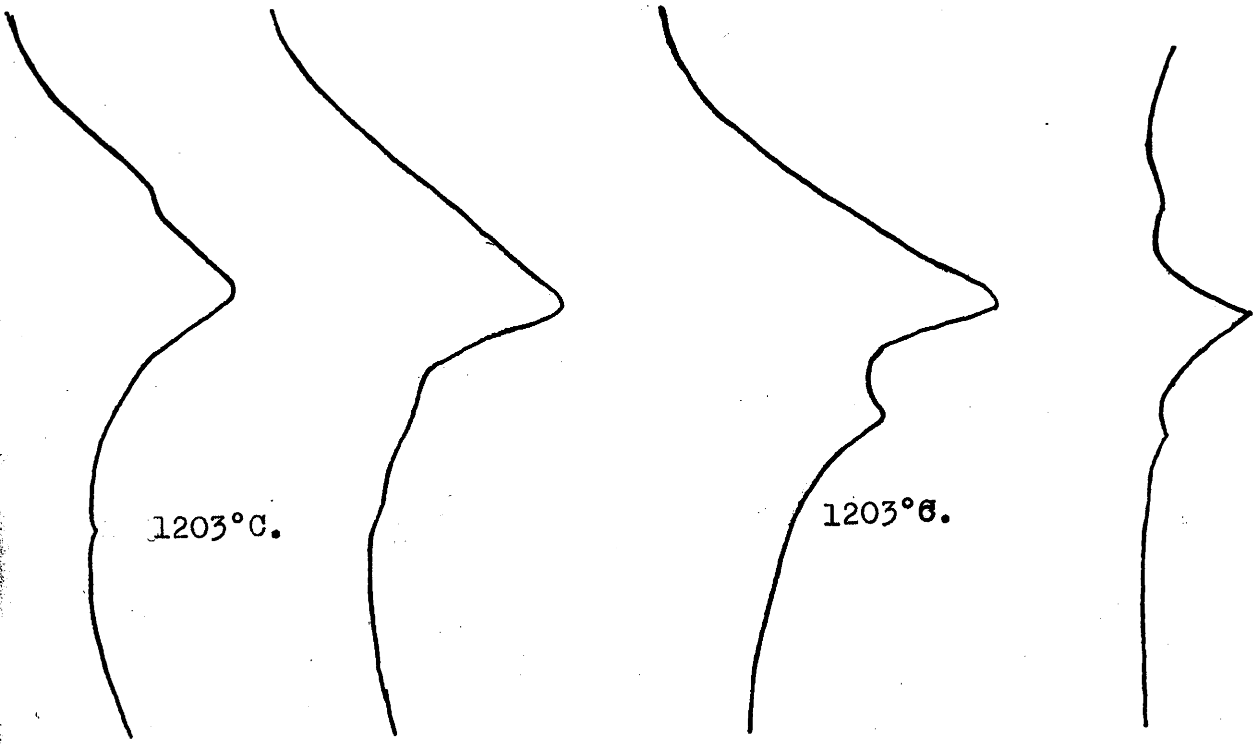


The rise in the freezing point is due to the dissociation of the ferric oxide and the formation of Fe_3O_4.

Cooling Curves.

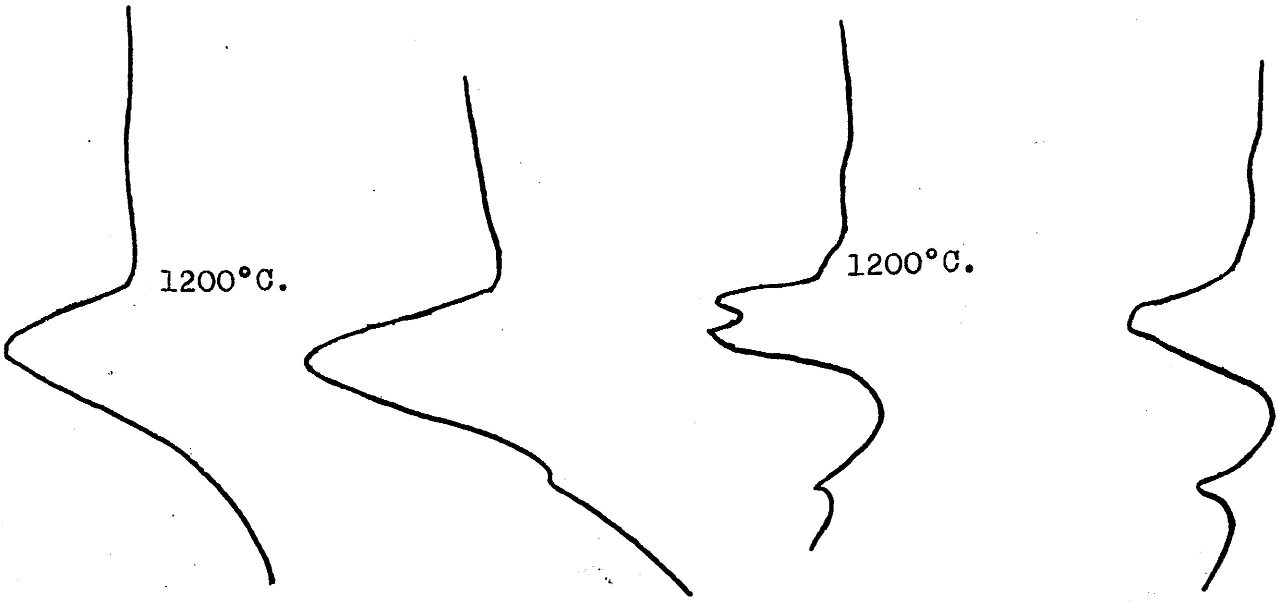


Heating Curves.



Differential Curves. Inverse Rate.

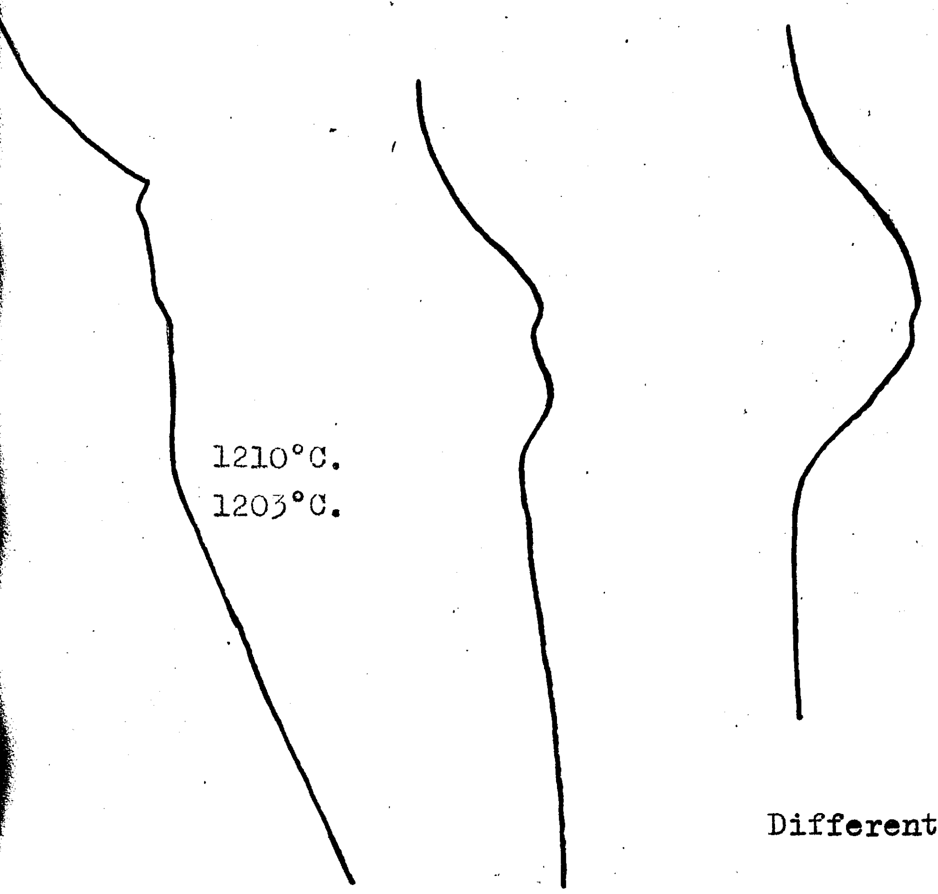
Cooling Curves.



Differential Curves. Inverse Rate.

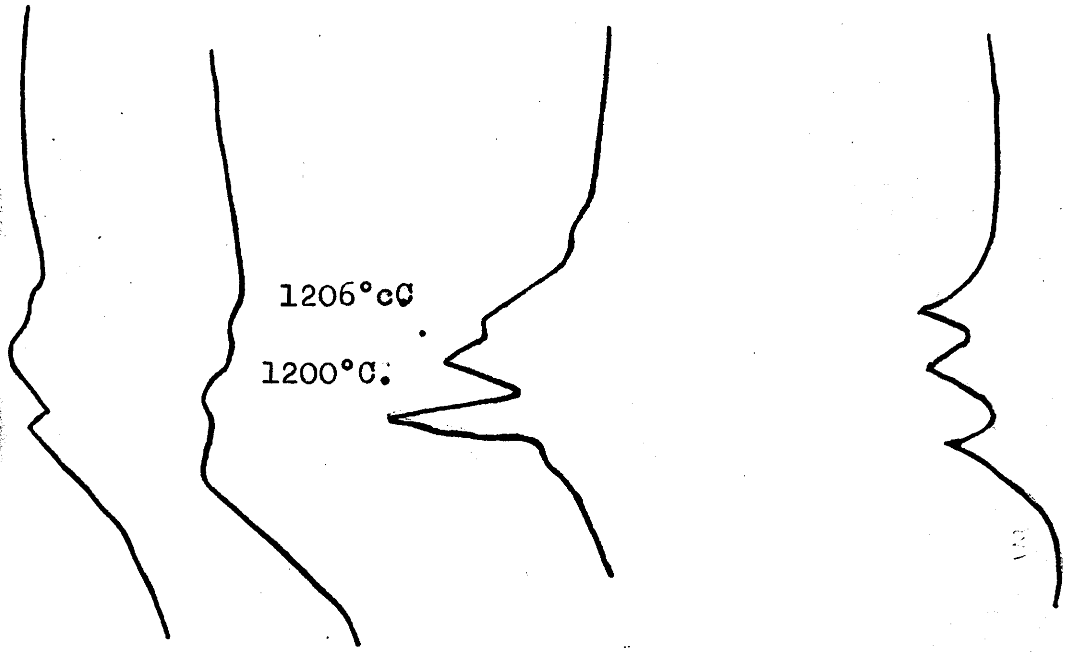
Fe_2O_3. 88%. CaO. 12%.

Heating Curves.



Differential Curves.

Cooling Curves.



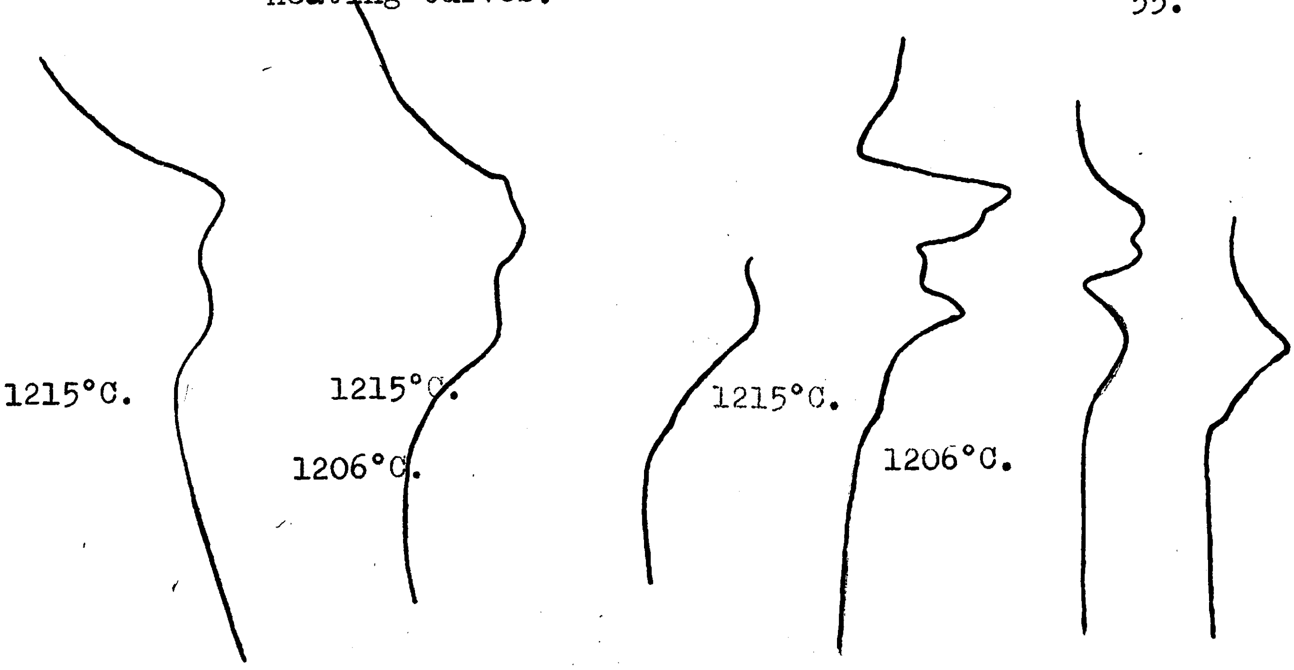
Differential

Curves.

Inverse Rate.

Fe_2O_3. 85%. CaO. 15%.

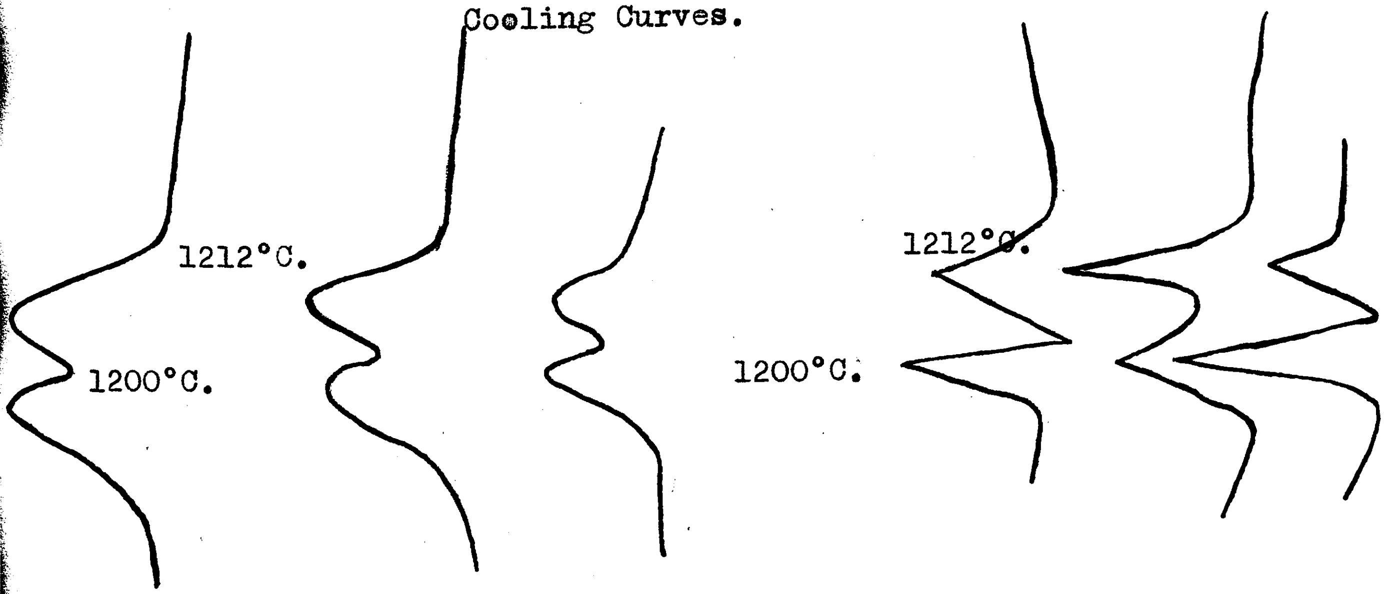
Heating Curves.



Differential Curves.

Inverse Rate.

Cooling Curves.

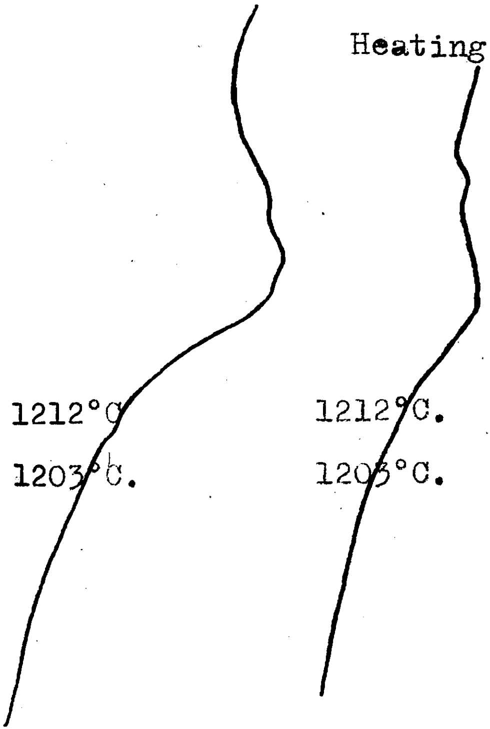


Differential Curves.

Inverse Rate.

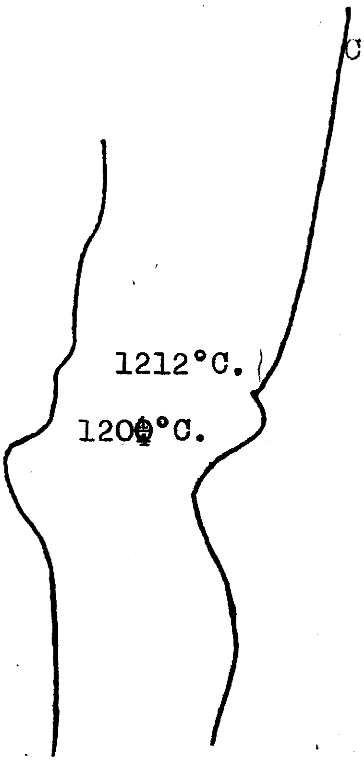
Fe_2O_3. 82.5% CaO. 17.5%.

Heating Curves.

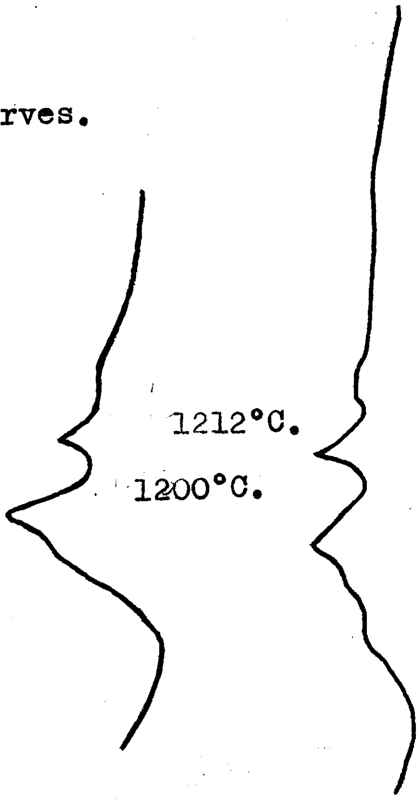


Differential Curves.

Cooling Curves.



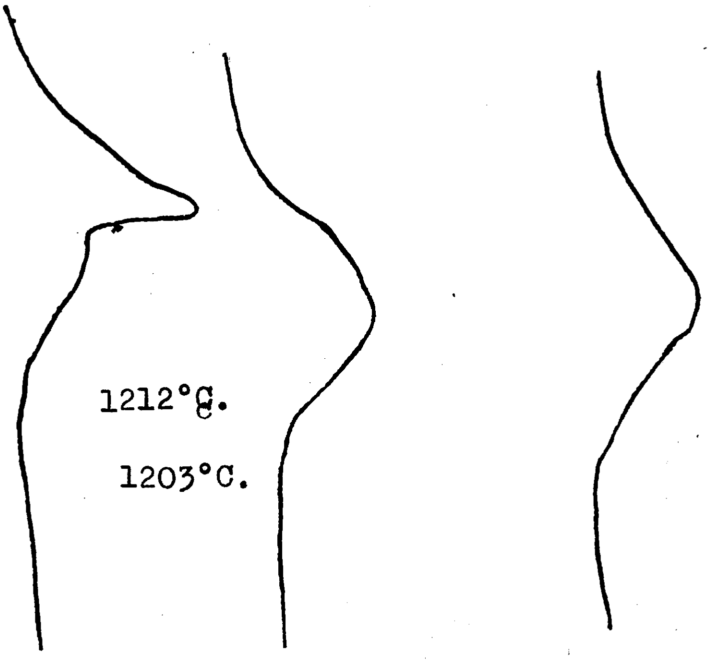
Differential Curves.

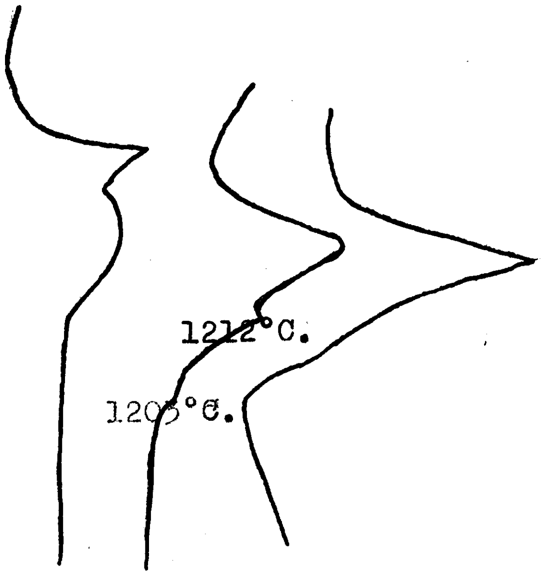


Inverse Rate.

Fe_2O_3. 80%. CaO. 20%.

Heating Curves.

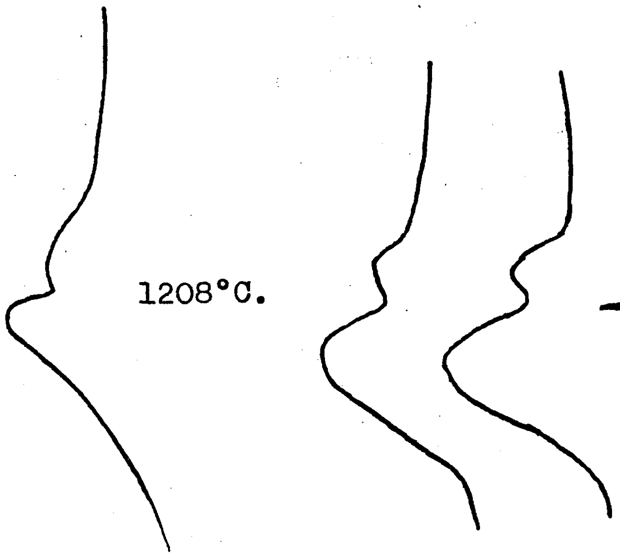


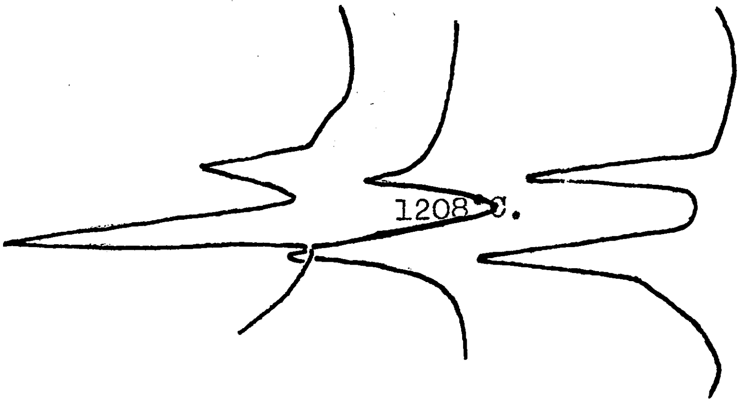


Differential Curves.

Inverse Rate.

Cooling Curves.



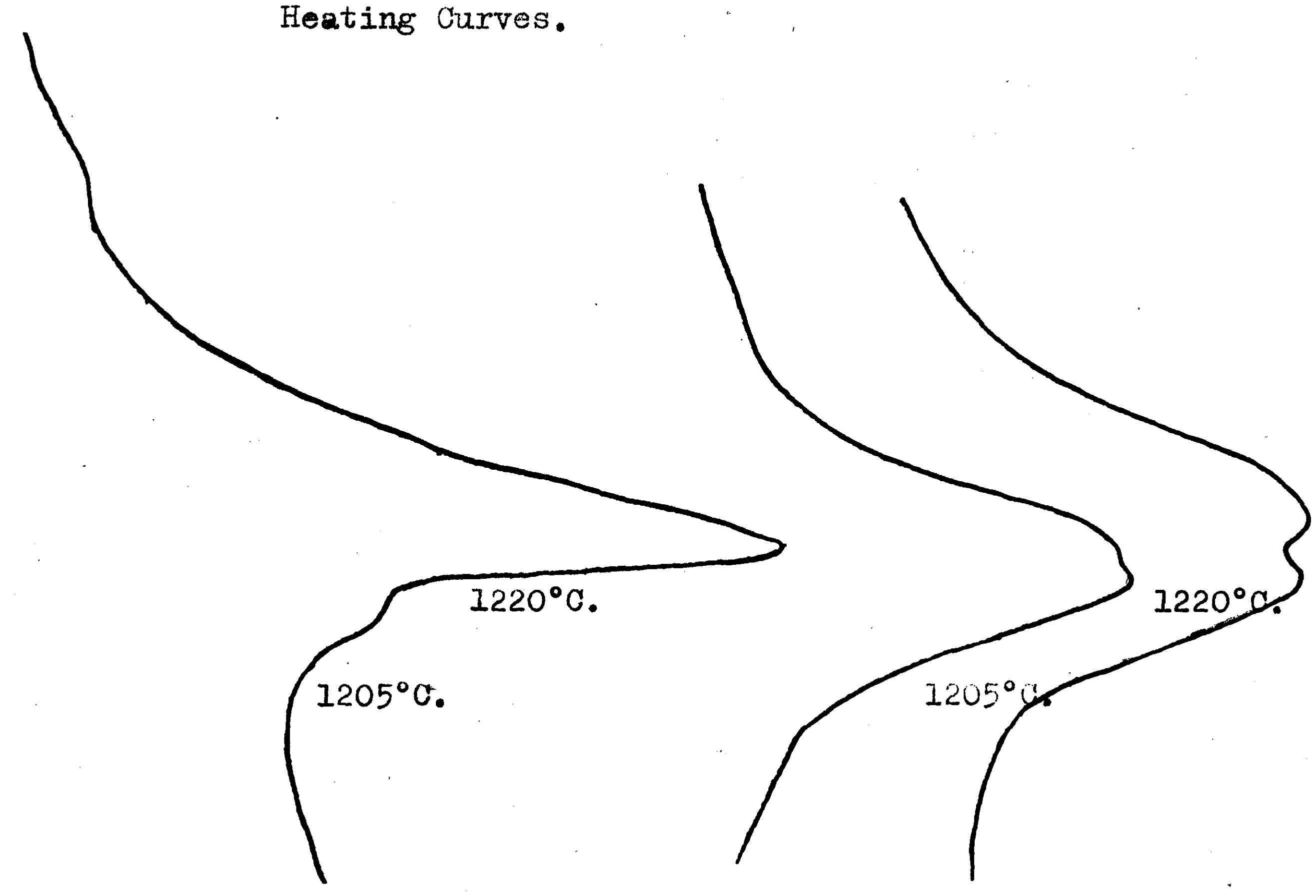


Differential Curves.

Inverse Rate.

Fe_2O_3. 77.5%. CaO. 22.5%

Heating Curves.

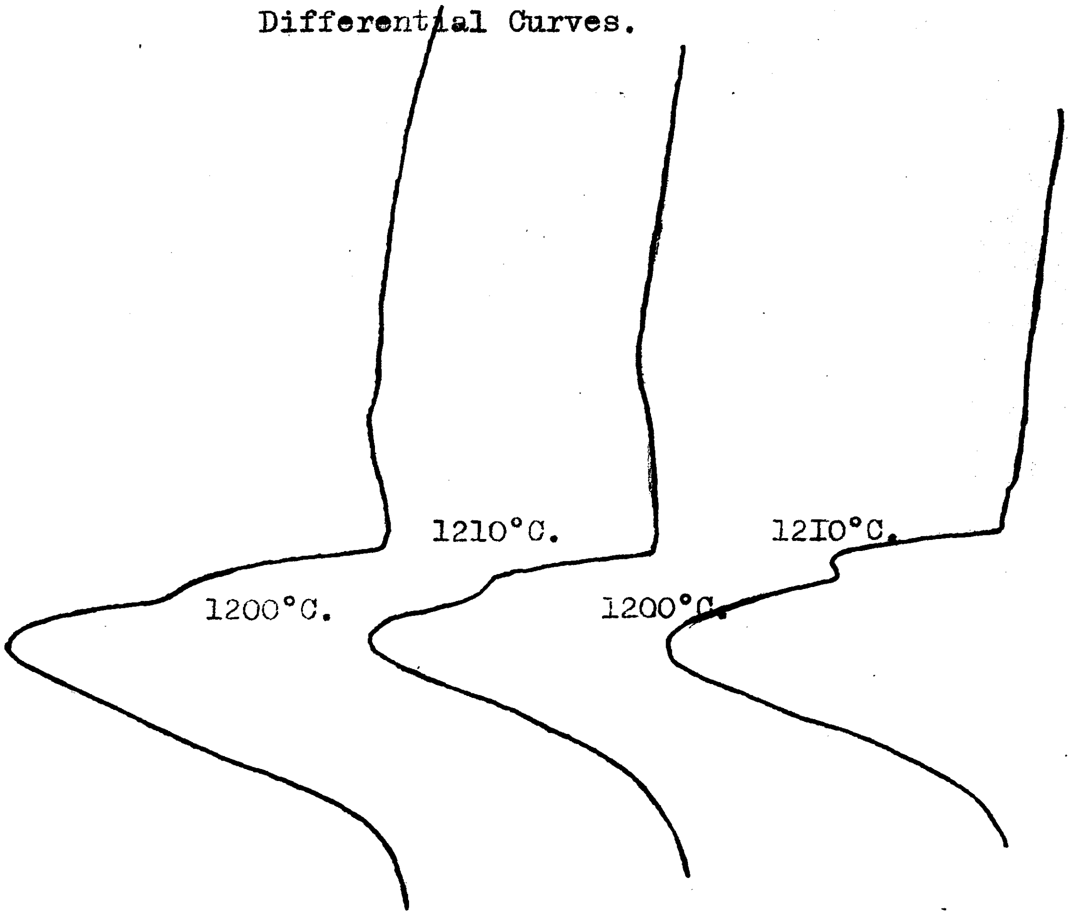


Differential Curves.

Fe_2O_3. 75%. CaO. 25%.

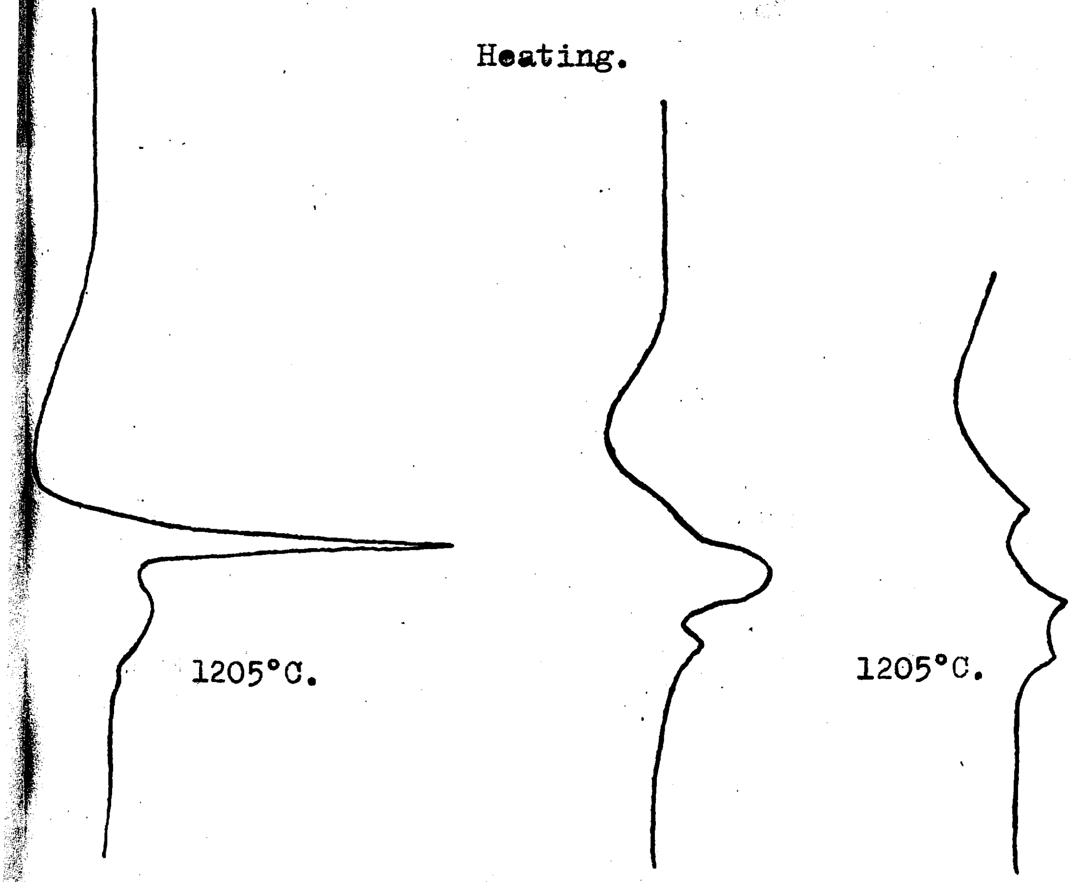
Cooling Curves.

Differential Curves.



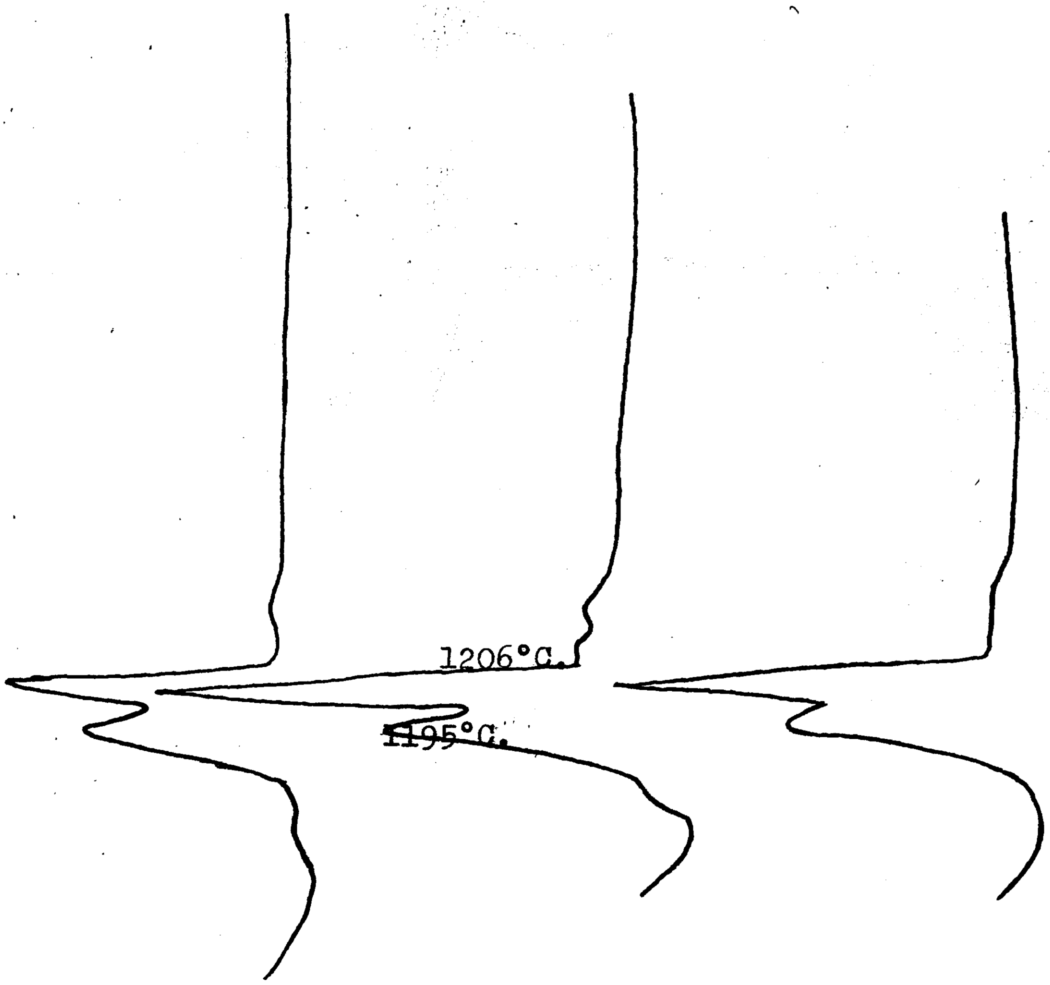
Inverse Rate Curves.

Heating.

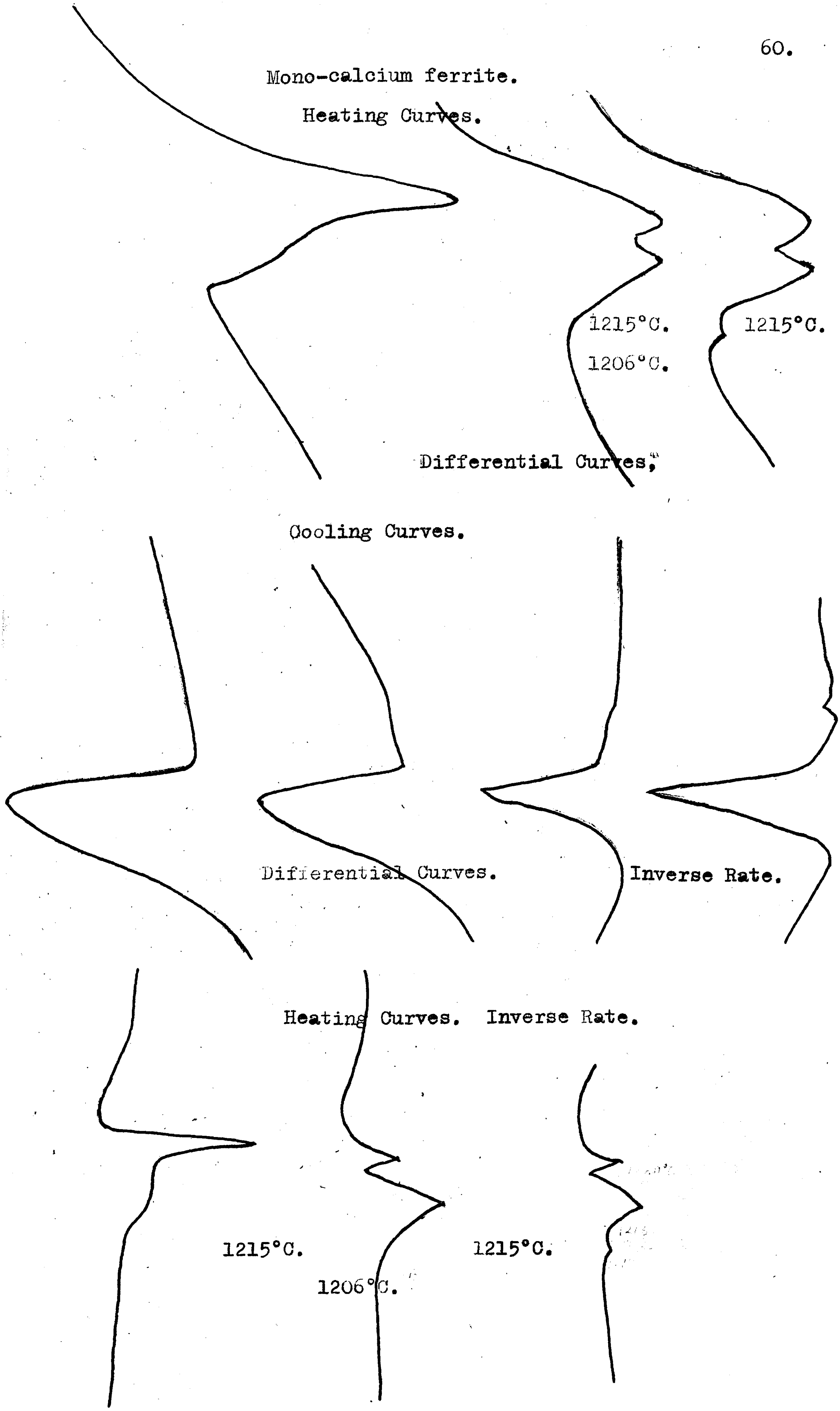


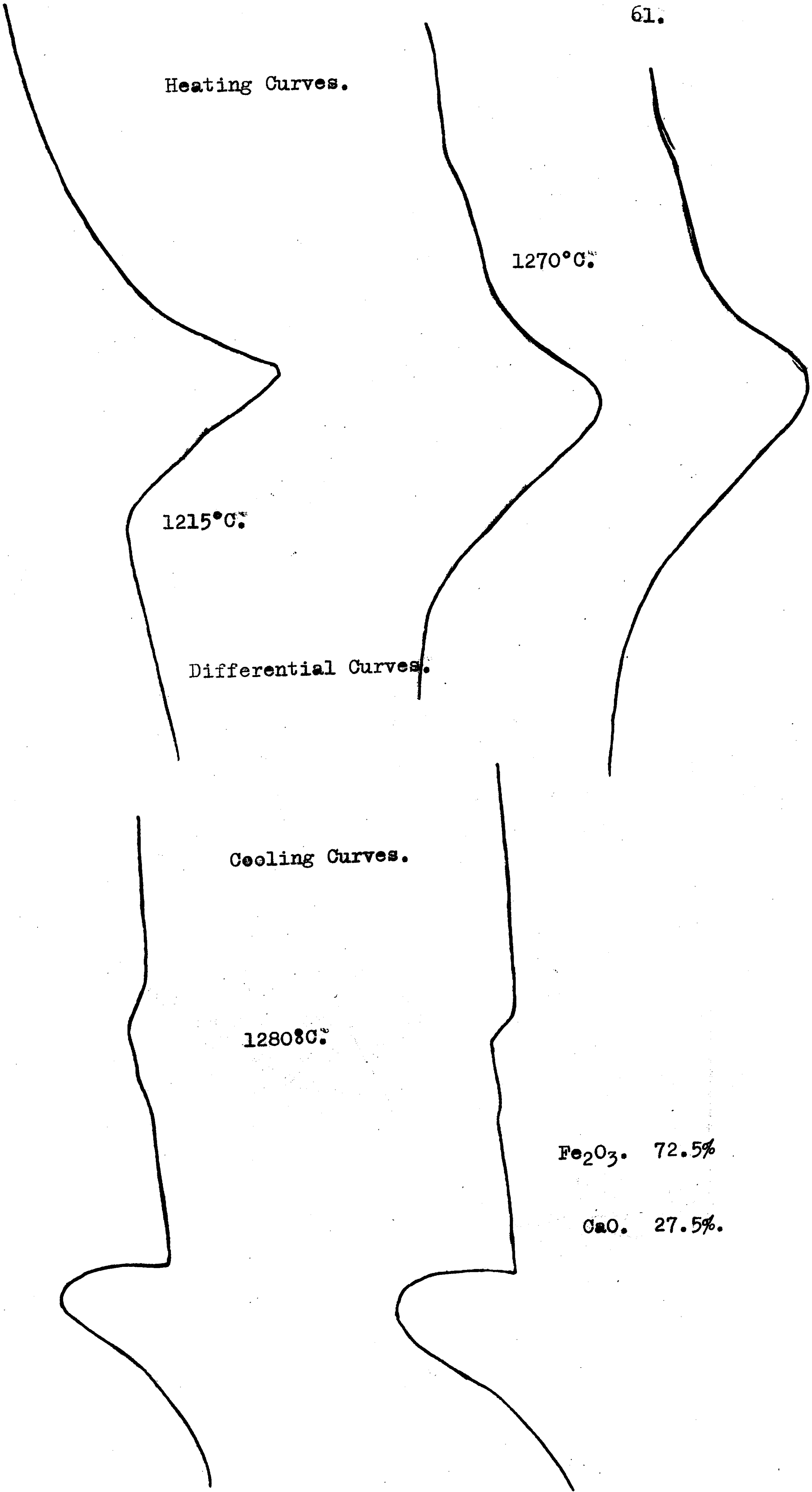
Fe_2O_3. 75%. CaO. 25%.

Cooling.



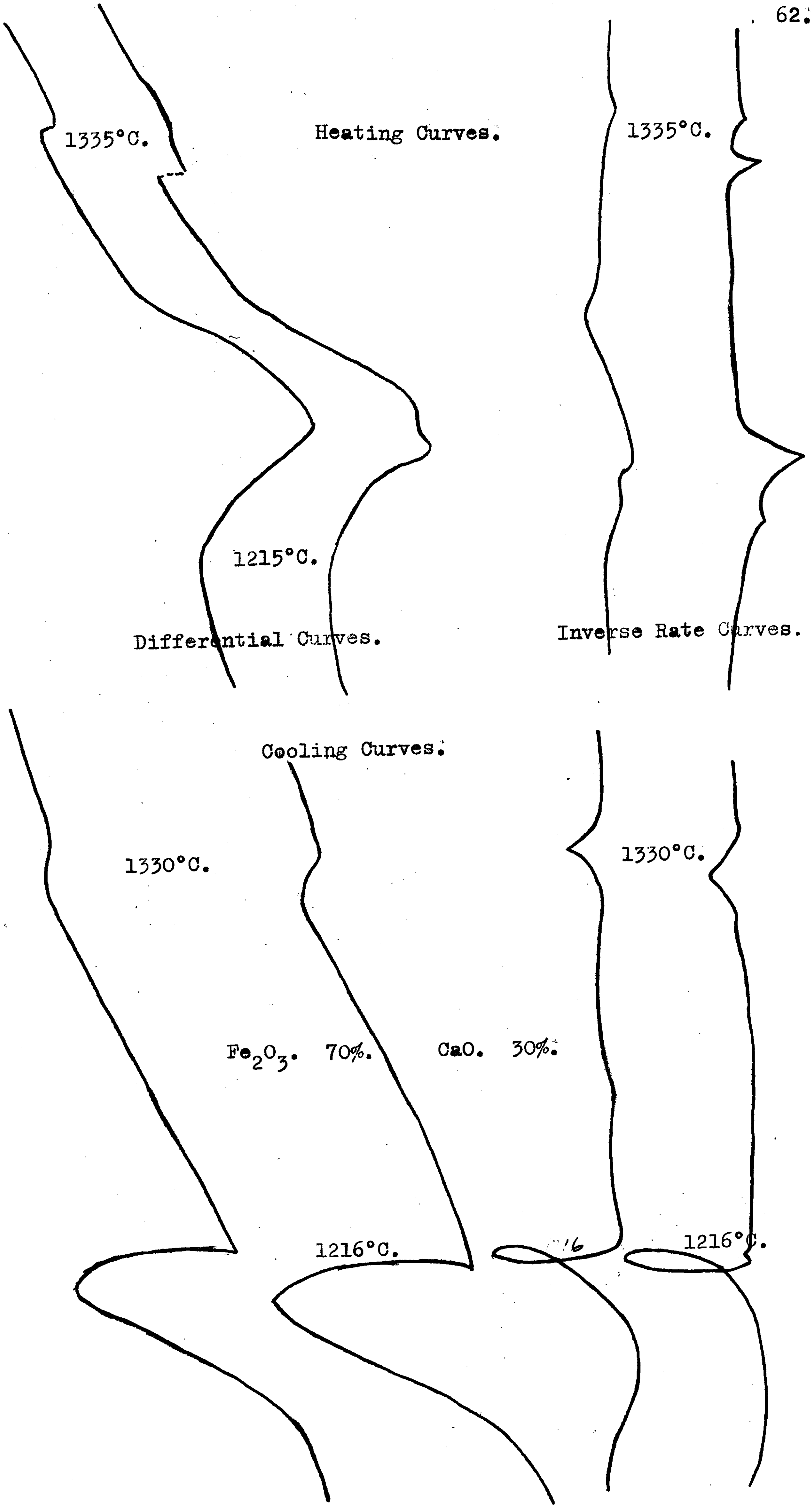
Mono-calcium ferrite.



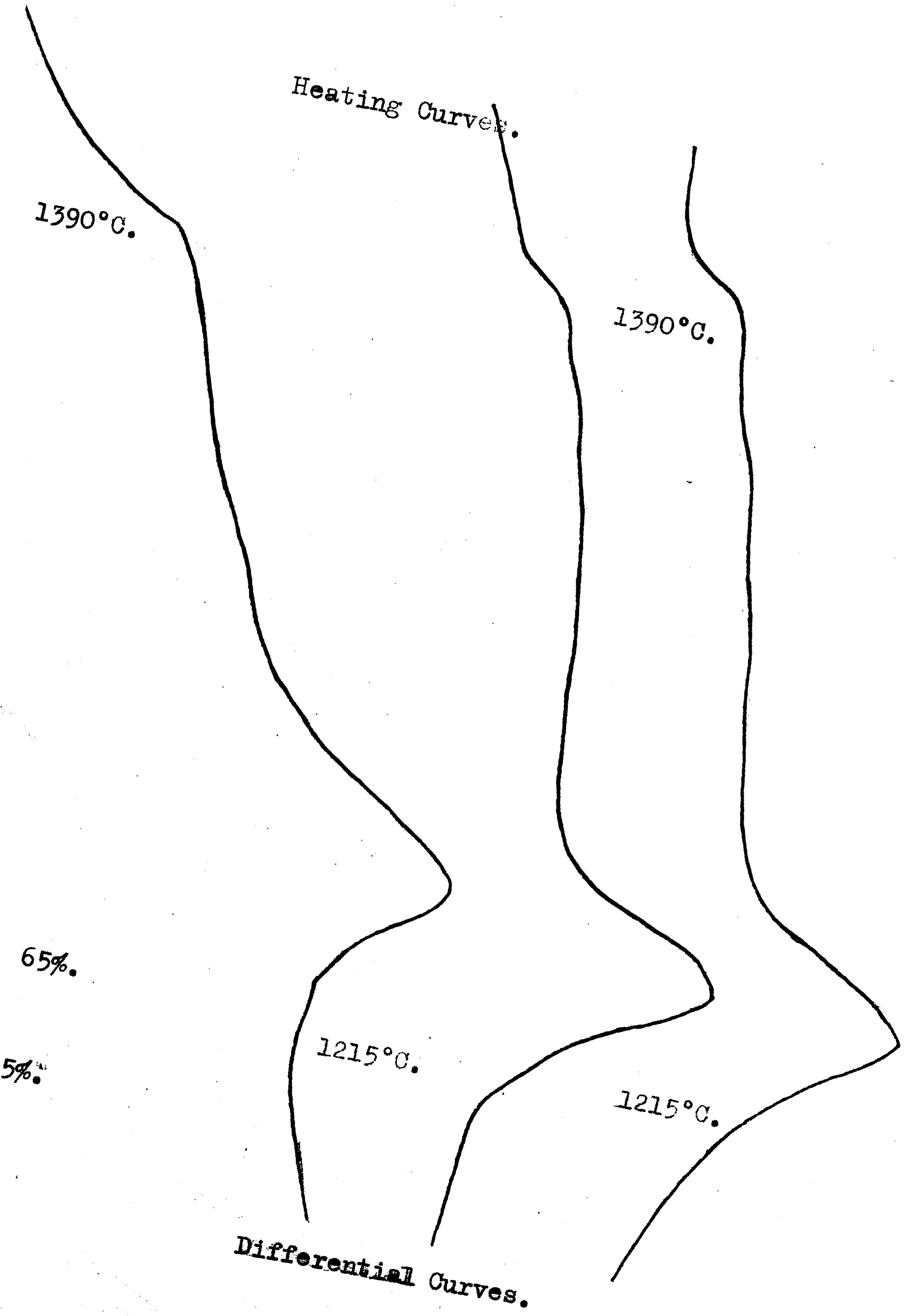


Fe_2O_3. 72.5%

CaO. 27.5%.

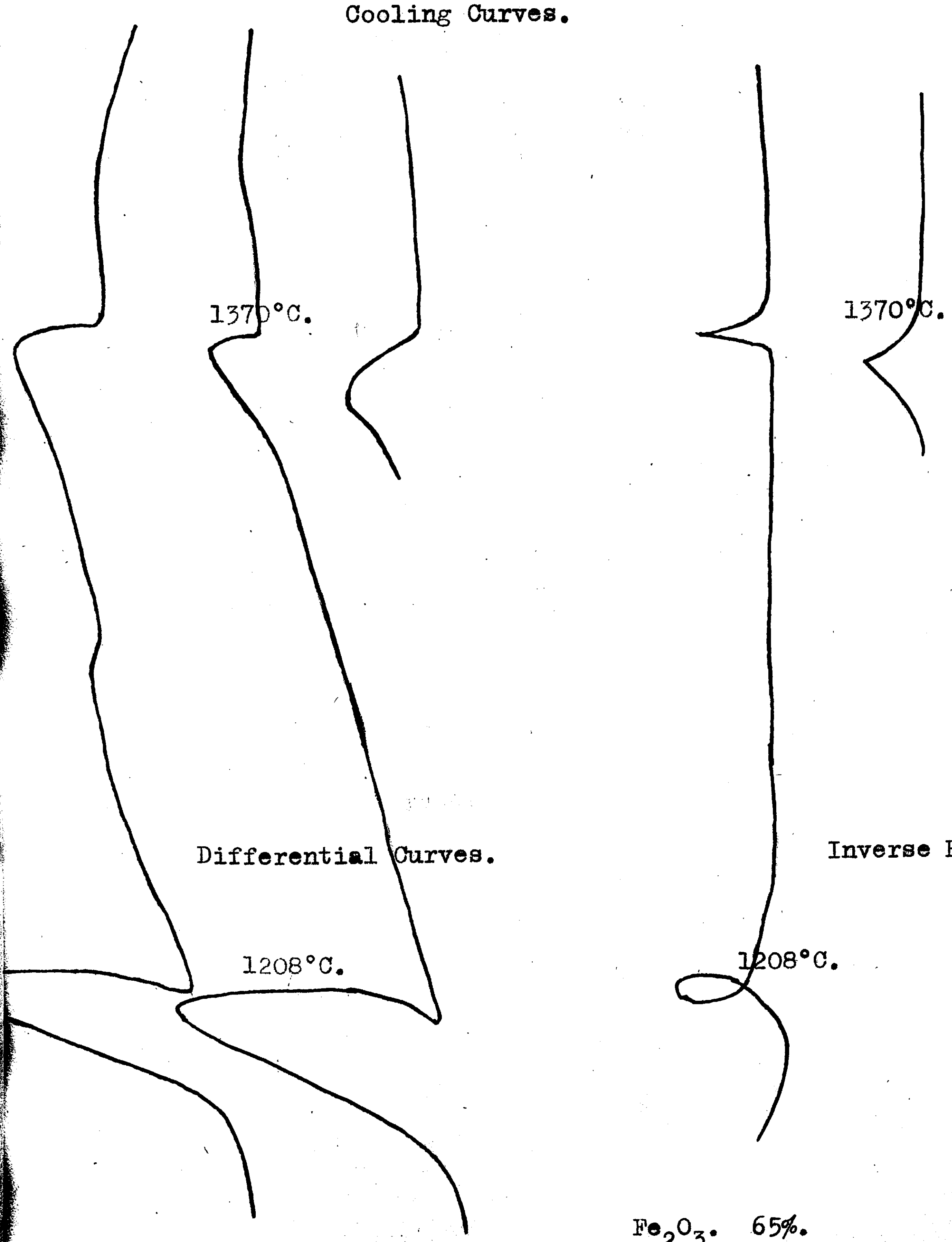


Fe_2O_3. 70%. CaO. 30%.



Fe_2O_3. 65%.

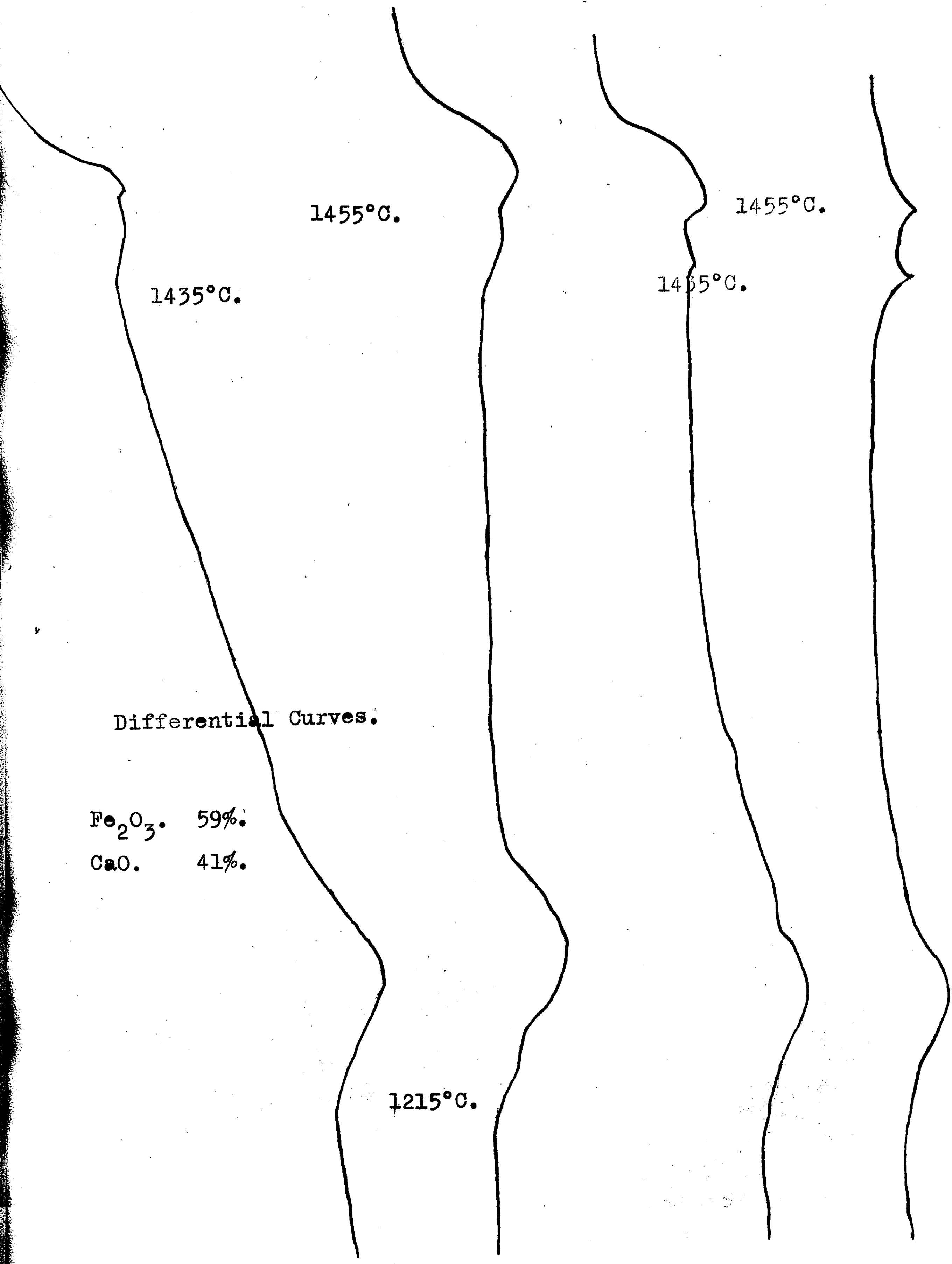
CaO. 35%.



Fe_2O_3. 65%.

CaO. 35%.

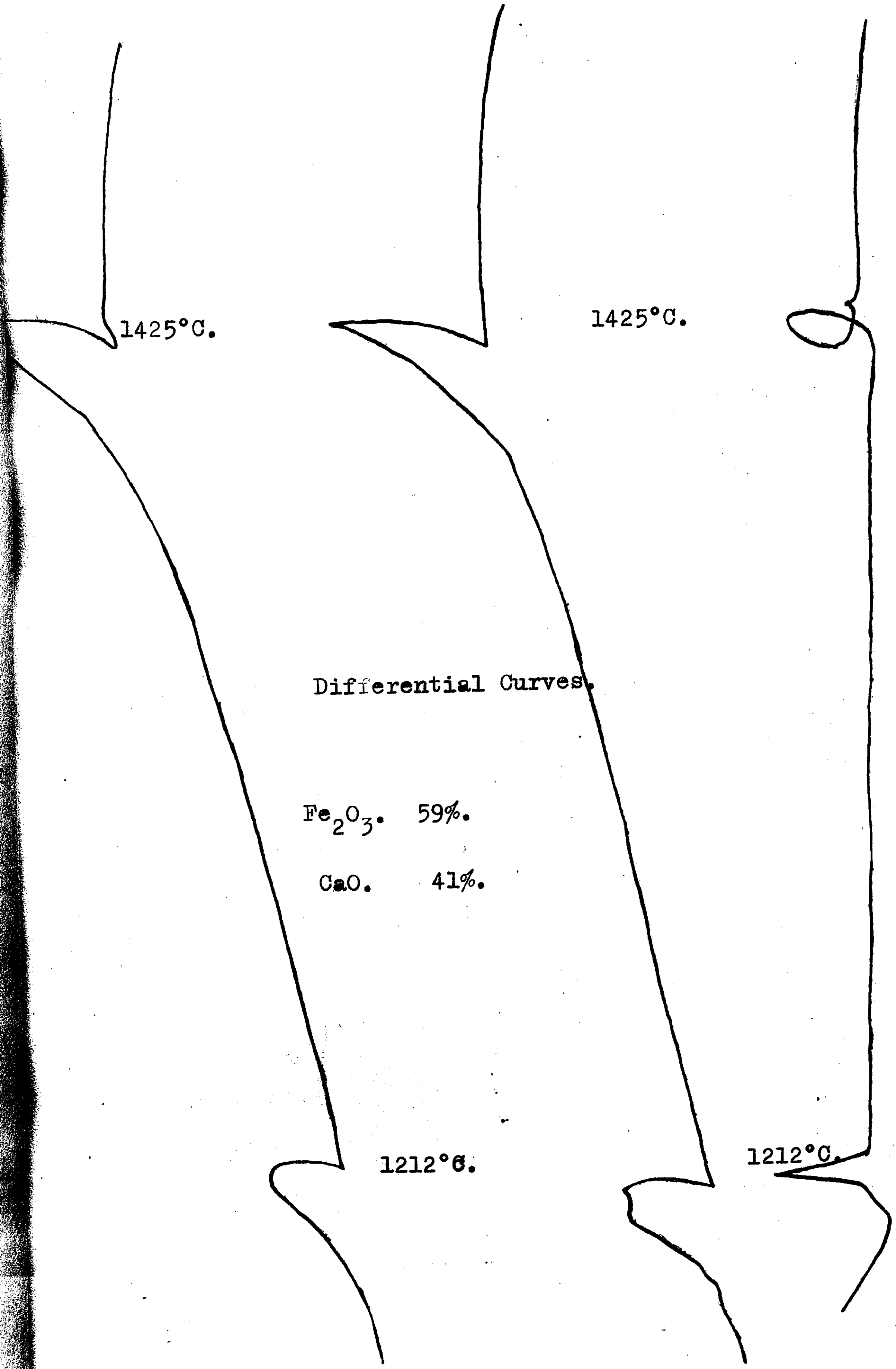
Heating Curves.



Differential Curves.

Fe_2O_3. 59%.
CaO. 41%.

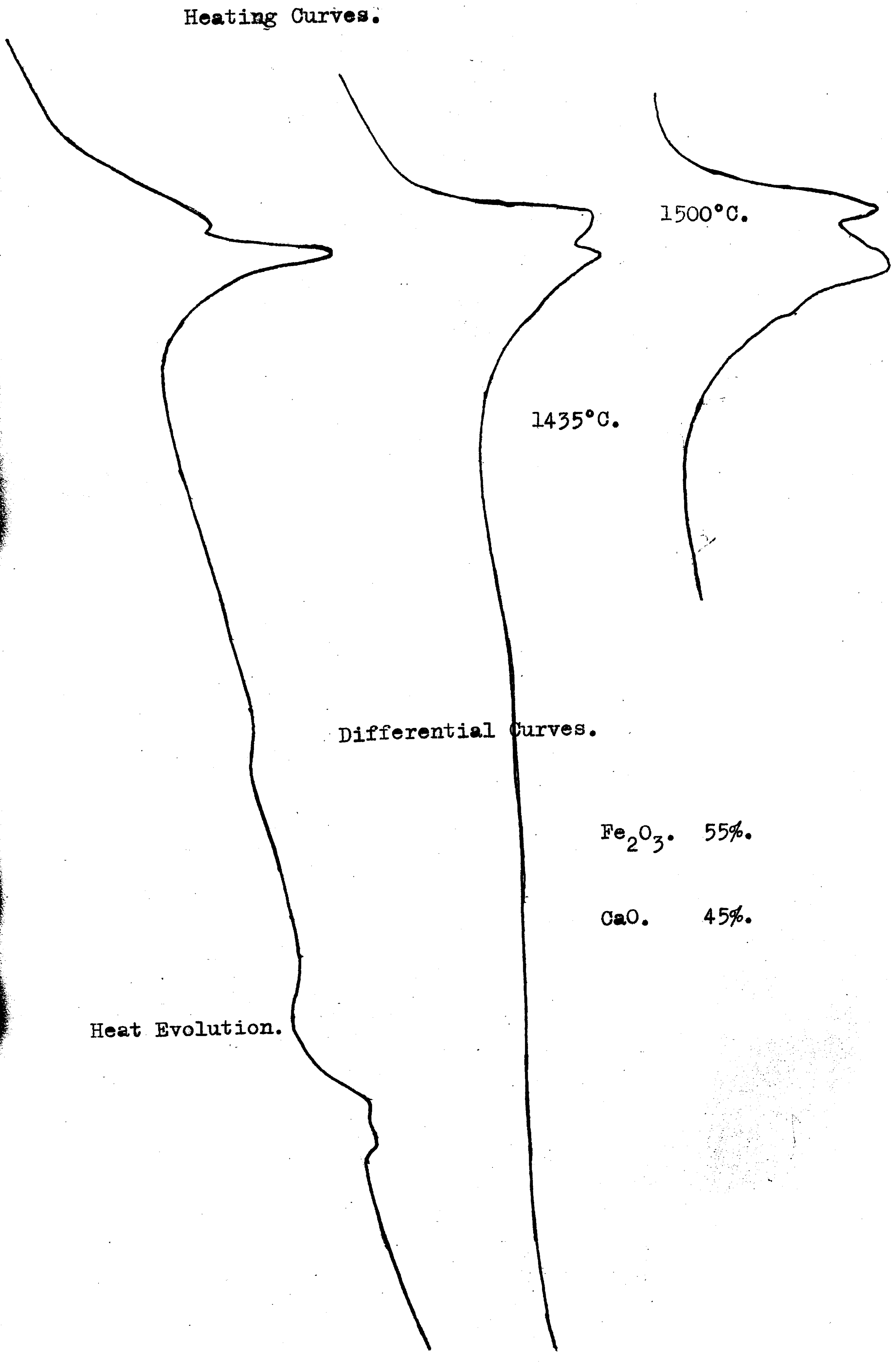
Cooling Curves.



Differential Curves.

Fe_2O_3. 59%.

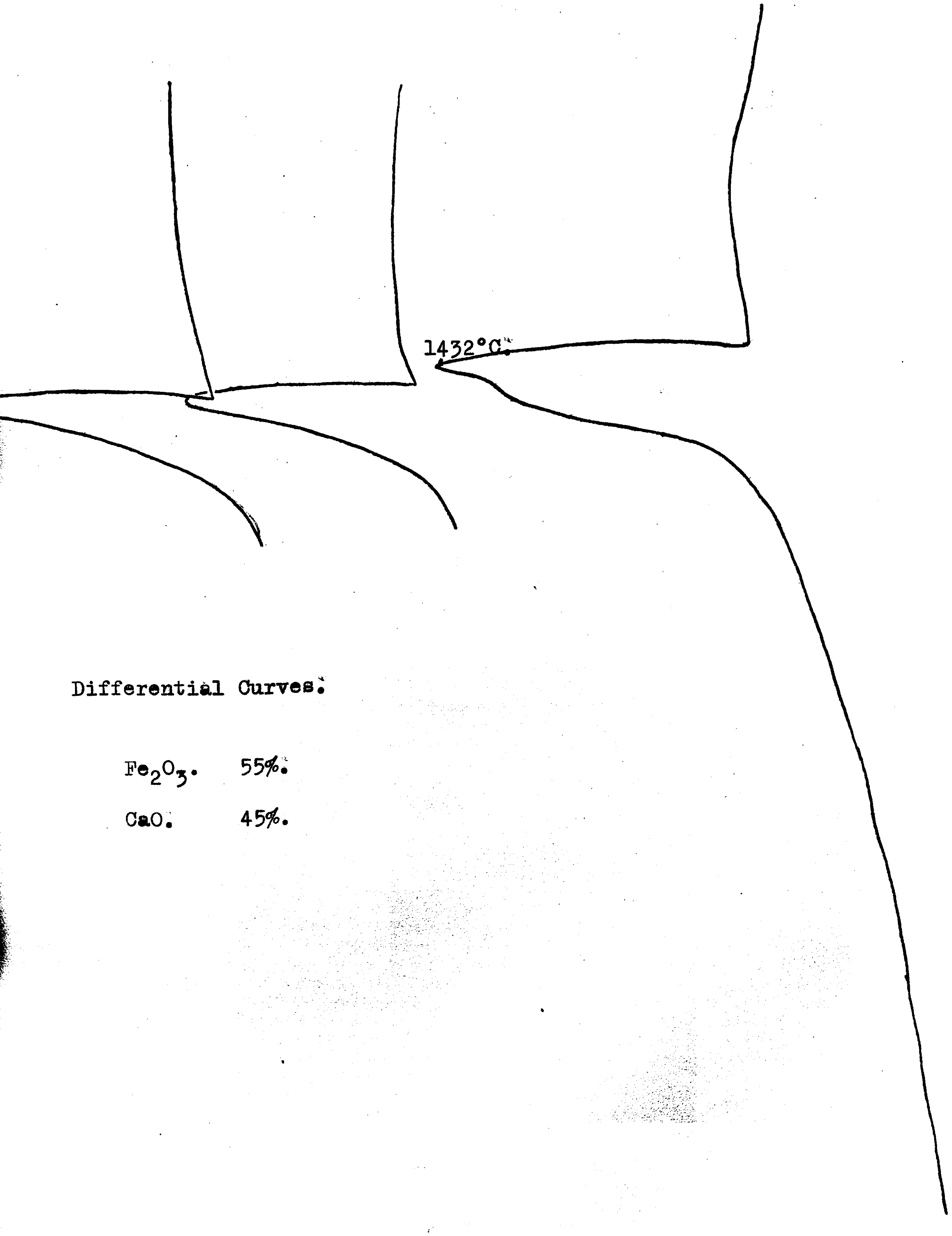
CaO. 41%.



Fe_2O_3. 55%.

CaO. 45%.

Cooling Curves.

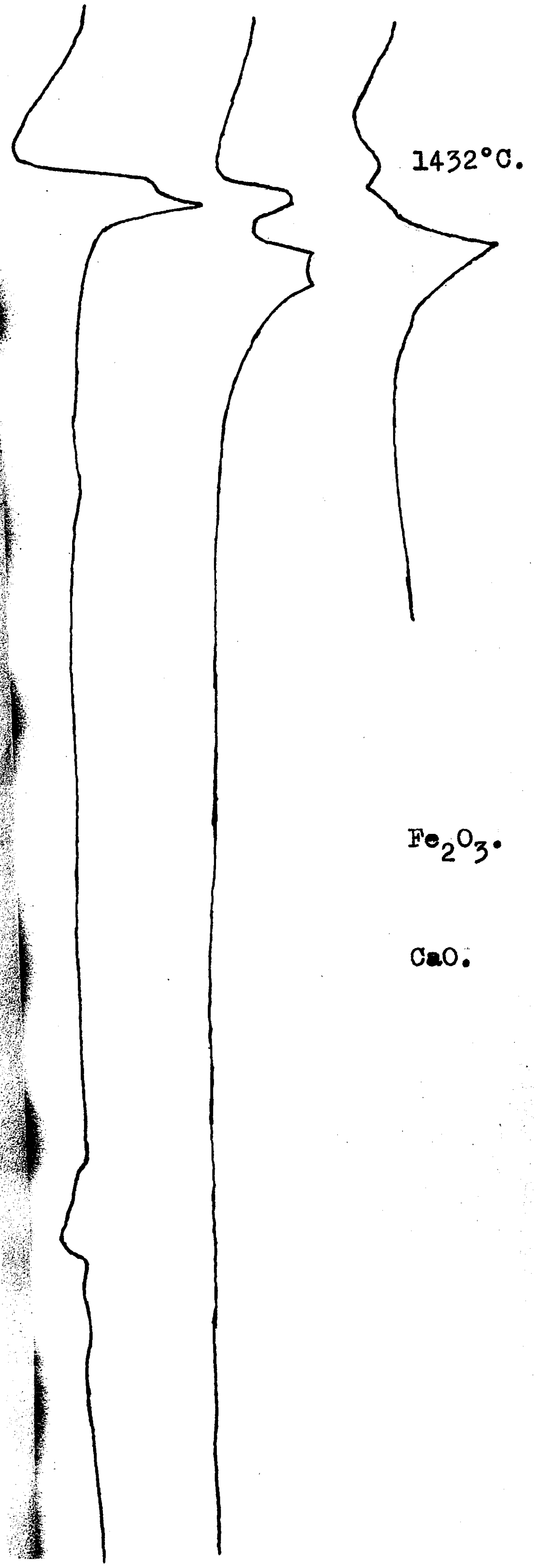


Differential Curves.

Fe_2O_3. 55%.

CaO. 45%.

Cooling Curves.



Inverse Rate Curves.

Fe_2O_3. 55%.

CaO. 45%.

THE EXAMINATION OF THE VARIOUS MIXTURES OF FERRIC OXIDE AND LIME.

Composition of Mixture. Fe_2O_3.	CaO.	Phases.	Colour.	Refractive Index.	Birefringence.	Pleochroism.	Extinction Angle.	Crystal Character.
100%.	0%.	Fe_2O_3.	Deep red.	2.95-3.1.	Strong.	Slight.	Straight.	Uniaxial Negative.
95%.	5%.	Fe_2O_3.	Deep red.	2.95-3.1.	Strong.	Slight.	Straight.	Uniaxial Negative.
		$CaO.Fe_2O_3$.	Red-brown.	2.5-2.6.	Strong.	Fair.	Straight.	Uniaxial.
92.5%.	7.5%.	Fe_2O_3.	Deep red.	2.95-3.1.	Strong.	Slight.	Straight.	Uniaxial.
		$CaO.Fe_2O_3$:	Red-brown.	2.5-2.6.	Strong.	Fair.	Straight.	Uniaxial.
90%.	10%.	Fe_2O_3.	Deep red.	2.95-3.1.	Strong.	Slight.	Straight.	Uniaxial.
		$CaO.Fe_2O_3$.	Red-brown.	2.5-2.6.	Strong.	Fair.	Straight.	Uniaxial.
88%.	12%.	Fe_2O_3.	Deep red.	2.95-3.1.	Strong.	Slight.	Straight.	Uniaxial.
		$CaO.Fe_2O_3$.	Red-brown.	2.5-2.6.	Strong.	Fair.	Straight.	Uniaxial.
85%.	15%.	Fe_2O_3.	Deep red.	2.95-3.1.	Strong.	Slight.	Straight.	Uniaxial.
		$CaO.Fe_2O_3$.	Red-brown.	2.5-2.6.	Strong.	Fair.	Straight.	Uniaxial.
82.5%.	17.5%.	Fe_2O_3:	Deep red.	2.95-3.1.	Strong.	Slight.	Straight.	Uniaxial.
		$CaO.Fe_2O_3$.	Red-brown.	2.5-2.6.	Strong.	Fair.	Straight.	Uniaxial.
80%.	20%.	Fe_2O_3.	Deep red.	2.95-3.1.	Strong.	Slight.	Straight.	Uniaxial.
		$CaO.Fe_2O_3$.	Red-brown.	2.5-2.6.	Strong.	Fair.	Straight.	Uniaxial.
77.5%	22.5%.	Fe_2O_3.	Deep red.	2.95-3.1.	Strong.	Slight.	Straight.	Uniaxial.
		$CaO.Fe_2O_3$.	Red-brown.	2.5-2.6.	Strong.	Fair.	Straight.	Uniaxial.

THE EXAMINATION OF THE VARIOUS MIXTURES OF FERRIC OXIDE AND LIME: contd.

Composition of Mixture.		Phases.	Colour.	Refractive Index.	Birefringence.	Pleochroism.	Extinction Angle.	Crystal Character.
Fe_2O_3.	CAO.							
75%.	25%.	Fe_2O_3. $CaO.Fe_2O_3$.	Deep red. Red-brown.	2.95-3.1. 2,5-2.6.	Strong. Strong.	Slight. Fair.	Straight. Straight.	Uniaxial. Uniaxial.
74.1%.	25.9%.	$CaO.Fe_2O_3$.	Red-brown.	2.5-2.6.	Strong.	Fair.	Straight.	Uniaxial.
72.5%.	27.5%.	$CaO.Fe_2O_3$. $2CaO.Fe_2O_3$.	Red-brown Light-brown.	2.5-2.6. 2.3-2.36.	Strong. Strong.	Fair. Strong.	Straight. Oblique.	Uniaxial. Biaxial.
70%.	30%.	$CaO.Fe_2O_3$. $2CaO.Fe_2O_3$.	Red-brown. Light-brown.	2.5-2.6. 2.3-2.36.	Strong. Strong.	Fair. Strong.	Straight. Oblique.	Uniaxial. Biaxial.
65%.	35%.	$CaO.Fe_2O_3$. $2CaO.Fe_2O_3$.	Red-brown. Light-brown.	2.5-2.6. 2.3-2.36.	Strong. Strong.	Fair. Strong.	Straight. Oblique.	Uniaxial. Biaxial.
59%.	41%.	$CaO.Fe_2O_3$. $2CaO.Fe_2O_3$.	Red-brown. Light-brown.	2.5-2.6. 2.3-2.36.	Strong. Strong.	Fair. Strong.	Straight. Oblique.	Uniaxial. Biaxial.
58.8%.	41.2%.	$2CaO.Fe_2O_3$.	Light-brown.	2.3-2.36.	Strong.	Strong.	Oblique.	Biaxial.
55.	45%.	$2CaO.Fe_2O_3$. CaO.	Light-brown. White.	2.3-2.36. 1.66 (approx.)	Strong. Nil.	Strong. Nil.	Obliwue. Isotropic.	Biaxial.

Since some of the ferric oxide dissociated before melting, it must be admitted that the melting point of the pure material is higher than the value given, but the difference is not very great, as the amount of ferrous iron found in the fused ferric oxide was very small. Knowing that Fe_2O_3 dissociates, the false phase change points occurring in ferric oxide rich mixtures are easily understood. This portion of the diagram therefore, unless a very high pressure of oxygen is kept on the mixtures while melting, is not a true binary system, but a section of a ternary system, and a ternary system in which pressure cannot be neglected, since one of the components is a gas. This danger was eliminated as far as possible by keeping a large oxygen pressure on the melting mixtures. 1¼ atmospheres was found to be sufficient to prevent the dissociation of mono- and di- calcium ferrites. Hence the portion of the diagram on tha lime side of mono-calcium ferrite is correct, although the solubility line for the true diagram on the ferric oxide of the mono-calcium ferrite is slightly steeper than represented.

The mono-calcium ferrite crystallised in plates, see appendix for photograph. Before melting under a pressure of 1¼ atmospheres of oxygen was adopted, it was found impossible to obtain this compound. It is stated in several chemical dictionaries that this compound can be prepared by a wet precipitation method; this claim could not be verified, and every time this method of preparation was tried, it was found that only ferric hydroxide had been obtained. An endeavour was made to first frit the materials together by keeping the temperature of the mixture at 1000°C. for a prolonged period before melting. This method did yield some of the compound but it was greatly contaminated with ferrous iron. The fritting of the materials was done in air. No difficulty whatever, was found in preparing the pure compound uncontaminated by ferrous iron, when melting under a pressure of 1¼ atmospheres was introduced.

The compound di-calcium ferrite is also very easy to prepare under the oxygen pressure, and it is extremely difficult to distinguish it from the mono-calcium ferrite in colour. The refractive indices of the two compounds, however, are different, as are the crystal characters, the dicalcium compound being bi-axial while the mono-calcium ferrite is uni-axial; it was possible to obtain photographs of the interference figures which are not, unfortunately, complete, but nevertheless serve to show the difference. Ferric oxide is itself uniaxial.

Only one mixture containing lime in excess of that required to form di-calcium ferrite, $2\ CaO.Fe_2O_3$, could be made due to limitations imposed by the lack of a refractory material capable of withstanding pressure at extremely high temperatures. This mixture was sufficient, nevertheless, to indicate that the solubility line follows such a gradient that no other compound is formed between lime and ferric oxide. In addition, the examination of the fused material showed free lime to be present.

Therefore in the equilibrium diagram of lime and ferric oxide only two compounds are formed. It is also to be noted that lime has a very stabilising effect on the dissociation of ferric oxide, as is shown that while the pressure developed by the pure oxide is of great magnitude at its melting point, yet a pressure of just over one atmosphere is sufficient to stop dissociation when lime is present. This fact has very great importance in actual slags , since it is to be believed that ferric oxide is the active oxidising agent of the carbon. So that while lime is added to a slag to raise the temperature of the slag and also to prevent its becoming too fluid and corrosive, it also has the effect of slowing down the rate of decarburisation of the liquid steel. It was also proved from dissociation data that Fe_3O_4 is soluble to some extent in Fe_2O_3, and this also has a very important bearing on actual slags because Fe_3O_4, by itself is a most infusible substance, and still it is, so to speak, the intermediary between FeO and Fe_2O_3, and as the ferric oxide is reduced to FeO in oxidising the carbon in the steel, it would seem necessary that Fe_3O_4 be formed in the cycle of oxidation.

The effect of alumina on a mixture of FeO, MnO, and SiO_2 was also examined. For this purpose, the eutectic composition of the ternary diagram was used and 5%, 10%, 7.5%, and 20%, of the weight of ternary eutectic mixture taken, was added of alumina. The 20% of alumina was added, although it never would occur in practice, because of the extraordinary infusibility of the 10% mixture. It was found that the mixture with 20% of alumina was easier to melt than the mixture with only 10%, thus indicating a ridge in the quaternary diagram and a possibility of the formation of a different phase. The ternary eutectic composition was FeO, 50%, MnO, 20%, and SiO_2, 30%. The results of the examination are listed below.

The ternary composition with 5% of alumina on examination, was composed of the following minerals, rhodonite, fayalite-tephroite, ferrous oxide and andalusite, an aluminium silicate.

The 7.5% of alumina mixture was composed on fusion of,the same minerals, as was the 10% alumina mixture. The 20% mixture however, was composed of knebelite, fayalite-tephroite, andalusite, and a manganspinel. The characteristics of these materials were noted and were used later in the examination of actual furnace slags.

Having determined the various major constituents occurring in slags, and their properties being known, Section B of the work was then commenced. This section deals with the examination of actual, typical furnace slags. The slags examined, however, were all obtained from normally run furnaces, which were producing plain carbon steels, as it was believed that special alloy steels would complicate,unduly,the minerals occurring in the slags.

Some basic slags, taken from a normally run furnace, which had been previously examined by another investigator, and thin geological sections of which had been prepared,were first examined. These slags had been annea~~l~~led. in air and sections of the annea~~l~~led portions had also been cut into thin sections. All examinations were, however, confined to the original slag. It was known that the series of slags covered the complete process of steel making, from "melting down" to tapping but beyond this the history of the slags, as regards additions,etc, was unknown. The thin sections were examined and compared with the examination by the powder method described in the last section; the annea~~l~~led thin sections were examined also but this practice was discontinued as these did not give information of any value, the slag having changed due to air oxidation.

THE EXAMINATION OF SLAG Number 1.

As stated, the slags were examined by the powder method already described, and number 1. gave the following results.

Colour of Phase.	Refractive Index.	Pleochroism.	Extinction Angle.	Birefringence.	Phase.
White.	1.64.	Nil.	Straight.	Low.	Apatite.
The surface of this mineral was pitted.					
White.	1.66-1.74.	Nil.	Isotropic.	Nil.	Andalusite.
Brown.	1.76.	Faint.	Oblique.	Very low.	Rhodonite.
Brown.	2.10.	Nil.	Isotropic.	Nil.	FeO-MnO.
Dull grey.	2.0	Nil.	Isotropic.	Nil.	Ferrous oxide.

There was also a trace of a red material of very high refractive index. The andalusite mentioned is an aluminium silicate.

The thin section of the slag, as taken from the furnace, showed only the phases which are noted above. Under even very high magnification, the thin section seemed to be composed of long needles of a white phase with a brown phase alongside. The red material of very high refractive index occurred in small isolated patches, of very small dimensions, as a boundary phase. The thin section examination bore out the powder examination, as regards data about the pleochroism, extinction angles and birefringence of the various phases, but only an approximate value of the refractive index of the different phases could be found as the section was embedded in canada balsam which has a very low refractive index itself, about 1.54.

The anneal~~l~~ed specimen showed scarcely anything under the microscope except ferrous oxide and opaque oxides of iron and manganese. So the examination of these sections was discontinued.

The material named andalusite is undoubtedly an aluminium silicate, but it appears to have a fair proportion of ferrous iron and magnesia in its composition, and this may account for its having a pseudo-cubic structure, instead of exhibiting polarisation colours, as it normally does.

From the minerals found it can be seen that the first materials to be oxidised in the process of steel making, are phosphorus, iron, silicon and manganese, chiefly. From the examination of the thin sections, which give a relative idea of the amounts of the different phases present, it can be argued that iron, and phosphorus are attacked first. The red material of very high refractive index is possibly a trace of one of the calcium ferrites. This would seem to bear out the assertion that the iron is first to oxidise, although it could have been due to iron oxide being present in the original materials charged into the furnace,; for as will be seen later, the calcium ferrites are supposed to be the most active oxidising agents in the basic open hearth slag, and it has been stated that the ferrites are the compounds, on whose oxidation and reduction, the mechanism of the process depends.

THE EXAMINATION OF SLAG Number 2.

This slag was examined in the same manner as slag number 1., but as in slag number 1., the heat treated thin section was of no value. The results of the powder examination are tabulated below.

Colour of Phase.	Refractive Index.	Pleochroism.	Extinction Angle.	Birefringence.	Phase.
White.	1.64.	Nil.	Straight.	Low. Uniaxial.	Apatite.
Dull grey.	2.00.	Nil,	Isotropic.	Nil.	Ferrous oxide.
White.	1.78-2.0.	Nil,	Straight.	Strong. Uniaxial.	Tephroite-Fayalite.
Brown.	1.76.	Faint.	Oblique.	Medium.	Rhodonite.
Brown-Light green.	2.12.	Nil.	Isotropic.	Nil.	FeO-MnO.
Red-Brown.	2.11.	Slight.	Straight.	Strong.	Mono-calcium ferrite

The thin section showed the same phases as those listed above. Since it is evident the powder method yields all the phases present in the slag, in future the thin section examination will not be referred to unless in exceptional circumstances, although it was carried out in every case. It is to be noted that a new phase has appeared in this slag as compared with the previous one; fayalite-tephroite. The aluminium silicate has apparently gone into solution in one of the other phases, since it could be found in neither the thin section nor by the powder method. In addition, the petrographic characteristics point to the red brown material being mono-calcium ferrite, while the refractive index seems to be nearer that of the di-calcium compound. This may be the phase which has dissolved the andalusite with a corresponding lowering in refractive index, since more petrographic characteristics point to the mono-calcium compound than they do to the di-calcium one. The amount of this phase has also definitely increased in proportion to the other constituents as can be seen in the examination of the thin section.

THE EXAMINATION OF SLAG Number 3.

This slag was examined in the usual manner and the various phases found in it are tabulated below.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Low. Uniaxial. Positive.	Straight.	Apatite.
White.	1.78-2.0.	Nil.	Strong. Uniaxial.	Straight.	Fayalite-Tephroite.
Brown.	1.76.	Faint.	Low.	Oblique.	Rhodonite.
Golden Brown.	1.78.	Nil.	Nil.	Isotropic.	Knebelite.
Dull grey.	2.00.	Nil.	Nil.	Isotropic.	Ferrous oxide.
Red.	2.5.	Slight.	Strong.	Straight.	Mono-calcium ferrite

From examination of the thin section, this slag seemed to be composed of knebelite, apatite, and ferrous oxide mainly. Thus it would seem that it takes some time for knebelite to form in the slag, and it is noteworthy that the refractive index of the mono-calcium ferrite has now returned to its proper value. Further, the FeO - MnO peritectic reaction material found in the first two slags has disappeared with the appearance of knebelite, and there can be no doubt that the solid solution of the two oxides has taken silica from somewhere to form the knebelite. Hence it would seem that at this stage of the process, the silicon in the metal had begun to oxidise fairly rapidly. Of course, much of the discussion is open to question since the full history of the slags is not known and there may have been additions made to the bath which have in some manner caused these changes to take place, but it is difficult to see how additions could cause the formation of knebelite, this being done by the addition of silica to the already existing material unless iron oxide addition had oxidised the silicon in the metal,

THE EXAMINATION OF SLAG Number 4.

This slag was examined also, by the powder method, and also in thin section, and the results are tabulated below.

Colour of Phases.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Low. Uniaxial. Positive.	Straight.	Apatite.
Brown.	1.76.	Faint.	Low. Biaxial.	Oblique.	Rhodonite.
Golden Brown.	1.78.	Nil.	Nil.	Isotropic.	Knebelite.
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown.	2.12.	Nil.	Nil.	Isotropic.	FeO-MnO.
Red.	2,5.	Slight.	Strong.	Straight.	Mono-calcium ferrite.
White.	1.66.	Nil.	Nil.	Isotropic.	Lime.

Apparently this slag has been drawn from the furnace just after the addition of lime, for free lime occurs as white transparent crystals. Their transparency must be due if not to actual fusion, then to a very near approach to fusion. It can be seen that evidently the presence of lime slows up the rate of working the furnace slag, for whereas, in the previous sample of slag, knebelite was present, the solid solution of FeO and MnO again appears, as such, in this slag. But since the phase, knebelite, is also present in this slag, it is also evident that lime cannot force this material to dissociate. Hence it would seem that the furnace gases have some place in the working of the slag for it is permissible to postulate that the FeO - MnO material is being caused by the oxidation caused by these gases, since the free lime is claiming the silica, or should be, from reasons of the heats of reactions of the various phases, which are to some extent, a measure of the affinity of one substance for another.

Unfortunately the heats of reaction of the compounds found in slags are not well known, nor is sufficient data extant to calculate them with any degree of accuracy, but it is known that calcium silicate will form quite easily at high temperatures. Thus although no calcium silicate is to be found , per se, in the slag, it is quite evident that it must be forming, for as was seen in the last slag, the silicon is being oxidised and yet the solid solution of FeO and MnO is appearing instead of the ternary solid solution, knebelite. Also, it is known that the addition of lime to a furnace makes the slag much more viscous and calcium silicates have very high melting points.

No free lime could be found in the thin section, but this is in all probability, due to the method of cutting. If water were used as a lubricant in grinding, then it would hydrate, although, slowly, the lime crystals. These crystals are also very brittle and so between grinding and hydration the lime would be entirely removed from the specimen. Some calcium silicates cannot be ground to thin section with water as a lubricant, because these become hydrated, and, like cements, form a supersaturated solution the excess material in the solution becoming deposited on the polishing pad and so removed from the section. When these are to be ground it is best to use paraffin oil as a lubricant.

THE EXAMINATION OF SLAG Number 5.

This slag was also examined and the results are tabulated below.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Low.	Straight.	Apatite.
Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
Brown.	1.76.	Faint.	Medium.	Oblique.	Rhodonite.
White.	1.78-2.0.	Nil.	Strong. Uniaxial.	Straight.	Fayalite-Tephroite.
Brown.	2.12.	Nil.	Nil.	Isotropic.	FeO-MnO.
Red.	2.45.	Slight.	Strong.	Straight.	Mono-calcium ferrite
White.	1.66	Nil.	Nil	Isotropic.	Lime.

Lime still exists, as such, in this slag, so apparently it does not all become absorbed by the slag at once. One noticeable feature of this slag is the relatively large amount of calcium ferrite that has appeared, as compared with that occurring in previous slags. The solid solution of FeO and MnO still co-exists with knebelite so it would appear that the lime is still reacting with the silica produced by oxidation. The amount of silica available must either be growing less or else the reactions are beginning to balance themselves for some of the lime is now reacting with the ferric oxide in the slag to form calcium ferrite as is shown by the increase of this substance. The calcium silicate does not appear as such, but there would seem to be a solution of this material in some other phase or phases, for there will be partition coefficients between the various phases although these will be very complicated. Not noted in the table because of the very small amount, there is also andalusite, or aluminium silicate occurring in this slag.

THE EXAMINATION OF SLAG Number 6.

This slag was also examined by the powder method and in addition by thin section examination both of the slag as received and also after the slag had been annealled.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.49.	Nil.	Very low.	Straight.	Tridymite.
White.	1.66+.	Nil.	Nil.	Isotropic.	Andalusite.
White.	1.64.	Nil.	Low. Uniaxial.	Straight.	Apatite.
Brown.	1.76.	Faint.	Medium.	Oblique.	Rhodonite.
White.	1.78-2.0.	Nil.	Strong. Uniaxial.	Straight.	Fayalite-Tephroite..
Red.	2.4.	Slight.	Strong.	Straight.	Mono-calcium ferrit
Brown	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.

In this slag the amount of knebelite and dull grey ferrous oxide is very small, while the relative amount of calcium ferrite has increased. The tridymite, while definitely present, was in such quantity as to preclude its belonging to the slag phases. It appears to be extraneous, being due, probably to one of the furnace bricks having fallen into the spot of sampling just before the drawing of the sample. The slag is now beginning to settle down to equilibrium as evidenced by the appearance of so many stable phases, the calcium ferrite being really the only one which can oxidise to any appreciable extent. The re-appearance of the phase, andalusite, argues to its having been in solution in some other phase.

THE EXAMINATION OF SLAG Number 7.

This slag appears to have been the finishing slag for the series, it was unlike the first ones, in that it is more or less coherent and is not full of gas holes, presenting the appearance of a piece of rock. The results of the examination are tabulated below.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.66.	Nil.	Nil.	Isotropic.	Andalusite.
Brown.	1.76.	Faint.	Medium.	Oblique.	Rhodonite.
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
Brown.	2.12.	Nil.	Nil.	Isotropic.	FeO - MnO.

There was also a little calcium ferrite in the slag.
The apatite has disappeared in this slag, and since it is a fairly stable substance, it has probably gone in solution in some other phase. The amount of knebelite present in the slag is very small and the calcium ferrite, in comparison, is of about equal quantity. This bears out the assertion of some investigators that the calcium ferrite is the active oxidising agent, for while there was carbon to oxidise, the amount of the calcium ferrite was kept down, but at the end when the carbon was less in

in quantity, the amount of the calcium ferrite increased. Andalusite occurs free, and the solid solution of FeO and MnO also occurs, as such. It would appear from an examination of the various slags that the andalusite had gone into solution in the ferrous oxide, since no andalusite is to be found in the slags in which ferrous oxide occurs free.

The components of the various slags have been tabulated, in order that the various differences in phases can be more easily seen ; the table is produced below.

Slag. No.1.	No.2.	No.3.	No.4.	No.5.	No.6	No.7.
Apatite.	Apatite.	Apatite.	Apatite.	Apatite.	Apatite.	Nil.
Andalusite.	Nil.	Nil.	Nil.	Andalusite.	Andalusite .	
Rhodonite.	Rhodonite.	Rhodonite.	Rhodonite.	Rhodonite,	Rhodonite.	
FeO - MnO.	FeO-MnO.	Nil.	FeO-MnO.	FeO-MnO.	Nil.	FeO-MnO.
Nil.	Calcium ferrite.	Calcium ferrite.	Calcium ferrite.	Calcium ferrite.	Calcium ferrite.	
Nil.	Ferrous oxide.	Ferrous oxide.	Ferrous oxide.	Nil.	Nil.	
Nil.	Fayalite-Tephroite.	Fayalite-Tephroite.	Fayalite-Tephroite.	Fayalite-Tephroite.	Fayalite-Tephroite.	
Nil.	Nil.	Knebelite.	Knebelite.	Knebelite.	Knebelite	
Nil.	Nil.	Nil.	Lime.	Lime.	Nil.	
Nil.	Nil.	Nil.	Nil.	Nil.	Tridymite.	Nil.

Slags 6 and 7 have been grouped together as regards the phases common to both, e.g. andalusite, rhodonite, and calcium ferrite, etc.

From the above table giving all the phases occurring in the slags taken at different periods of the steel making process, it can be seen that apatite is formed from the materials charged into the furnace and persists right to the finishing slag. It could not be found in the finishing slag but could have gone into solution in some other phase. This formation and persistence of apatite is to be expected from the fact that phosphorus must be aboutthe first component of the charge to be oxidised and removed from

from the molten metal and further, it must be kept in the slag in a stable condition, so that it will not be reduced and return into the metal, thus contaminating it. Andalusite, aluminium silicate, only occurs as such in the slags which do not contain any free ferrous oxide. Andalusite is very stable and is not easily reduced to aluminium and silicon so it must, from the data appearing, dissolve in the ferrous oxide, thus reducing the effectiveness of this compound if it be the active oxidising agent in the slag, which is questionable. Once manganous oxide and silica have reacted to form rhodonite, this material is stable at least as regards the oxidation of the carbon in the steel. Fayalite and tephroite are also very stable as regards the oxidation of the carbon in the steel, although fayalite may dissociate at elevated temperatures and thus be of some minor importance in the decarburisation process. Thus these materials, ordinarily, when they have once been formed, simply act as diluting materials in the slag and are of minor importance in the study of the mechanism of oxidation, but they may have a rather greater importance where the cleanliness of the steel is concerned. Their specific gravity is less than that of the steel, so if they do occur as inclusions, there are two ways in which their presence may be explained; first, they may have been washed in due to swirling during tapping and secondly, they may occur as reaction products of some other inclusion with the steel itself, thus being formed while the steel is cooling and solidifying. The material which would appear to be most active in the production of this latter type of inclusion would be ferrous oxide, this being known to occur in fairly large quantities in the finishing slag, and also to be to some small extent, dissolved in the steel itself.

However, ferrous oxide seems to occur, in the first slag s examined, at least, in the free state, only in the slags which were drawn earlier on in the process, and towards the end it appears associated with manganous oxide, but this would not prevent its reduction by the manganese and silicon dissolved in the steel itself, so it is still feasible that it could give rise to inclusions.

It is therefore possible that ferrous oxide could give rise to inclusions of the second type, the type produced in the steel during solidification, but as regards oxidation of the carbon in the molten steel, it is doubtful if the ferrous oxide is of more than minor importance. In the first place, the heat of formation of ferrous oxide is fairly large, and in the second , ferrous oxide would rather oxidise further to ferric oxide in the oxidising atmosphere which exists in the furnace, rather than be reduced to iron and oxygen. The ease of further oxidation of ferrous oxide was well illustrated in the preparation of ferric oxide from it, when the temperature of the material was raised by about 200°C. due to the oxidation. Thus it could be that the ferrous oxide acts as an oxygen carrier for the ferric oxide or for the calcium ferrites. These compounds have a very high vapour pressure of oxygen at the temperature of the molten slag and it is very probable that this is the oxygen that performs the oxidation of the carbon, silicon and manganese, in the molten metal. So the process might be imagined as consisting of the oxidation of ferrous oxide to ferric oxide with the formation of calcium ferrites and these compounds then react with the molten metal oxidising the various constituents in it. This view is borne out by the increase of calcium ferrite in the slag as the amount of oxidisable material in the molten steel decreases. Knebelite does not seem to be an oxidising agent of great importance, since it itself seems to be more of a reaction product, occurring only after the slag has commenced to oxidise the molten metal, and not in the first two slags.

So it would seem from the examination of this slag, that

calcium

calcium ferrites are the chief oxidising media in the process of carbon elimination in steel making, the other constituents of the slag being more or less the products of reaction which have assumed a more or less stable form and are not of more than secondary importance in the process, while the more active oxidising ferrites are present. The ferrite exists only in traces when the slag is first formed but the amount increases as the process proceeds, but not th the extent that might be imagined since it is postulated that it is the most active oxidiser, but this relatively small increase till the process is nearly finished, is in itself a proof that the material must be performing some operation since it cannot grow in amount as it would if it were more or less inert. While many side reactions are taking place with the ferrous oxide, e.g. the formation of fayalite, and a solid solution with manganous oxide, nevertheless this material seems to be the oxygen carrier for the calcium ferrites and if this assumption is correct, then the statement that 15% of the oxidation in the basic steel making process is caused by the furnace gases is very probably correct.

From the point of view of inclusions in the finished steel, it is very important therefore, that the calcium ferrites in the slag should be in as small quantity as possible at tapping. Otherwise they will be liable to react with the silicon and manganese in the finished steel and produce inclusions of manganese and silica. Relatively speaking the only danger from the other components of the slag examined above, is that they might be mechanically entrapped in the solidifying steel, although they too, would in a lesser degree react with the steel itself producing inclusions, since they are not by any means inert in carbon elimination, but only relatively so when compared with ferrites. Consequently, the chief components of inclusions in the steel made under the above slag would consist of oxides of iron, manganese and silicon, .

THE EXAMINATION OF SLAG SERIES Number 2.

This series of slags were also taken from a normally run basic steel furnace; and while the complete history of the slag was known, no attempt was yet made to correlate changes in the slag with the different additions made from time to time. The slag was examined by the powder method, thin sections were also cut, and the " Ultro-pak" illuminator was employed to examine pieces which had been polished in the usual metallurgical manner. A diagram of the illuminator is given on page 4 . The instrument is so constructed as to ensure that no light is seen in the ocular of the microscope which has not been reflected from the surface of the specimen being examined. Thus minerals are made to exhibit their natural colours, and a fair degree of differentiation between them can in this way be effected.

The preparation of thin sections proved no small difficulty. Firstly, the slags are extremely hard, but at the same time extremely brittle. Then it was found that one particular component of the slag is liable to crystallise on the outside of the massive specimen, leaving the others to crystallise in the centre of the specimen; so great care had to be taken to ensure including all the possible components of the slag in the piece selected for cutting to thin section. The centre of the slag is usually of a porous nature and full of minute pinholes and these tend to make the slag still more friable. The following technique was adopted after experiment, in the cutting of thin sections.

Having chosen a sample of the slag likely to contain all the components, usually a piece extending from within a quarter inch of the surface to the centre of the sample, this was roughly ground on a wheel to square shape. The sample was ground so as to have two faces about ½ inch long and about the same broad, while the section was as thin as possible. The two large faces should be as near parallel as possible. Then one nearly flat face is ground to optical flatness on a machined steel surface

surface, using, first, coarse carborundum powder as a grinding medium with water as a lubricant. If calcium ferrites or silicates are expected to occur in the section then paraffin oil is used as the lubricant. When the flat face is grinding uniformly on the flat steel face, the grinding medium is changed to F F F grade carborundum powder and grinding is continued on this medium till deep scratches and as far as possible, pinholes are eliminated. The face is then polished on a selvyt pad with putty powder, (finely divided stannic oxide,) using 25% glycerine and 75% oil as a lubricant. Polishing is continued till the face reflects light well. Here, some authorities recommend that the face be cemented to a glass plate and fixed with shellac cement, and the section be removed from the glass plate by means of a block of plaster of paris and then cleaned of shellac before finally cementing to the microscope slide with canada balsam. This was not found to be necessary, however, if proper care were observed in fixing the section to the microscope slide with canada balsam alone and then continuing the grinding. The balsam must be very carefully "cooked" so that while setting hard, it does not set brittle, nor yet is it under "cooked". In the one case, the brittle balsam tears the section by breaking into small hard pieces and in the other, the plastic balsam allows the section to be pulled to bits by the force of grinding. "Cooked" to the proper degree, the balsam is sufficiently hard to allow of grinding, and yet is sufficiently elastic not to chip. While the balsam is being "cooked" it is best to have the specimen immersed in it, for the balsam percolates into the pores and helps to consolidate the rather friable material. While the balsam is cooling, the specimen should be pressed into it uniformly, and when the slide is cool the section is again ground with the F F F grade of carborundum powder. Great care is essential to ensure that the two faces of the specimen are parallel for if not, trouble is experienced in finishing the grinding when the section is very thin. Till the section is translucent the parallelism of the faces should be be checked with calipers; when the section becomes translucent, the microscope can be used to ensure uniformity of grinding. For finishing off to the required degree of thinness, the section is ground on a glass plate with putty powder with the glycerine-oil lubricant. When sufficiently thin, the section is carefully cleaned and a spot of canada balsam is spread uniformly over the surface and a cover glass is slid on, care being taken to avoid air bubbles, and also to avoid undue pressure on the specimen for it is very easily broken up and disintegrated. The section should be allowed to sit until the balsam has hardened before an examination is made on the specimen.

For examination in dark field light by the "Ultro-pak" illuminator, one face only of the slag specimen need be polished. This face is polished in the same manner as for thin sections, i.e., grinding with coarse carborundum powder, fine carborundum powder, and finally with putty powder on a selvyt pad.

THE EXAMINATION OF SLAG Number 1. SERIES 2.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	High.	Nil.	Weak.	Straight.	Apatite.
White.	Very high.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown.	High.	Slight.	Medium.	Oblique.	Rhodonite.
Brown.	Very high.	Nil.	Nil.	Isotropic.	Knebelite.
Red.	Very high.	Slight.	Very strong.	Straight.	Calcium ferrite.

The brown, isotropic phase could easily have been called ferrous oxide, for it is nearly opaque. The apatite appeared with a pitted surface, which is characteristic of the mineral.

These minerals listed above, are all the phases which could be differentiated in the thin geological section of slag number 1. The crystals in the section were extremely small and a magnification of about 400 had to be used in the examination. The normal manner of drawing the samples was to take a spoon full

full of the liquid slag from the desired spot in the furnace, and then to cool this by pouring on the floor plates. This manner of drawing did not tend to give large crystals in the cold sample, so a sample of the slag had been allowed to cool in the spoon in which it had been drawn from the furnace, but when a section of this slowly cooled sample was prepared,the size of the crystals had not increased sufficiently to warrant the extra slow cooling, so latterly the examination was confined to one sample of the slag which had been cut to thin section, and the slowly cooled sample was neglected.

Having examined the sample of slag in thin section, the material was then powdered and examined by the powder method. The technique was the same as previously described, and the following phases were found; Apatite, Andalusite, Fayalite-Tephroite, Knebelite and a very little ferric oxide. The characteristics of these phases have been given previously. It is noteworthy that what was supposed to be calcium ferrite in thin section turns out to be ferric oxide when examined by the powder method.

The polished sample was examined by the "Ultro-pak" illuminator and the phases were seen as follows;

Apatite.	The crystals appear brown in colour and seem to be speckled here and there with very bright white spots.
Fayalite-Tehproite.	The crystals appear very bright, and would seem to be lighted up internally, being dazzlingly white.
Rhodonite.	The crystals of this material appear brown but there is no polish on them, they appear with a matt surface.
Knebelite.	This material appears as a dark brown phase, darker than rhodonite but with a matt surface resembling that of the rhodonite.
Ferric Oxide.	The crystals of this material appear a brilliant red colour.

THE EXAMINATION OF SLAG Number 2. SERIES 2.

This slag was first examined by thin section and the results are tabulated below.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	High.	Nil.	Weak.	Straight.	Apatite.
White.	Medium.	Nil.	Nil.	Isotropic.	Collophanite.
Brown.	Very high.	Slight.	Medium.	Oblique.	Rhodonite.
Brown. (Light in colour.)	Very high.	Nil.	Nil.	Isotropic.	Knebelite.
Brown.	Very high.	Nil..	Very weak.	Straight.	Manganspinel.
White.	Very high.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Red.	Very high.	Nil.	Strong.	Straight.	Ferric oxide.

Again the apatite pesented a pitted surface; collophanite appears in somewhat distorted cubic crystals, and the manganspinel presents a somewhat fuzzy appearance.

Examination of this slag by the powder method revealed the following phases to be present; Apatite, Fayalite-Tephroite, Knebelite, Collophanite, Rhodonite, Manganspinel and a trace of ferric oxide.

The appearance of these phases under the microscope fitted with the "Ultro-pak" illuminator is as follows;

Apatite.	The crystals are brown in colour, speckled with white spots here and there and show a pitted surface.
Ferric oxide.	The crystals of this material are of a deep brilliant red colour.
Fayalite-Tehproite.	The crystals of this phase were dazzlingly white in appearance and gave the impression of being internally lighted.
Rhodonite.	This phase appeared brown but does not reflect the light very well.
Knebelite.	This phase is of a dark brown colour and is an even worse light reflector than rhodonite.
Collophanite.	The crystals of collophanite are white in appearance

appearance but are not glassy like the fayalite, presenting a matt surface.

Manganspinel. This phase is light brown in colour, appearing lighter than rhodonite, but is still not a good reflector of light.

THE EXAMINATION OF SLAG Number 3. SERIES 2.

The thin section of this slag showed the phases listed below.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	High.	Nil.	Weak.	Straight.	Apatite.
White.	Medium.	Nil.	Nil.	Isotropic.	Collophanite.
Brown.	Very high.	Slight.	Medium.	Oblique.	Rhodonite.
White.	Very high.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown.	Very high	Nil.	Very weak.	Straight.	Manganspinel.
Light brown.	Very high.	Nil.	Nil.	Isotropic.	Knebelite.
Red brown.	Extremely high.	Slight.	Medium.	Straight.	Mono-calcium ferrite

The basal sections of the apatite had a roughly hexagonal shape and were isotropic. The collophanite occurred as rough cubes, and again, the manganspinel presented a somewhat fuzzy appearance.

The slag was powdered and examined by the powder method and the following phases were identified; Apatite, Fayalite-Tephroite, Knebelite, Mono-calcium ferrite, Collophanite, Rhodonite, and Mnaganspinel.

With the dark field reflected light, the phases presented the appearances listed.

Fayalite-Tephroite. The crystals present an exceedingly dazzling appearance with a glassy look.

Mono-calcium ferrite. The crystals are small and red in appearance, but lack the red fire of the ferric oxide crystals.

Manganspinel.	The crystals of this material are light brown in appearance, but bad light light reflectors.
Rhodonite.	The crystals are dark brown in appearance, speckled with pin point patches of light.
Apatite.	In this slag the grey brown tinge of the apatite was lighter than in the last, but the white streaks were present as before.
Collophanite.	The crystals are white with a matt surface.
Knebelite.	The crystals are very dark, nearly black in appearance and are very poor light reflectors.

THE EXAMINATION OF SLAG Number 4. SERIES 2.

This slag was also examined in thin section and the results are tabulated below.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	High.	Nil.	Weak.	Straight.	Apatite.
White-brown.	Medium,	Nil.	Nil.	Isotropic.	Collophanite.
Red-brown.	Extremely high.	Fair.	Strong.	Straight.	Mono- calcium ferrite.
Light brown.	Very high.	Nil.	Medium.	Straight.	Manganspinel.
Brown.	Very high.	Nil.	Nil.	Isotropic.	Knebelite.
Brown.	High.	Slight.	Medium.	Oblique.	Rhodonite.
White.	Very high.	Nil.	Strong.	Straight.	Fayalite-Tephroite.

The slag, on examination after grinding to a powder, showed the following phases when examined by the powder method; Apatite, Fayalite-Tephroite, Knebelite, Calcium ferrite, Collophanite, and Rhodonite.

These phases presented the following characteristics when examined in the dark field reflected light microscope.

Fayalite-Tephroite.	The crystals were very bright in appearance, with a glassy look.
Collophanite.	The crystals appear white with a matt surface.
Manganspinel.	This material appears of a light brown colour but with a matt surface and the reflecting of light is stronger than with rhodonite or knebelite.
Mono-calcium ferrite.	These crystals are of a red brown colour and are not so intensely red as the crystals of ferric oxide.
Rhodonite.	The crystals are dark brown and do not reflect the light very well.
Apatite.	The crystals appear of a brown-white colour with white streaks through them.

THE EXAMINATION OF SLAG Number 5. SERIES 2.

The thin section yielded the characteristics of the listed phases on examination.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	High.	Nil.	Weak.	Straight.	Apatite.
White.	Medium.	Nil.	Nil.	Isotropic.	Collophanite.
White	Very high.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown.	Very high.	Nil.	Nil.	Isotropic.	Knebelite.
Red brown.	Extremely high.	Faint.	Strong.	Straight.	Mono-calcium ferrite.
Brown.	High.	Slight.	Medium.	Oblique.	Rhodonite.
Light brown.	Very high.	Nil.	Medium.	Straight.	Manganspinel.

The slag, examined by the powder method, showed the presence of the following phases; Apatite, Fayalite-Tephroite, Mono-calcium ferrite, Rhodonite, Manganspinel and Collophanite.

When examined in the dark field reflected light microscope, the phases exhibited the following characteristics;

Apatite.	The crystals exhibit a brownish white colour with white striae running through them.
Fayalite-Tephroite.	The crystals of this phase are very bright and glassy in appearance.
Knebelite.	The knebelite in this slag is of a golden brown appearance and much better as a light reflector than the material in the last slag.
Mono-calcium ferrite.	These crystals are very red in colour but are not brilliant.
Rhodonite.	The crystals of rhodonite are very dark brown, resembling a piece of very dark amber.
Mnaganspinel.	The crystals are light brown, but with a dull matt surface.

THE EXAMINATION OF SLAG Number 6. SERIES 2.

The slag on cutting and examining a thin section, showed the following phases to be present.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	High.	Nil.	Weak.	Straight.	Apatite.
White.	Medium.	Nil.	Isotropic.	Isotropic.	Collophanit
Brown. (Golden)	Very high.	Nil.	Isotropic.	Isotropic.	Knebelite.
White.	Very high.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Light Brown.	High.	Faint.	Medium.	Oblique.	Rhodonite.
Light Brown.	Very high.	Nil.	Medium.	Straight.	Manganspinel.

The phase called knebelite could be the solid solution of ferrous and manganous oxides, for there is no definite degree of differentiation obtainable in thin section examination. The rhodonite appeared in abundance.

The slag when examined by the powder method, proved to contain the following phases; Apatite, Fayalite-Tephroite, very little Knebelite, Rhodonite in abundance, Manganspinel and a trace of mono-calcium ferrite.

These constituents, in dark field illumination by reflected light, exhibited the following appearances;
Rhodonite was of a deeper colour than in the last slag, while knebelite had become more golden in tinge, indicating a probable loss of iron in its composition, and mono-calcium ferrite seemed to have become rather scarcer. The other constituents showed the same characteristics as those listed in the examination of the last slag.

The various components of all this series of slags are tabulated on page 97 . The components have been found by either or both methods of examination, i.e. by either thin section examination or by the powder method.

The table shows that the phases do not change greatly from one period of the steel making process to another, as can be seen for instance, from the persistence of apatite and rhodonite in the slag. However, even although the phases persist in the slag, nevertheless, there are changes in them. Apatite, at first, is white in thin section, although it shows a brown tinge in dark field examination, then later, the phase becomes darker until the period of the boil is reached. After this is past, the colour of the apatite again gradually becomes whiter. This indicates that some dark material is dissolving in the apatite, probably one of the metallic oxides,, and that this dissolved material is eliminated or changed into some other phase as the carbon in the steel is reduced.

As in the first series of slags, the fayalite-tephroite phase also persists throughout the slag from the beginning of the process to the end. This is to be expected, however, for these materials are stable and will not easily oxidise to higher oxides of the iron and manganese.

TABLE SHOWING THE PHASES IN THE VARIOUS SLAGS EXAMINED IN SERIES 2.

SLAG No.1.	SLAG No.2.	SLAG No.3.	SLAG No.4.	SLAG No.5.	SLAG No.6.
Apatite.	Apatite.	Apatite.	Apatite.	Apatite.	Apatite.
Fayalite-Tephroite.	Fayalite-Tephroite.	Fayalite-Tehproite.	Fayalite-Tephroite.	Fayalite-Tephroite.	Fayalite-Tephroite.
Knebelite.	Knebelite.	Knebelite.	Knebelite.	Knebelite.	Knebelite.
Ferric oxide.	Ferric oxide.	Nil.	Nil.	Nil.	Nil.
Nil.	Nil.	Mono-calcium ferrite.	Mono-calcium-ferrite.	Mono-calcium ferrite.	Mono-calcium ferrite.
Nil.	Collophanite.	Collophanite.	Collophanite.	Collophanite.	Collophanite.
Rhodonite.	Rhodonite.	Rhodonite.	Rhodonite.	Rhodonite.	Rhodonite.
Nil.	Manganspinel.	Manganspinel.	Manganspinel.	Manganspinel.	Manganspinel.

The relative amount of the fayalite-tephroite phase does not seem to change at different periods of the process, however.

Rhodonite occurs in every slag examined, but varies greatly in amount. Thus, at the beginning, its relative proportion, as seen in the thin section is fairly large, but it decreases in relative quantity till just after the boil when the proportion again rises till it is again fairly large in slag number 6. Knebelite is practically the same as rhodonite as regards quantity and follows practically the same gradation throughout the process, but as the boil is approached, the colour of the knebelite becomes darker and darker, thereby indicating that ferrous oxide is increasing in amount in the solid solution; but after the boil the knebelite again loses the ferrous oxide as is shown by the progressive lightening in colour of the knebelite.

The calcium ferrite behaves in rather a curious way; at first the slags contain no calcium ferrite, but only ferric oxide. Then in slag number three, calcium ferrite appears, but not in large quantity. This quantity of ferrite increases but little and in slag number five, just after the boil, the amount of ferrite is very small, but it increases in quantity in the finishing slag.

Collophanite and manganspinel are present, at most, in small quantities and do not appear to have any major bearing on the working of the slag as regards the decarburisation of the molten metal. It is interesting to note, that compared with slag series number 1., the alumina has appropriated some of the manganous oxide to form manganspinel, whereas in the first series, it formed andalusite.

This slag would seem to have been produced in a furnace, in which the charge was high in manganese. This is shown by the alumina being able to obtain some of the manganous oxide to form manganspinel whereas in the first series it had to form andalusite with the silica in the slags. There seems to have been a deficiency of either ferric oxide or lime in this slag series; for free ferric oxide appears in the first slags, and then there is the

the banking up of ferrous iron in the knebelite just before the boil. This ferrous oxide could have been more usefully employed in oxidising to ferric oxide with the formation of calcium ferrite, than it would be acting as an oxidising agent by itself. This appears to have been the case, for the ferrous oxide is worked out of the knebelite as the boil proceeds and the only place it could go without the formation of another phase or phases, would be to the metal as iron and its oxygen would oxidise the carbon. If the ferric iron were deficient then gas oxidation in the furnace would not be functioning properly, and this would not seem to be feasible; but if lime were lacking in the slag, this would explain the formation of ferric oxide in the earlier slag samples, and since the ferric oxide has a very high vapour pressure of oxygen, it could not exist by itself, but would dissociate to ferrous oxide. If sufficient lime had been present, then, as was seen in the lime - ferric oxide diagram, the vapour pressure of the oxygen would not be so much, so that less ferrous iron would have formed and the slag would ~~have~~ probably have worked more efficiently. So theoretically, this slag was probably not quite satisfactory in the earlier stages of the process and this assertion seems to be borne out by examination of pieces of the slag. Slag number 1. is clinker like in appearance, full of blow-holes and shots of metal, and has a rather low specific gravity. Slag number 2. has lost all metallic lustre, and blow-holes are scarce while the density of the slag has risen. Slag number 3. looks like a piece of brown flint, but breaks with a conchoidal fracture and is free of blow holes. Slag number 4. presents the same appearance of flint and also breaks with a conchoidal fracture and the density has still further increased. Slag number 5. is black in colour and is very dense breaking with a conchoidal fracture, Slag number 6. is grey in colour and breaks in straight planes and not with a curved fracture, and is much more coherent than any of the others.

These data seem to show that the slag, generally, was of a somewhat pasty consistency, which would not allow of proper oxidation

oxidation by the furnace gases. This occassionally does happen when the gases seem to glide off the surface of the bath without heating the slag properly, and also without oxidising properly. As postulated previously, slags high in manganous oxide should be pasty, so in addition, it would seem that slags high in manganous oxide are also bad heat conductors. Unfortunately no analysis was made on the slags, so that the percentage of manganese cannot be stated.

From the discussion it would seem that the calcium ferrites must be the active oxidising agents in the slags, as was postulated in the case of the first series of slags.

THE EXAMINATION OF SLAG SERIES Number 3.

Having examined two series of slags taken over the complete process of steel making, and tabulated the changes which occur in them at different periods in the process; the next question to be decided was, whether were the slags homogeneous throughout the bath at any particular period of time, or was the slag heterogeneous, varying in composition from place to place at the same instant. This series of slags were drawn to find the proper place to obtain representative samples of the complete slag covering for any particular period of the process. To ensure that the slag should have a fair chance of being homogeneous throughout, the finishing slag was first examined, and samples were drawn as detailed below. The details of the furnace charge were as follow; the furnace was being run in a normal basic manner; and samples were drawn one hour before tapping; the carbon in the steel at the time of drawing the samples was 0.18% -0.12%; and the final carbon content for the steel was to be 0.08%, so that the carbon in the steel was being eliminated at the normal rate of 0.02% per ten minutes, approximately. The slag was in a fluid condition when the samples were drawn, and lime had been the last addition made to the furnace, but the lime had been so long in the furnace that it was all incorporated in the slag. The gas was passing in the furnace from door 5. towards door 1.. Doors 1 and five are on the front of the furnace and doors 6 and 7 are on the back of the furnace with door 1. nearly opposite door 7 and door 5 nearly opposite door 6. The results of the examination of the slags are tabulated below.

All the slags in this series were examined by the powder method, since it was found in the last series that the thin sections do not offer any advantage, beyond being able to be preserved as a permanent record, to which reference can be made.

THE EXAMINATION OF THE SLAG FROM DOOR 1.

SERIES 3.

The slag recorded underneath was drawn from the surface of the slag bath, and the results represent the composition of the slag to a maximum depth of four inches.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
Dark brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
White.	1.66.	Nil.	Nil.	Isotropic.	Collophanite.
White.	1.78-2.0.	Nil.	Nil.	Isotropic.	
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Golden brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
Red brown.	2.12.	Slight.	Medium.	Straight.	Mono-calcium ferrite.

The apatite is present in small quantity, and the white, isotropic phase which has not been named was present in the form of square crystals.

As the above slag was drawn from the surface of the slag, another was drawn from the same spot, but was drawn from the slag-metal interface. The results of examination of this slag are recorded below.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
White.	1.66.	Nil.	Nil.	Isotropic.	Collophanite.
Dark brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
White.	1.78-2.0.	Nil.	Nil.	Isotropic.	
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tehproite.
Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
Red brown.	2.12.	Slight.	Medium.	Straight.	Mono-calcium ferrite.

The slag from door 1. being examined the slag sample which was drawn from door 2. at the same time to within two minutes, was also examined, and in this case too, samples of the slag at the surface and a sample from the slag-metal interface were compared, both being drawn at the same time.

THE EXAMINATION OF THE SLAG FROM DOOR 2.

SERIES 3.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
Dark brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
White.	1.78-2.0.	Nil.	Nil.	Isotropic.	
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown (Golden)	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
Red brown.	2.12.	Slight.	Medium.	Straight.	Mono-calcium ferrite.

The slag whose components are listed above was drawn from the surface of the bath, but the sample, drawn simultaneously, from the slag-metal interface, contained the same phases and hence there is no difference in the phases to be found in the slag at this part of the furnace.

Slags were drawn at the same time as those from door 1., from the middle door of the furnace, door 3. Deep samples and shallow samples were drawn in the usual manner. The phases found were identified and are listed below.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
Brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
White.	1.78-2.0.	Nil.	Nil.	Isotropic.	
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
Red brown.	2.12.	Slight.	Medium.	Straight.	Mono-calcium ferrite.

Since door 7. is nearly opposite door 1. therefore the slag in the sample from door 7. should, even admitting that the slag as a whole is heterogeneous, be practically the same as that from door 1. and if this is not so, then it would appear that the slag is very heterogeneous indeed, since it would then be varying in a distance of about three feet. Accordingly, the results of the examination of the slag from door 7. are recorded here for comparison. The results recorded are taken from the surface of the slag covering.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
White.	1.66.	Nil.	Nil.	Isotropic.	Collophanite.
Dark brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
White.	1.78-2.0.	Nil.	Nil.	Isotropic.	
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
Red brown.	2.12.	Slight.	Medium.	Straight.	Mono-calcium ferrite.

A slag drawn from the slag-metal interface in door 7. was also examined and the results were compared with those of the slag drawn from the surface, and they were found to agree in every respect, so they have not been listed here.

It is evident from the results set out above that the slag does not vary in composition, at least, as far as can be seen from examination of the cooled slags, at the gas exit end of the furnace; neither does the slag appear to be different on the surface of the bath from that in contact with the metal at least at the gas exit end of the bath.

The unnamed phase listed above is probably an aluminium silicate, but for the purpose at present under consideration it is not essential to know what the compound actually is.

In the slag from door 3. there is also an extremely small amount of the solid solution of ferrous oxide and manganous oxide. The slag drawn from the slag-metal interface also showed the same phases. So the vertical section of this slag from the centre of the furnace is also homogeneous as regards visible phases.

At the same time as samples were drawn from door 2. they were also drawn from door 4. The samples were as usual, drawn from the slag-metal interface as well as from the surface of the bath. The results are listed below.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
Brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
White.	1.78-2.0.	Nil.	Nil.	Isotropic.	
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
Red brown.	2.12.	Slight.	Medium.	Straight.	Mono-calcium ferrit

The slag drawn from the slag-metal interface, at the same time, was composed of the same phases.

At the same time as samples were drawn from doors 1. and 3., they were also drawn from doors 5 and 7. The usual shallow and deep samples were drawn and the phases were examined and identified.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
Brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
White.	1.78-2.0.	Nil.	Nil.	Isotropic.	
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
Red brown.	2.12.	Slight.	Medium.	Straight.	Mono-calcium ferrit

All the slags drawn from doors 5 and 7. exhibited exactly the same phases whether drawn from the slag-metal interface or from the surface of the bath.

A very large quantity of slag had been withdrawn from door 4. and this had been allowed to cool very slowly and then it was examined in the usual powder method. It exhibited the same phases as those slags that had been cooled quickly, the only difference being, that the slowly cooled slags were rather easier to examine, since the crystals had developed to a larger extent, and were more easily seen than the very small crystals found in the quickly cooled slags.

From the results given above it can be seen that, for finishing slags in the basic open hearth steel process, if a sample be drawn from any part of the slag covering, that sample will normally contain, on cooling, representatives of all the phases that could occur in the entire slag covering if it were solidified. The only phase that does not occur in all the slag samples is collophanite, As has been postulated in previous slag examinations, this material has not any great importance on the working of the process, so its presence in the slags next the gas outlet ports can be neglected. Although all the phases given exist throughout the slag covering, this does not mean, however, that the degree of oxidation of the oxidisable phases, is the same throughout. Knebelite, as stated above, is a solid solution of the oxides of iron, manganese and silicon, which may be present in varying amounts, within limits This phase occurs in the slags, sometimes of a golden brown colour and at other times as a darker brown phase. This dark brown colour probably means that the iron in its composition has increased, and this variation in the colour of knebelite occurs throughout the series of samples which were examined. In a steel furnace, the slag does not lie static on the metal,, but constantly circulates, generally running against the direction of flow of the gas. If the supposition of the darker colour of knebelite being due to more ferrous oxide in in its composition be true, then this explains why the knebelite occurring in the slag from doors 4, 5, and 6, is reported as being brown. The ferrous oxide is being formed due to the gas oxidation and is being dissolved in the knebelite. Also the amount of calcium ferrite found in slag from door 5, is greater than that found in the slag from door 1. So it would seem that calcium ferrite is also being formed from gas oxidation. It is plausible to assume, then, that the calcium ferrite is being formed on the surface of the slag, circulates against the gas flow, and travels along the slag-metal interface, where the ferric iron is reduced to ferrous by the carbon of the steel, this ferrous iron then again being oxidised to ferric by either the furnace gases or some other agent.

From the examination of the slags recorded above, it seems feasible to state that any sample of slag taken from the slag covering during the finishing period is representative of the entire slag for that period.

The slag being found to be homogeneous in the finishing stages of the steel making process, it was then decided to find out how early on in the process this stage of homogeneity was reached. To this end, samples of slag were taken from the same furnace as series 3, but the period chosen was earlier in the process. The furnace was being run in precisely the same manner as when the third series of slags were drawn, and the steel to be produced was the same, with a final carbon content of 0.08%. The samples were drawn from the same places in the furnace and the direction of flow of the gas was the same. The period of the process was chosen, such that all the scrap and pig-iron had just melted and lifted clear of the bottom. The only additions which had been made to the furnace were seven to nine hundredweights of fluorspar to thin the slag, and a very small feed of lime. At the time of drawing the slag samples the ferrous oxide content of the slag was 10%, and the carbon in the steel amounted to 0.1%. The results of examination of the various slags are noted below.

THE EXAMINATION OF SLAG SERIES Number 4.

The first slag examined was taken from door 1..

Colour of Phases.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
Dark brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
Dark brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
White.	1.78-2.0.	Nil.	Nil.	Isotropic.	
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Black.	2.0.	Nil.	Nil.	Isotropic.	Ferrous oxide.

In addition to these phases a very slight trace of calcium ferrite was found.

All of these phases were found in the sample of slag from the slag-metal interface, with the exception of the calcium

calcium ferrite and the knebelite. The results given above were obtained by the powder method, and a thin section was prepared in the manner already described. Examination of this section showed very little beyond the dark brown dendritic needles of knebelite and long dull grey striae of ferrous oxide. A few traces of red calcium ferrite were, however, found in the section.

The examination of the slag from door 2..

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
White.	1.78-2.0.	Nil.	Nil.	Isotropic.	
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
Black.	2,0.	Nil.	Nil.	Isotropic.	Ferrous oxide.
Light brown.	2.1.	Nil.	Nil.	Isotropic.	FeO-MnO.

The sample of slag from the slag-metal interface showed the same phases except apatite, and there was one phase which does not appear in the shallow sample, andalusite. The thin section of the slag which had been prepared, showed the slag to have a large amount of a brown phase which crystallises in long needles similar to those in the slag from door 1..

The examination of the slag from door 3.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
Brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
White.	1.78-2.0.	Nil.	Nil.	Isotropic.	
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
Red brown.	2.1.	Slight.	Medium.	Straight.	Mono - calcium ferrite

All of these phases with the exception of the apatite, were found in the sample from the surface of the metal.

The examination of the slag from door 4.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
Brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
White.	1.78-2.0.	Nil.	Nil.	Isotropic.	
Black.	2.0.	Nil.	Nil.	Isotropic.	Ferrous oxide.
Red brown.	2.1.	Slight.	Medium.	Straight.	Mono-calcium ferrite

The sample from the slag-metal interface showed these phases also, with the exception of apatite, rhodonite, ferrous oxide, and also the phase which has not been named.

The examination of slag from door 5.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
Brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite.
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Black.	2.0.	Nil.	Nil.	Isotropic.	Ferrous oxide.
Red brown.	2.12.	Slight.	Medium.	Straight.	Mono-calcium ferrite.

The sample taken from the surface of the metal showed the same phases with the exception of apatite. The calcium ferrite in both the samples, the deep drawn and the shallow, was about equal in amount, and this was verified from the thin sections which were cut of both samples of slag.

The slag from door 1. was under the gas outlet from the furnace while that from door 5. was under the incoming gases. The time of drawing the first and last samples was very nearly the same covering a period of only three minutes. To compare the components of the different samples of slag examined, the following table was drawn up.

Slag No.1.	Slag No.2.	Slag No.3.	Slag No.4	Slag No.5.
Apatite.	Apatite.	Apatite.	Apatite.	Apatite.
Rhodonite.	Nil.	Rhodonite.	Rhodonite.	Rhodonite.
Nil.	Andalusite.	Nil.	Nil.	Nil.
Knebelite.	Knebelite.	Knebelite.	Knebelite.	Knebelite.
Fayalite-Tephroite.	Fayalite-Tephroite.	Fayalite-Tephroite.	Fayalite-Tephroite.	Fayalite-Tephroite.
Ferrous oxide.	Ferrous oxide.	Nil.	Ferrous oxide.	Ferrous oxide.
Calcium ferrite.	Calcium ferrite.	Calcium ferrite.	Calcium ferrite.	Calcium ferrite.
Nil.	FeO-MnO.	Nil.	Nil.	Nil.

From the table it can be seen that slag covering, at this stage of the process cannot be considered to be homogeneous. Thus, andalusite occurs in only one slag, and in that slag it would appear to have taken the manganous oxide in preference to the silica, for no rhodonite occurs in that slag. The table was drawn up,with the phases included whether they appeared in both or one of the samples examined. What is of more vital importance than the heterogeniety of the slag covering as a whole, is that the slag next to the metal is different from that at the surface of the bath. It is noteworthy, that the slag next the incoming gases is more oxidised than the slag at the exit end of the furnace. Apatite appears to exist on the surface of the bath, but it is to be remembered that only a very small amount of lime has been added, and the phosphorus of the steel has probably combined with all of it thus leaving none free to react with the phosphorus being oxidised.

being oxidised later, so that the oxide of phosphorus will not be able to form apatite on the surface of the metal. It would seem from the results of the examination that the slag was fast settling down to homogeneity, but had not quite reached that state. The behaviour of the ferrous iron, illustrates this, in one sample of slag forming knebelite, and in another sample of slag taken near-by, it is combined with manganous oxide alone. Accordingly, it must be stated that a representative, single sample could not be obtained of the slag at this period.

THE EXAMINATION OF SLAG SERIES Number 5.

Since the slag was not homogeneous, and could not be examined representatively by a single sample, it was decided to take a series of slags from a basic furnace at regular intervals from the period of melting down, and to find when the slag did become homogeneous. The slags were taken, as before, from a normally run basic furnace. The state of the furnace was as follows; at 6.40, there had been no ore additions to the furnace, the gas was flowing from door 5. towards door 1. and the ferrous oxide amounted to 2% of the slag. Samples were drawn at both ends and also at the middle of the furnace, both from the slag-metal interface and from the surface of the slag. The furnace had "Melted down" at 6.15. ,so that all the material in it was liquid. All the slag samples were examined by the powder method and the results are tabulated below.

The examination of the slag from door 1. at 6.40.

Series 5.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction. Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
White.	1.66+.	Nil.	Nil.	Isotropic.	Andalusite.
Brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
White.	1.56.	Nil.	Nil.	Isotropic.	Collophanite
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Black.	2.0.	Nil.	Nil.	Isotropic.	Ferrous oxide.

The results tabulated above were obtained from the examination of the shallow-drawn slag, and the following phases were found in the deep-drawn slag; Apatite, Andalusite, Rhodonite, Collophanite, Fayalite-Tephroite, Ferrous oxide. From these results it seems that the slag is homogeneous from top to bottom. Of course, there was the usual difference in degree of oxidation between the shallow sample and the deep one; the slag on top seems to be always rather more oxidised than that on the surface of the metal. It is interesting to note that the alumina is capable at this stage of the process to form aluminium phases of its own, andalusite.

The examination of the slag from door 3. at 6.40.

Series 5.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
White.	1.66.	Nil.	Nil.	Isotropic.	Andalusite.
Brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
White.	1.56.	Nil.	Nil.	Isotropic.	Collophanite.
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
White.	1.78.	Nil.	Nil.	Isotropic.	

The phases in the sample from the slag-metal interface are exactly the same as those from the slag in the surface of the bath, so apparently, the cross section of the slag at the middle of the furnace is homogeneous at this period. Of course, the usual reservation must be made, that the bottom slag is less rich in oxygen than the top slag.

The examination of the slag from door 5 at 6.40.

Series 5.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
White.	1.66.	Nil.	Nil.	Isotropic.	Andalusite.
Brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
White.	1.56.	Nil.	Nil.	Isotropic.	Collophanite.
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Brown.	1.78-2.0.	Nil.	Nil.	Isotropic.	Knebelite
Brownish black.	1.66-1.74.	Nil.	Nil.	Isotropic.	Hercynite.

The phase , Hercynite, is composed of alumina and ferrous oxide. Again in this slag, the phases which occur in both the sample from the top and the sample from the bottom of the slag covering are the same, the usual reservation being made as regards the state of oxidation.

In the table given below, all the phases which occurred in the slag samples from the three doors are given;

Slag sample. 1.	Slag sample. 3.	Slag sample. 5.
Apatite.	Apatite.	Apatite.
Andalusite.	Andalusite.	Andalusite.
Rhodonite.	Rhodonite.	Rhodonite.
Collophanite.	Collophanite.	Collophanite.
Calcium ferrite.	Nil.	Nil.
Fayalite-Tephroite.	Fayalite-Tephroite.	Fayalite-Tephroite.
Traces of FeO.	Ferrous oxide	Nil, but Knebelite and Hercynite.

From the phases reported in the previous table, it can be seen that this period of the process is not capable of being represented by a single slag sample. The important constituents calcium ferrite, ferrous oxide and knebelite, do not occur uniformly throughout the slag. It is to be expected that knebelite would exist in the slag from door 5., since this is directly under the oxidising action of the entering gases, and since the slag flows against the gas flow, the oxidation from the gases would be at a maximum where the gas impinges on the slag most. This happens in the centre of the furnace, and then it is natural to expect to find the oxidised material at the gas entrance end of the furnace. The presence of calcium ferrite in the slag from door 1. does not seem to fit into this theory of oxidation, but it must be remembered that all of the oxidation is not caused by the gas but is also caused, and probably to a larger extent, by the additions of iron oxide to the slag. There had been an addition of ore and it is probable that the stabilising action of the lime on ferric oxide had allowed the calcium ferrite to exist to some extent, thus accounting for its presence in this sample, and further, only a small quantity of the ferrite was found. The other phases recorded are normally expected to be present, due to the oxidation of the impurities in the scrap, ore and pig iron. The apatite seemed to have fluorspar in its composition, as was evidenced by a somewhat higher refractive index than that given in the tables, but the majority of the pieces of apatite had the refractive index given, the higher refractive index material having all the characteristics of apatite, but being of a somewhat darker colour, being brown in appearance.

The examination of the slag from door 1. at 7.00 .

Series 5.

The material in the furnace had now been completely liquid for approximately one hour; there had been a fairly large amount of ore added between 6.40 and 6.50. and the gas was still travelling from door 5. towards door 1.. The amount of ferrous oxide in the slag had risen to 7%

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
White.	1.56.	Nil.	Nil.	Isotropic.	Collophanite.
Brown.	1.76.	Slight.	Medium.	Oblique.	Rhodonite.
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.
Light brown.	1.78-2.0.	Nil.	Medium.	Straight.	Manganspinel.
Grey.	2.0.	Nil.	Nil.	Isotropic.	Ferrous oxide.
Red brown.	2.12.	Slight.	Medium.	Straight.	Calcium ferrite.
Brown.	1.78.	Nil.	Nil.	Isotropic.	Knebelite.

The slag which was taken from the slag-metal interface was composed of the same phases. The apatite seemed in some crystals, to have a certain amount of fluorspar in its composition as shown by the slight rise in its normal refractive index, and also by the darker colour of these crystals. These darker coloured crystals had an extremely weak birefringence and at first appeared to be isotropic.

The examination of slag from door 3. at 7.00.

Series. 5.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
Brown.	1.78.	Nil.	Nil.	Isotropic.	Knebelite.
White.	1.56.	Nil.	Nil.	Isotropic.	Collophanite
Brown.	1.74.	Slight.	Medium.	Oblique.	Rhodonite.
Light brown.	1.78-2.0.	Nil.	Medium.	Straight.	Manganspinel
Black.	2.0.	Nil.	Nil.	Isotropic.	Ferrous oxide.
Red brown.	2.12.	Slight.	Medium.	Straight.	Calcium ferrite.
White.	1.78-2.0	Nil.	Strong.	Straight.	Fayalite-Tephroite.

There was one notable feature in this slag. The phase collophanite was found to be more abundant in the slag from the surface of the bath than it was in the deeper sample. The explanation for this was found when the slag wasbeing examined by the powder method; collophanite was found to have a low specific gravity and floated in monobromonaphthalene. Floating in this liquid would mean that it would float much more readily in the liquid slag. This is a further indication, that to obtain a representative sample of slag from the furnace, it is necessary to either stir the slag or else to draw a very large sample.

The examination of slag from door 5. at 7.00.

Series 5.

Colour of Phase.	Refractive Index.	Pleochroism.	Birefringence.	Extinction. Angle.	Phase.
White.	1.64.	Nil.	Weak.	Straight.	Apatite.
White.	1.56.	Nil.	Nil.	Isotropic.	Collophanite.
Brown.	1.76.	Slight.	Medium.	Oblique..	Rhodonite.
Brown.	1.78-2.0.	Nil.	Medium.	Straight.	Manganspinel.
Red brown.	2.12.	Slight.	Medium.	Straight.	Calcium ferrite.
Grey-black.	2.0.	Nil.	Nil.	Isotropic.	Ferrous oxide.
White.	1.78-2.0.	Nil.	Strong.	Straight.	Fayalite-Tephroite.

The deeply drawn sample of this slag showed the same phases on examination. The relative amount of calcium ferrite had increased in this slag as compared with the last one.

On comparing the constituents of the three slags, however, it is to be seen that all three contain the same essential phases, although the relative amounts may vary slightly. Hence a sample, drawn from, say, door, three, would be a representative one for the furnace under the given conditions, i.e. the phases representative of the slag would be present but the proportions would not be correct.

Since the slags from period 7.00., are homogeneous with respect to the distribution of the phases, but not with respect to quantitative distribution, another sample was drawn at 7.25. In the interval the direction of flow of the gases had been changed, and a further small addition of ore had been made, the ferrous oxide content of the slag having now risen to 11.5%. On examining the slag samples from the three doors, the samples being drawn, as before, both from the slag surface and the metal surface, they were found to be rather more homogeneous as regards distribution of phases.

From the examinations made on a series of five typical basic slags, the following deductions can be made.
The slag covering of the molten metal in the basic open hearth steel process varies with the period of the process of steel making. The slag at the beginning of the process is very heterogeneous, and even varies in the cross section of the depth. Thus at this period no representative single sample can be obtained. The period of heterogeneity varies but can be said to exist for about one-sixth of the total time for working the charge from beginning to end. The slag can be represented by a single sample of slag drawn preferably just after a gas reversal from the middle door of the furnace, just before the commencement of the boil. The additions of ore and lime alter the slag and time should be allowed to allow these additions to be incorporated in the slag before samples are drawn. There are certain components of the basic slag which persist from the time of melting down till the tapping stage is reached, but these components are stable and usually are not easily reduced nor oxidised. Some components seem to appear and disappear according to the altering of the conditions in the slag.
Thus calcium ferrite seems to be the chief oxidising component of the slag and disappears nearly completely after the boil, but again makes its appearance towards the end in much larger quantity. This is to be expected from the high oxygen vapour pressure of this compound, at high temperatures. From the point of view of cleanliness of the finished steel, these are expected to be the important components of the slag, since the others are rather inert towards the metal. The materials which are expected, therefore, to have most effect on the clean or dirty steel point of view, are calcium ferrites, knebelite, (iron and manganese silicate) and the oxides of iron.

The cleanliness of the finished steel, must of course, in addition to being affected by the reactive components of the slag, be affected largely by the physical state of the finishing slag.

A clean fluid slag would not be nearly so difficult to separate from the metal as would a very viscous slag, nor would one of low specific gravity be so difficult to separate as one of higher specific gravity.

From the above considerations, it is possible for inclusions to occur in the metal from two distinct types of slags. Firstly, the inclusions could occur due to mechanically entrapped slag particles from a viscous slag, and, secondly, inclusions could occur due to reaction between the components of the slag and the metal itself. The two types cannot be separated, as an inclusion could start as one of them and end by acting like the other, say, a piece of mechanically entrapped slag, this would, while the metal was cooling, probably react with it, and so could be classified under the second category.

The types of slag most likely to give rise to mechanically entrapped inclusions are the slags high in manganese and silica, or lime, since these materials make the slag viscous and difficult to separate from the metal. The slag component which would give rise to inclusions due to slag metal reaction would be the calcium ferrites, due to their high oxygen content and their willingness to oxidise. These compounds would still be oxidising the carbon, manganese, etc, in the steel for they increase in quantity in the finishing slag, and so would be carried into the steel on tapping, giving rise to inclusions which would cause a strain on the metal, due to formation after the metal had partially solidified.

From this, the oxides likely to be encountered in non-metallic inclusions in steel, would be those of calcium, iron, silicon, and manganese, with a certain amount of aluminium oxide due to the method of deoxidising the steel in the ladle.

THE QUALITATIVE EFFECT OF THE VARIOUS COMPONENTS OF A TYPICAL BASIC SLAG ON STEEL, BUT AT TEMPERATURES BELOW THE MELTING POINTS OF THE COMPONENTS.

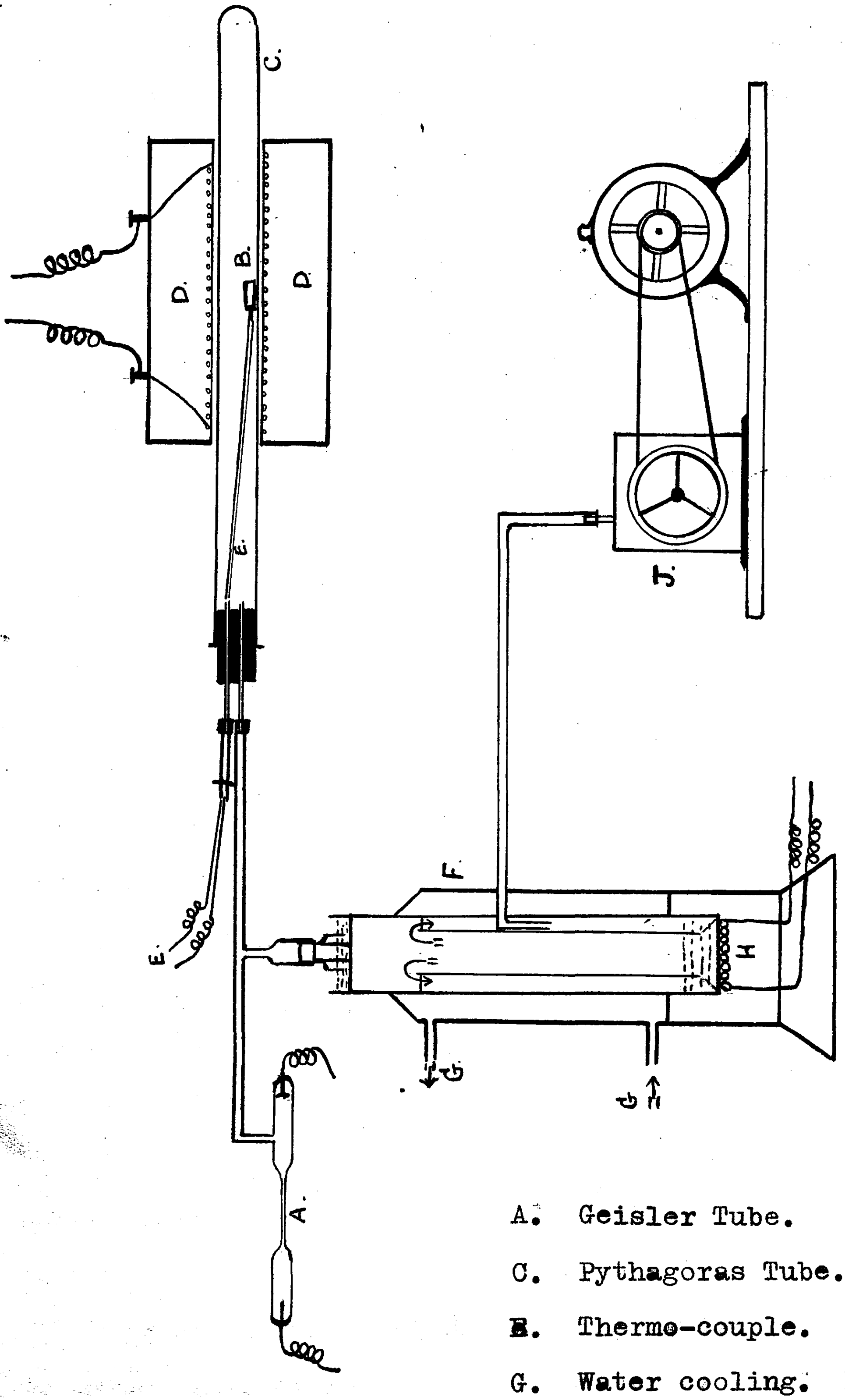
Various synthetic slags having been made, their components noted and applied to actual slag determinations, it was then decided to find the effect of these components on steel at relatively low temperatures. These temperatures compare with those which would be employed in heat treatment, but are somewhat higher.

The steel chosen for decarburisation or slagging had a carbon content of 0.75%. This steel was taken because the effects of slagging could be most easily seen in this steel, since it contains a large amount of pearlite. The steel was obtained in rod form, one inch in diameter and the same rod was used throughout the series of experiments. A two inch length of the rod was sawn off and a half inch hole was drilled centrally in this to a depth of one and a half inches. This hole was packed with the inclusion and a plug of the same steel was fitted tightly into the crucible.

The inclusions used had to be prepared synthetically. The pure materials used have been already described and the method of preparation of these was the same as already described. For the compounds, the components were mixed in the required proportions and then fused in large quantity in a fire-clay crucible. Only the material from the centre of these large melts was used as the outside was contaminated to some extent by the components of the fire-clay. Fire-clay was used because of the impossibility of obtaining a molybdenum crucible of sufficiently large size. All the material placed in the steel crucible was exceedingly finely powdered to the same degree of attrition. If some extraneous matter did creep in from the fire-clay fire-clay crucibles, its presence could be neglected, for the examination was only qualitative, and in addition, the material from the crucible would be non-reactive with the steel.

The steel crucible with a base metal couple attached to it, was placed in a " Pythagoras " tube . This temperature resisting gas tight tube, was placed in a nichrome wound electric resistance furnace, capable of reaching a temperature of 1200°C.. The temperature was controlled by altering the current to the furnace by means of a large rheostat, this rheostat being of such dimensions that a change of 0.25 amp. could be made. The temperature of the crucible was measured by the base metal couple, chromel-alumel; and the millivolts were measured on a recorder of a sensitivity of 0.0002 volts. The refractory tube was closed by means of a large rubber bung, through which passed two gas tight tubes, one carrying the thermo-couple wires, the other being used to evacuate the tube. The tube was evacuated by means of a mercury vapour pump, backed by a " Cenco Hyvac " oil suction pump. This arrangement was capable of producing very nearly an X-Ray vacuum in the " Pythagoras" tube. The method of examination originally used was to examine the furnace gases by means of a Geisler tube and a microscope, fitted with a small spectroscope on top. The idea was to examine the spectrum of the furnace gases when a discharge took place in the Geisler tube. It was found, however, that when the furnace and tube were cold, and no decarburisation was taking place, that such a low vacuum was obtained that the glass of the Geisler tube fluoresced. The bright lines due to this flourescence were noted when the tube was cold and completely evacuated. The microspectroscope consists of a small short focus ocular used to view the spectrum given by a triple Amici prism. Alongside the spectrum from the source to be examined, a small reflecting mirror can cast a standard spectrum and the whole instrument replaces the ocular of the microscope.
The Geisler tube used was made of soda glass and it was found that this material could not hold a vacuum completely at the very

very low pressures which existed inside the tube.. It was found that sufficient air leaked through the glass in ten minutes to make Crooke's dark space disappear. Thus the Geisler tube had to be clipped off from the furnace, as in sketch, and constantly evacuated unless when a determination was being made. The very small amount of air necessary to destroy Crooke's dark space, was sufficient to nullify the determination of the commencement of decarburisation unless the above precaution was taken. It was found that the following technique gave very good reproducible results. The refractory tube was completely sealed off, to make it gas tight. The tube was then evacuated, and the temperature of the tube was raised a definite increment. The Geisler tube was then evacuated of all infiltered air and was connected to the refractory tube by undoing the clip on the connecting tube. The movement of the striae in the Geisler were watched and if no change took place on connecting to the refractory tube then no gas was being given off due to the reaction between the slag and the steel. If on the other hand the striae moved and finally disappeared, it meant that the slag and steel were reacting and giving off a gas. It was hoped by means of the microspectroscope to identify this gas from its spectral lines but this was found not to be possible, since, after a time the electrodes of the Geisler tube became coated with carbon and no reliability could be placed on the results. This carbon is due to the decomposition of carbon monoxide under the influence of a high tension discharge to carbon dioxide and carbon. In addition the instrument was capable of being read to only 100 A° and this is of no great use for determination of spectral lines which must be read to an accuracy of at least 1A°. Therefore the movement of the striae was taken as being the more reliable method of determination, and a movement of half an inch of the striae was equivalent to a very slight flattening of the meniscus of a mercury manometer. A movement of one eighth of an inch was taken as the beginning of decarburisation of the steel by any particular inclusion.



A. Geisler Tube. B. Specimen.

C. Pythagoras Tube. D. Furnace.

E. Thermo-couple. F. Mercury pump.

G. Water cooling. H. Heater.

J. Ceneo Hyvac backing pump.

The temperatures of the crucibles containing the various inclusions were raised by definite increments and the evolution of gas was then tested for. If there were none, then the temperature was raised still further to another predetermined value and another determination made. In this way a series of temperatures of the commencement of the decarburisation by the various inclusions was made.

When the temperature of commencement of decarburisation by the inclusion had been determined, the crucible was heated to a certain temperature and held there for forty five minutes. The crucibles were then cooled and sectioned for examination. Photographs are to be found in the appendix, showing the effect of the various inclusions on the steel at different temperatures.

One very interesting fact was found by accident, during this series of experiments. A crucible was being heated to discover whether any oxidation would occur on an empty crucible. The surface of the crucible had been polished and etched to discover if the sample were quite clean, and then this polished, etched crucible was heated in the tube and by mistake, the tube of the of the connection to the glass Geisler tube was left unclipped. A very small amount of air had leaked in through the soda glass and oxidised the surface of the specimen. When the crucible was removed after cooling, it was found that the outlines of both the " α " and the " γ " crystals were to be seen on the same specimen. A photograph was taken and is to be found in the appendix.

The crucibles containing the slag components were heated to three temperatures, 1100°C., 900°C., and 700°C., and the effects of the inclusions were examined at these different temperatures.

The spectroscopic method of examination gave promise of results, at first, because of the change of colour in the discharge from pink to a pale blue colour, but because of the difficulties mentioned the method had to be abandoned. None of the large number of spectra recorded were of any use, since they did not give corresponding results for the same inclusion.

Nevertheless the Geisler tube was a very fine method of measuring the temperature at which decarburisation commenced, because the striae in the tube give a very good indication of the state of the vacuum in the tube, and had exceedingly fine apparatus been used the method could have perhaps been made quantitative. To find out a relative value of the decarburisation of the different inclusions, the specific gravity of the crucibles was found before and after heating, but owing to the formation of scale on the outside of the crucibles , the impossibility of ensuring that all the inclusion had been removed from the crucible after heating, and the variations in area of action of the inclusion on the crucible, definite results could not be obtained.

Several experiments were made with each inclusion; the first ones were made roughly, the temperature being increased 50°C., at each step, but in subsequent ones the temperature increment was made much smaller. In this way the temperature of the commencement of decarburisation was obtained within a very narrow range.

The sections were polished,and etched in 1% alcoholic nitric acid. The steel was photographed at a magnification of 190 diameters. This magnification did not give the best photographs obtainable, but it was necessary to use it, in order to show a fair length of the reaction side of the crucible. The results of the examinations are tabulated below, on page 127.

In addition to the results given, experiments were made with the " Pythagoras " tube empty, to ensure that the results were not being nullified by the gases which might be occluded on the sides of the tube. These were found to be removed if they existed by the mercury vapour pump. An experimental heating with one of the crucibles empty, showed that no interference was occurring from this source, and the various inclusions were also heated alone to find if they evolved gases themselves at the temperatures of the experiments but this was found not to be the case.

Substance.	700°C.	900°C.	1100°C.
Ferrous oxide.	No decarburisation. The pearlite is spheroidal.	Moderate decarburisation. Grain size enlarged. The reaction commenced at 850°C.	Extensive decarburisation. Overheated structure.
Fayalite.	No decarburisation.	No definite decarburisation, but the edge near the inclusion is frayed.	Less decarburisation than FeO, commenced to evolve gas at 1030°C.
Knebelite.	No reaction.	No reaction.	Decarburisation with a ring of pure ferrite at the edge.
Manganous oxide.	No decarburisation. Very minute blow holes.	No decarburisation recognisable, but edge corroded with blow holes. Reaction commenced at 900°C. (Gas evolved).	No decarburisation recognisable. Gas evolved Numerous blow holes.
Rhodonite.	No blow holes. No reaction.	No decarburisation. Edge the same as fayalite case.	Similar to manganous oxide. The start of the reaction spreads over a range. Very little gas evolved.

The results of the examination of the specific gravities as stated, could not be made to yield reliable results, as can be seen from the following table.

Substance.	Specific gravity 700°C.	Specific gravity. 1100°C.
Blank.	7.803.	7.803.
Ferrous oxide.	7.803.	7.603.
Fayalite.	7.803.	7.715.
Knebelite.	7.803.	7.617.
Manganous oxide.	7.803.	7.598.
Rhodonite.	7.803.	7.623.

From the photographs in the appendix, and from the results noted above, the conclusion can be drawn that ferrous oxide by itself, is the worst inclusion that could occur in a piece of steel which has to be heat treated. Unfortunately, ferrous oxide is one of the inclusions most likely to be encountered in steel, but the ferrous oxide may not be so bad as regards the properties of the steel for it only decarburises the pearlite. Manganous oxide, on the other hand causes a real slagging action at high temperatures. This is seen by the blowholes it causes in sound steel with which it is in contact. Were it to occur in the centre of a very thin heat treated section its action would be very great on the mechanical properties of the steel for it would tend to produce a void and hence lower the strength of the material. Were it near the surface its action would be to produce a hair line crack which would later allow of internal oxidation of the steel. This action of manganous oxide is very strange; it may come about by the action of the oxide on the pearlite, the metal, manganese being produced. Manganese has a great affinity for carbon, so it may be that manganese carbide is formed thus taking more carbon from the pearlite; if this carbide forms a solid solution with the ferrite or with the cementite, and this solid solution

solution has a very low fusion or softening temperature, then this would explain the presence of the blowholes and also the lack of evidence of decarburisation by the manganous oxide. The similarity of the actions of fayalite and rhodonite must be attributed to the silica in these compounds. Fayalite is known to dissociate at temperatures not exceeding 1100°C. by very much, although the dissociation is very small. Nevertheless, if the products of dissociation were removed as fast as formed, then the factor is of major importance. The oxygen liberated would oxidise the carbon in the pearlite, and the ferrite left behind would also oxidise very readily, so that the ferrous oxide would tend to react with the silica in the fayalite to form a solid solution of the remaining fayalite and the ferrous oxide. This would probably account for the frayed edge that the crucible presents. In the case of rhodonite, knebelite would tend to be formed.

Thus it has been shown that if inclusions do occur they are very apt to cause failures in the steel, especially if the steel has been heat treated. Around the inclusion would be found a decarburised area which would normally be a potential source of weakness, and in the case of some the distribution of the inclusions after they had acted on the steel e.g. round the grain boundaries would be a still more serious matter. Thus the inclusions should never be compounds of manganese, and the inclusions of fayalite. The presence of rhodonite as an inclusion in steel would be very deleterious if the steel were to be rolled for this would give rise to strings of inclusion and unsound metal after rolling. The distribution of the inclusions, globular or granular, are discussed under the next heading.

THE IDENTIFICATION OF NON - METALLIC PARTICLES IN STEEL.

The identification of non-metallic particles in steel has occupied a considerable part of the literature during the last quarter of a century, and various methods have been adopted to try to find a suitable procedure for the identification of the slag particles. The chief method used was examination of the inclusions in the steel by the microscope and deductions were drawn from the colour, shape, and etching effects of the inclusions. In addition to these methods, use has been made of vertical polarised light to identify slag inclusions, and a quantitative method has been introduced for their estimation.[10.] Some of these methods were used to try to identify inclusions, but the methods used are subject to the following limitations. Colour is of no use whatever, by itself, as a means of identifying inclusions. While it may be used in conjunction with another method as a confirmatory test, its disadvantage lies in the fact that no allowance can be made for the changes introduced by material in solution. Small amounts of dissolved materials can greatly alter the appearance and even the crystal structure of a substance. Also it is difficult to describe the colour of an inclusion as they are nearly all dark, and such entirely different substances as rhodonite and ferrous oxide are reported as being dark grey and grey respectively. It is absolutely impossible to tell the difference unless the materials occur together.

Shape can to a certain extent, be used to denote the family to which the inclusions belong, whether oxide or silicate but this property depends too, on the treatment to which the steel has been subjected. Rolling for instance, will deform most inclusions, as will forging. If the inclusion be a manganese one then, as seen in the last section, it may disappear entirely, leaving only a string of blowholes.

Etching effects have been used to some extent to identify non-metallic inclusions, but their use does not seem to have been adopted. The general refractoriness of the inclusions to ordinary etching agents, however, militates against this method of determination.

From a consideration of the difficulties set out above, it is evident that these methods can at most, give only some idea as to the nature of an inclusion and while they were used to some extent in the present work, these difficulties were kept in mind and allowed for accordingly.

The quantitative method of estimating the inclusions gives the total amount of inclusions in any given sample, but makes no claim to identifying the inclusions.[10.] This method was also used to confirm some tests as will be seen later. The methods adopted in the identification of non-metallic inclusions in steel were, to a limited extent, those mentioned above, and the examination of a polished section by the " Ultro - pak " illuminator, a diagram of which has already been given. Vertical polarised light was also used but only to the extent of determining whether the inclusion were isotropic or anisotropic. Most, but not all oxides are isotropic, whereas all silicates, with very few exceptions are anisotropic, so a fair amount of differentiation could be obtained from this method of examination. It is well nigh impossible to tell the extinction angle of a mineral, or the crystal character of the mineral by vertical polarised light, for in being reflected the light becomes to a large degree scattered, thus not being properly polarised when it passes through the analyser, and thus upsetting determinations depending on the polarised character. Examination was also made of the inclusions by means of the microspectroscope. This method at the beginning seemed to hold out a fair degree of success, owing to the spectrum of the incident light being obtained alongside the reflected light spectrum. It was intended to measure the intensity of the two spectra and compare them, thus obtaining the absorption bands of the mineral.

To measure the intensity of the spectra, it was intended to use a photo-electric cell. The plate on which the spectra were recorded was to be placed in front of the cell, one part of the spectra, say from 6000 A° units to 5900 A° units, was to be exposed through a fine slit and the cell would record the candle power of the light passed by that part of the spectrum. Then the other spectrum of the same wave length was to be exposed in the same manner, and a comparison made as to the same or less intensity. The developement of the plate did not interfere since both spectra were on the same plate and developed alongside, fixed and dried and washed together. Unfortunately, the instrument gave spectra which could be read to only 10 A° units and thus it was very difficult to standardise the scale from a sodium flame, the standardisation being necessary to be correct to 5896 A° units. In addition it was difficult to correct for the absorption by glass of the lenses of the microscope and also to obtain a spectrum from the incident light which was of approximately the same intensity as the reflected light spectrum. So the method had to be neglected.

Since the above methods were all limited in their application, and since the method of identification of the inclusions had of necessity, to be a microscopical one, then it was decided to try microchemical methods. Microchemical tests are used in chemistry to identify very small amounts of material in solution, and many tests are available.[11.] It was decided to etch the inclusions in a suitable reagent, and to analyse the resultant solution, and the microchemical tests are usually very sensitive.

Accordingly, the method was tried out with ferrous oxide and manganous oxide. These materials were prepared and fused .

In the literature, the tests for iron are not very plentiful, and most of them depend on colour reactions. The chief ones are the blue colour produced with ferrocyanide and another precipitation test where a phosphate is precipitated. The colour test is sensitive enough, but it was felt that a precipitation test would be more satisfactory, while the colour test

test could be used as a confirmatory one. The phosphate test is one that can occur with several metals, notably manganese and zinc, so that it cannot be used in the identification of iron. Further, the precipitate is at first amorphous or sub-crystalline microscopically, so it was felt that this test was not definite enough. A general consideration of all the salts normally used in microchemical tests showed that the compounds formed are to some extent, slightly soluble in the liquid from which they are precipitated, and quite a few of them have water of crystallisation in their make-up. Accordingly a search was made for an iron compound which would fulfil these conditions. The reason for the slight solubility in the liquid is to allow crystallisation to proceed at such a rate that definite recognisable crystals will form. The possible salts which might be of use for tests were noted from reference books and these were tried but in most of the cases the precipitate obtained was an amorphous one. Acridine hydrochloride was found, however, to yield a recognisable precipitate, and this precipitate was easily enough obtained so that the conditions of precipitation were elastic enough for the purpose. The test consisted in mixing with the suspected iron solution a drop of 1% solution of ammonium thiocyanate, and then adding to the mixture a drop of a 1% solution of acridine hydrochloride. If iron is present, square red crystals are precipitated. These crystals are fairly stable but the colour is not red if ferrous iron is present. If ferrous iron is present, the crystals are green in colour and on exposing to air for a fair length of time these turn red. The following precautions are to be observed, however, in the precipitation of the compound. Acridine hydrochloride is rather easily hydrolysed to acridine itself, so it is necessary to have a chloride ion present to prevent this dissociation. Ammonium chloride, or hydrochloric acid itself will keep the salt from hydrolysing. Ammonia causes the hydrolysis of the salt and so must be absent. A mixture of nitric acid and hydrochloric acid prevents the precipitation

precipitation of the red iron crystals though the acids alone do not. Hydrogen peroxide not only inhibits the precipitation of the red iron crystals but if added after the crystals are precipitated, it redissolves them. Sulphuric acid inhibits the precipitation of the iron crystals and bromine, although it does not stop precipitation completely, slows it up very considerably. The test repeated with no iron present gave no precipitate. Sufficient iron is obtained by etching a piece of ferrous oxide, after fusion, with N/10 hydrochloric acid, to give this test. Another confirmatory test which was used was the purple colour developed with thioglycollic acid when mixed with an iron solution in the presence of ammonia. This test is exceedingly delicate, and very slight traces of iron can be detected by it.

This acridine hydrochloride test was then adopted as the main test for iron and a photograph of the crystals produced by the test appears in the appendix. The colour tests were used only as confirmatory ones.

Having found a test for iron, the next step was to find one for manganese. A list of the probable compounds which would serve for a test was made and the followingaare a few of the compounds which were tried.

Manganous carbonate; this compound is precipitated in neutral solution by sodium carbonate, but the precipitate is amorphous. Manganous ferrocyanide could not be used because of the blue colour which would be obtained when iron was present, and in addition, the precipitate was amorphous.
Ammonium manganous molybdate, would not give a crystalline precipitate in either neutral, hydrochloric acid, acetic acid, or ammoniacal solution; and manganous sodium phosphomolybdate behaved in the same manner.

Eventually manganous oxalate [11.] was tried and was found to fulfil the conditions. The salt could be precipitated by potassium oxalate but excess of this reagent redissolves it, but then adding acetic acid reprecipitates the manganous oxalate.

The inclusion is etched with dilute hydrochloric acid and a few drops of a 25% solution of acetic acid is added to the solution after which is added a drop of a 10% solution of potassium oxalate. If manganese is present, manganous oxalate is precipitated by the potassium oxalate in the form of crystals shown in the photograph in the appendix. These long needle crystals are truncated at the ends and have the following characteristics. The needles are very strongly birefringent and the angle of e extinction is , from a series of determinations, 64°, 63° 30', 63° 30', 64°. If the manganese be present in large amount, then the oxalate is liable to crystallise out as square dome shaped crystals which have the same characteristics as the needles, which come out on slower crystallisation.

The following precautions are to be observed with regard to the precipitation of this salt. The reagent potassium oxalate, as stated, in excess, dissolves the compound, so acetic acid must be present. Free oxalic acid also dissolves the compound , as does sulphuric acid, and if too large an excess of acetic acid is present, then crystals of acid manganous oxalate are precipitated and these are decomposed by light. Iron does not interfere with the precipitation nor does hydrochloric acid if acetic acid be present.

Then it was decided to find a test for silica. This material is very refractory towards acids, so a test was found in which hydrofluoric acid could be used. Sodium fluosilicate is used as a microchemical test for silica, and this was the test adopted. The inclusion was polished and then commercial hydrofluoric acid was diluted four or five times and the inclusion was etched with this weak acid. The test drop of solution was then placed in a very weak solution of sodium hydroxide and after a very short time the crystals of sodium fluosilicate were seen to crystallise. The test can be performed slightly better if a very dilute solution of sodium chloride is is used instead of the caustic soda. A photograph of the crystals produced by the test is to be seen in the appendix. The following precautions must be observed; the acid must be placed on the material to be tested with a clean platinum wire, and the slide on which the crystals are grown must be protected from the attack of the fluosilicate by coating it with some non-reactive material.. For this purpose, it was found to be best to coat the glass slide with a thin coat of properly cooked canada balsam. The objective of the microscope should be protected with a layer of collodion. None of the other elements like iron or manganese interfere in the reaction and on the whole the conditions of the test are very elastic and the test is a very sensitive one.

The test adopted for the identification of calcium was the tartrate test.[11.] Sulphate can also be used as a test for calcium, but the calcium sulphate must be crystallised from hot water to yield good crystals whereas the tartrate gives good crystals in the cold. The tartrate is easily precipitated in acid solution but acetic acid is best. If too much acid is present, them the crystals while being precipitated, are very badly distorted and are unrecognisable. A photograph of the typical crystals is to be found in the appendix. Sulphuric acid cannot be used because it tends to precipitate crystals of calcium sulphate which are too small for identification. Strong hydrochloric acid is very bad, if present, for it completely alters the crystal structure of the calcium tartrate.
The conditions that are most favourable is to obtain the calcium in a dilute solution of hydrochloric acid, to which is added two or three drops of 25% acetic acid and a drop of ammonium acetate of 10% strength. Then a drop of a 10% solution of normal sodium tartrate is added to the solution and the crystals are quickly precipitated. The normal tartrate must be used, for the test does not work with the acid tartrate nor with the sodium, potassium tartrate.

The last metal for which a test was sought was aluminium. Tests are available for aluminium but due to the slight amphoteric nature of alumina, these tests all call for a definite knowledge of the acidity factor of the solution from which it is proposed to precipitate the aluminium compound. It is impossible under the conditions recorded here for testing non-metallic inclusions to obtain any more than a very approximate idea of the"ph" value of the solution to be tested, so that the tests are of no use in this case. Thus a very fine test for aluminium in which a very crystalline precipitate is obtained, the oxime test, had to be neglected for it called for a "Ph " value in the testing solution and a precipitating temperature of 60°C. The amount of aluminium in the complex precipitate obtained is only 5.87%. Added to the difficulties of finding a proper test was the difficulty of dissolving aluminates when they occur in inclusions. Thus a test was sought which would have a fluoride or double fluoride in it. Such a test was found, and the procedure is as follows. The inclusion is etched in hydrofluoric acid and a drop of concentrated hydrochloric acid is added to the solution and a drop of a solution of ammonium fluoride. Then a small crystal of potassium is placed touching one end of the liquid and in a little time small white octahedra of potassium aluminium fluoride are precipitated.($K_3Al F_6$). The crystals are very small but the test is quite sensitive and is elastic enough in the conditions of precipitation for the purpose on hand. The same precautions are to be taken as with the silica test, i.e. protecting the slide and the objective. In this case properly prepared canada balsam was also used and found to be satisfactory. The material used in the oxime test is 8 - Hydroxyquinoline.

Another very delicate test for aluminium is the alizarin red S test. This dye with solutions of aluminium produces a purple colour which can be compared with the original colour of the dye when two capillary tubes containing the two liquids are placed side by side.

Tests for iron, manganese, silica, lime and alumina, having been worked out or obtained from the literature, and the conditions of these tests having been examined, it was then decided to apply them firstly, to large samples of the materials which would occur in inclusions. For this purpose, the synthetic slags which had been made in the examination of the equilibrium diagrams were used. These materials were polished and etched in the same manner as would be a piece of steel which was to be examined for non-metallic inclusions.

Ferrous oxide was first examined. The polished slag was etched with a drop of dilute hydrochloric acid and the test was made as described. Good crystals of the iron compound were obtained but these were small and there were a great many of them. If the slag were only lightly etched, then the crystals appeared light red in colour, but if a heavy etch were made, then the crystals were black in colour. Under the dark field microscope these black crystals proved to be deep red in colour. The test drop was examined for the other materials, manganese, silica, lime and alumina, but the results were negative in each case.

A mixture of ferrous oxide and manganous oxide in the ratio 50% to 50%, yielded the red iron crystals on examination. The manganese test yielded the characteristic long needles of manganous oxalate, but it was found that a very much less time of etching was sufficient to give a manganese test than was required for a satisfactory iron test. This shows that the manganese test is much more sensitive. The test drop in this case was also tested for silica, lime and alumina but none of the tests gave positive results. If too much manganese is present in the test drop then the dome shaped crystals and not

not the needle shaped crystals were obtained.
Rhodonite was next examined; it was found in connection with this compound that it is very important that the surface of the material be washed very clean for a definite test for iron was obtained and was due to polishing the rhodonite on emery paper which had been previously used for steel polishing. The small particles of iron had become fixed in the crevices in the slag in sufficient quantity to give the test for iron when the material was etched. So the slag was washed very carefully. The rhodonite was found to be very resistant to hydrochloric acid even when this was concentrated; so the slag was etched in hydrofluoric acid and the test for silica was obtained, very good crystals being obtained. It was also found that if the hydrofluoric acid used for etching is not too strong, and if sufficient acetic acid is added to the solution, then the acid used in etching does not interfere in the test for manganese.

Fayalite was then tested. It was soluble in sufficient quantity in hydrochloric acid to give the test for iron, and the etching with hydrofluoric acid gave the test for silica. All other tests were negative as was the case with the tests for iron, lime and alumina when the rhodonite was examined.

Therefore the tests do not interfere with each other and it is possible to identify iron, lime, manganese, silica, and alumina in presence of each other.

Then a sample of the calcium ferrites was examined and a satisfactory test was obtained for the lime and also for the iron. A sample of the quaternary mixture of silica, iron oxide, manganese oxide and alumina was next examined and good results were obtained for all the tests although the crystals obtained for alumina were rather small.

Since the tests for the components of the inclusions likely to be found in steel had been obtained, the next point was to find a method of preventing the steel from interfering in the examination of the inclusions. It was first proposed to plate the metal with some other metal which would be resistant to hydrochloride acid. Chromium and rhodium are resistant to the acid so these two metals were chosen. It is known that if non-metallic particles are present in steel which has to be plated, difficulty is encountered in obtaining a perfect surface on the metal, due, it is supposed to the inclusions refusing to be plated. Chromium plating was tried and although the method seemed to offer a solution to the problem of protecting the steel, nevertheless it had to be abandoned. There were two reasons; the first was that the conditions of plating are not simple but the difficulties in the technique could have been overcome had it not been for the second difficulty. This was that the chromic acid used in plating was attacking the inclusions and was eating them out and leaving only a gap where they had been. Accordingly this method was abandoned. The rhodium plating was too expensive, although the metal offers a complete resistance to hydrochloric acid, and the plating conditions are easy to obtain. A further difficulty of the chromium plating was that the small amount of chromium which did dissolve in the acid was sufficient to interfere with the test for iron, chromium giving green crystals when tested for, with the materials and in the same manner as for iron. Accordingly another method had to be adopted to protect the steel from the acid.

Commercial inhibitors are sold to lessen the sost of piping failures due to acid corrosion but none of these could be used as they do not completely inhibit the action of the acid on the metal but seem to act by depositing a protective skin.
The following is a short list of the various inhibiting agents mentioned in the literature.
A thiazole derivative, e.g. dihydro-toluidine.[12].

A substance of the general formula,[13.]

$N R' : C (X R'') NR_2$

Where R' is an alkyl, aryl, or acyl group or H_2.

R'' is another of the same groups or a similar group.

X is sulphur, selenium, or tellurium.

An example of a compound of this type is ψ- benzylthiourea.

Xanthane hydride.[14.]

The higher aliphatic acids.

Tests were made with some kindred compounds of these. Pine oil was used in polishing the specimen and was found to resist the action of the hydrochloride acid to some extent but not completely. Of the higher aliphatic acids, oleic, palmitic, and stearic were tried and found to resist the action of the hydrochloride on the steel in the order given. So the steel was polished with stearic acid mixed with the polishing powder. This was found to give the steel a very good temporary resistance to the action of hydrochloric acid and even to the action of hydrofluoric acid but not for so long as in the case of the hydrochloric acid. To test the efficiency of the protection a sample of steel was prepared containing no ferrous iron as inclusion, but containing manganous oxide. This was polished with the stearic acid and etched with hydrochloric acid and the resultant solution was tested for iron but was found to contain none.

It was found that after fifteen minutes exposure to the action of concentrated hydrochloric acid, the steel began to show signs of etching in spite of the stearic acid, but with dilute acid the time was very much longer. As the time of etching occupied only half a minute at most, there is therefore very little danger of the acid attacking the steel and nullifying the results. To further test the stearic acid polishing a sample of wrought iron was polished and etched. The iron had been inhibited, and as can be seen from the photograph in the appendix the inclusions were etched and the iron was not. A corresponding photograph is also given, unfortunately not at the same magnification, of what happens when the iron is etched with the

the hydrochloric acid without being inhibited. These photographs show definitely that the stearic acid does protect the steel from etching and hence from interference in the tests. The method of polishing was to polish in the usual manner down to the 000 grade of emery paper and then to wash the specimen very thoroughly to rid it of small pieces of iron that had been removed by the polishing. The specimen was then polished for a prolonged time on a selvyt pad with a mixture of stearic acid and alumina polishing powder. The lubricant used was paraffin oil. This method of preparation was therefore assumed to be sufficient to protect the steel from the action of the acid used to etch the inclusions.

One curious feature occurred in connection with the etching of the inclusions was noted. When the acid is placed on the inclusion in the steel all of the inclusion was etched out before there was any visible sign of an etch on the steel. From this it was argued that the solution potential of the inclusions might be higher than that of the steel. This was investigated by measuring the solution potential of pure iron and that of a mixture of the oxides of iron. The pure carbonyl iron used was polished in the usual manner and placed in a solution of neutral ferrous chloride in a half cell apparatus. The ferrous chloride was later changed to ferrous sulphate since no acid had to be present, and the ferrous chloride oxidised to ferric chloride which always dissociates to form hydrochloric acid. Had it not been for this the chloride salt would have been used for the speed of the chloride ion and that of the ferrous ion are about equal, whereas the suphate ion mobility and the ferrous ion mobility are a little different though not too far differing to allow of their use. The half cell with the carbonyl was used in conjunction with a standard calomel half cell and the voltage across the cell thus made was measured. The solution potential of the iron was found to be 0.439 volt. Then the semi-fused oxides were placed in the half cell in place of the carbonyl iron and the solution potential was found to be 0.63 volt. So this explains why the inclusion dissolves before the iron in the steel. This also helps to some extent to aid the inhibiting polish on the steel.

A method of investigating the inclusions being developed, and a method of preventing the steel from interfering in the examination being also known, it was then decided to make some steels with synthetic inclusions in them and to investigate these inclusions. The inclusions used were, ferrous oxide, manganous oxide, a mixture of ferrous and manganous oxides in the ratio 50% - 50%, calcium aluminate, and calcium silicate.

The method of preparation of the steel containing the inclusion was to melt the steel in a high frequency furnace and add the synthetic inclusion. The weight of ingot obtained was about one to two pounds, and photographs of the sectioned ingots are to be seen in the appendix. It was easy to melt the steel , but it was somewhat difficult to introduce the inclusion into the molten metal, so the following technique was adopted. The inclusion when merely thrown the surface of the molten metal lay there and did not melt, nor did it mix with the metal.; so one of the rods of steel of which the ingot was made was drilled out and the inclusion was packed inside. This rod was either placed at the bottom of the high frequency furnace crucible, where it was about the last to melt, or else the steel was melted first and then the hollow rod was added. The photographs of the ingots containing the ferrous oxide and also the manganous oxides show that this method on introducing the inclusion was successful. The ingots were cast in a small chill mould and then sectioned and examined. The sections were photographed actual size and also the polished unetched section was photographed at a medium magnification to show the mode of occurrence of the various inclusions. All of these photographs are to be seen in the appendix.

The steel used in making the small ingots was almost pure iron. The examination of the ingot containing ferrous oxide showed that no matter what the pouring temperature, ferrous oxide in the steel will give rise to blowholes. This was proved, because the ferrous oxide made the steel so sticky that the whole ingot could not be poured at once, and the second or top half of the ingot was poured at a much lower temperature than the bottom half of the ingot and yet the amount and dispersion of the blowholes is about the same. The blowholes in most cases showed temper colours indicating that the steel was being oxidised. The inclusions of ferrous oxide are round in shape and a few are very intimately mixed with the iron of the ingot. They were grey brown in colour with a pink tinge when examined in vertical illumination. In dark ground illumination, they showed to be a dark brown colour and are much harder than the steel as is shown by the scratches across the specimen becoming more narrow when crossing the inclusion. Some of the inclusions showed some cracks in the centre like contraction cracks.

The steel was protected by the stearic acid method from attack by hydrochloric acid and the inclusions were etched out and examined. The red crystals of the iron compound with the acridine hydrochloride and the ammonium thiocyanate were easily obtained but all other tests for the other inclusions were negative.

The ingot containing the manganous oxide was prepared in the same manner as that containing the ferrous oxide. About one pound of steel was melted in the small high frequency furnace and then the inclusion was added inside a hollow rod of the steel. The rod melted and the inclusion mixed with the steel. The steel when tapped into a chilled mould exhibited a sound exterior, but the ingot had risen by about 25% to 30%. The ingot, when sectioned, was photographed and this is to be seen in the appendix. As can be seen, the ingot is very unsound inside, and it is to be noted that

that the place of maximum unsoundness is where the surface of the metal would normally have been. The crystals of the manganous oxide inclusion are dove grey in colour with a pink tinge, in vertical illumination. In dark ground illumination when polished perfectly flat, they appear black, but if they have a rough surface the crystals appear to be a brilliant green colour. At very high magnifications the small inclusions of manganous oxide present a cubic structure somewhat like that of bismuth. When the inclusions are larger, they appear to be round or globular, and it was noticed that in the very large ones, the steel seemed to run along the crystal boundaries of the inclusion. When the section was examined microchemically good results were obtained for the manganese test but all other tests including the iron one were negative.

One very interesting result was obtained when an inclusion containing ferrous oxide 50%, and manganous oxide 50%, was introduced into the steel in the manner described above. It was found on examining the inclusion at high magnification that the inclusion was duplex in structure thus bearing out the examination of the powdered synthetic slag recorded in the first section of the work. This proves that the equilibrium diagram of ferrous oxide and manganous oxide cannot be a complete solubility diagram in the liquid and in the solid states. A photograph of this duplex structure is shown in the appendix. The inclusions from the mixture of the oxides showed a colour mid way between those of the oxides at low magnifications, and when tested by the microchemical method for iron and manganese the results were satisfactory. The inclusions are globular in most instances as can be seen from the photograph in the appendix, but in one or two cases the inclusions appeared to be inter - granular. This was especially so with the larger inclusions. The amount of blowholes in the ingot were equivalent in number to those found in the ingots containing the oxides singly.

The ingot prepared containing calcium silicate shows no blowholes equivalent to those found when iron and manganese oxides are present, as can be seen from the photograph given in the appendix. The calcium silicate slag used was chosen so that its melting point was the same as that of the steel, so that a very good degree of mixing of the slag and metal was obtained. Calciumsilicate would seem to be a very dangerous inclusion in steel as can be seen from the photograph, for the inclusion is intergranular. When etched in hydrofluoric acid the silica test was obtained, but it is somewhat difficult to see the crystals of sodium fluosilicate for they have very nearly the same refractive index as the liquid from which they are precipitated so that they are nearly invisible unless careful search is made. They usually exhibit a pink colour due to this equivalence of refractive indices. This is called the "Christiansen " effect. The lime test was also obtained, the crystals being fairly well formed unless excess acid were present when they were distorted. Tests for iron, manganese, and alumina were negative.

The calcium aluminate inclusion was also chosen so that its melting point was similar to that of the steel. The ingot obtained with this inclusion in it was also much sounder than that with the oxides in the ingot. The inclusions of calcium aluminate were very small and a great deal of care was required in the polishing, for the inclusion was very brittle. The particles were too small to photograph. Nevertheless the tests were obtained and the only drawback was the extreme small size of the crystals in the alumina test.

The ingots with the calcium silicate and calcium aluminate inclusions are as sound as that ingot which was completely deoxidised in the crucible and no trace of inclusion was to be found in the body of the ingot, although they were found in the pipe. This ingot was also photographed and is shown in the appendix.

The above results indicate to some extent, the factors to be avoided in the steel making process, as regards inclusions in the finished product. Thus there can be no doubt that pin-holes in the finished steel are due to oxides of iron. These pin-holes are more common in cast steel than they are in rolled steel but nevertheless, they affect the rolled steel and may, if large enough cause a roke. From the photographs it is seen that an aluminate inclusion is less dangerous than a silicate one as regards the properties of the steel, for the aluminate inclusion is globular whereas the silicate one in intergranular and so would be a major cause of a failure. On the other hand a steel which is completely deoxidised, as shown in the appendix, pipes to a large extent and the inclusions form in this pipe, so that it would not seem to be an advantage to have the steel in this condition. The calcium ferrites in the steel bath slag would give rise to these silicate inclusions and also to the aluminate inclusions, so that the use of aluminium as a deoxidiser would not seem to have a bad effect on the purity of the steel, for as shown, these inclusions rise into the pipe and so leave the part of the steel which is normally used, free from non-metallic inclusions.

It was then decided to examine a piece of steel from the head of an ingot, where inclusions were most likely to be seen. This steel was polished and examined and was found to contain inclusions. On making the steel safe by the stearic acid inhibitor from the attack of the etching acid, and examining the solution obtained from the etch, the following elements were found to be present, manganese, silicon, iron and calcium. A portion of this steel was electrolysed to find the total inclusions in the manner described in reference 10. Great care was taken to keep the voltage across the steel anode less than 1 volt and the inclusions were caught in the small collodion

collodion bag. These were then washed carefully to rid them of soluble salts and were examined by qualitative analysis in the usual manner. This analysis proved that only the four metals mentioned, silicon, iron, manganese, and calcium were present.

The method therefore, of examining the steel for the constituents of the inclusions, is to polish the steel in the normal way till the 000 grade of emery paper is reached. The specimen is then washed carefully. Polishing is done on a clean selvyt pad with an alumina polishing powder to which has been added an equal quantity of stearic acid. Polishing is continued for a prolonged time, and paraffin oil is used as the lubricant. The polished specimen is placed under the microscope and the inclusion is etched in dilute hydrochloric acid which is applied to the inclusion by means of a capillary tube. When etching has proceeded sufficiently far, the liquid is drawn off from the steel in another capillary tube which causes the liquid to run up it by capillary attraction. This liquid is then tested for the various metals according to the methods given on the previous pages. When a silicate is encountered, hydrofluoric acid has to be applied by means of a platinum wire and removed in the same manner.

The research recorded here gives a method of correlating the finishing slag with the inclusions to be found in the finished steel. The finishing slag can be examined by the powder method, and it has been demonstrated that the slag at that stage of the process is homogeneous, and the phases composing it can be determined from the data mentioned. The finished steel can be examined by the microchemical method recorded in the last section of the research and the metals forming the inclusions can thus be found. Knowing these, the

the material composing the inclusion can be deduced from the other data given. The effect of this inclusion can also be qualitatively foretold from the results recorded in section three of the research, and further evidence of the nature of the constitution of the basic open hearth steel furnace slag's effect on the metal can be deduced from the examination of the cast ingot.

It has been shown that the calcium ferrites have a great effect on the working of the basic process of steel making, and it has also been shown that calcium silicate would be very bad as an inclusion in the finished steel, so it can be stated that the slag in the furnace at the time of tapping is the chief factor in the question of clean or dirty steel. Of course many other factors enter into the question, such as the treatment which the steel receives before and during heat treatment, but it is certain that the constitution of the furnace slag is the prime factor in the quality of the finished steel.

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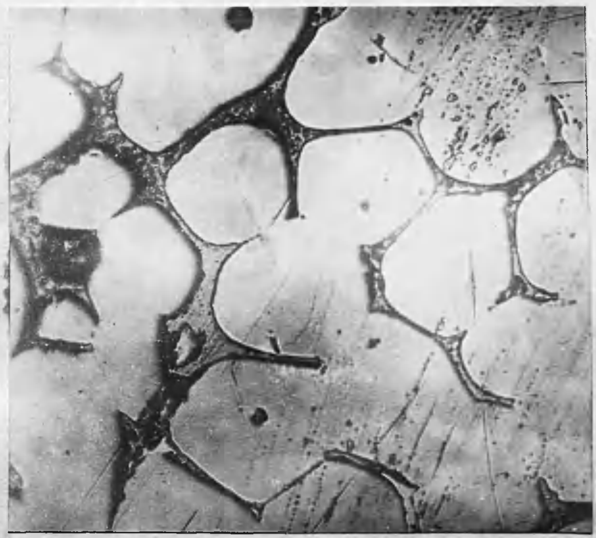
APPENDIX.

100%. Ferrous oxide. Melted in
a platinum crucible in vacuo.
Magn. 250. Diameters.

Massive piece of ferrous
oxide. Etched in HCl.
Magn. 4 diameters.



Ferrous oxide, showing the
effect of improper polishing.
Magn. 250. Diameters.

FeO. 50%. MnO. 50%.

Etched in HCl.

Showing the duplex structure of the mixture.

Fe_2O_3. CaO. 20%.

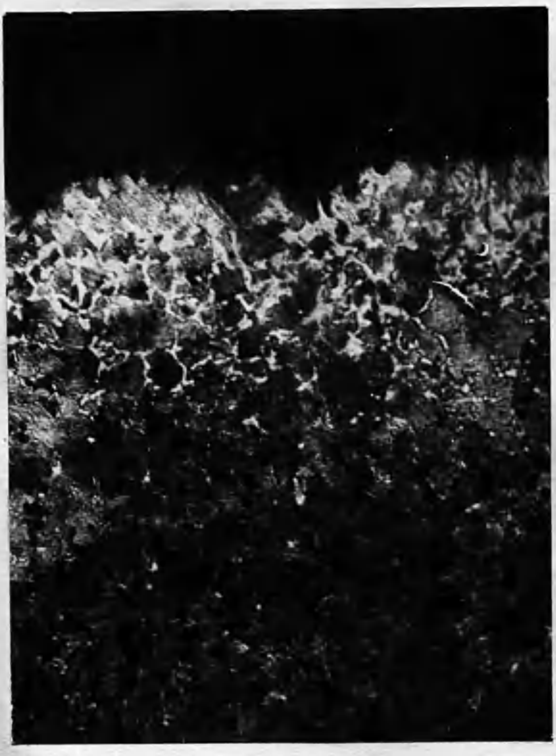
Showing the definite crystal structure of the slag in the crucible. Actual size.

Interference figure of Fe_2O_3 .

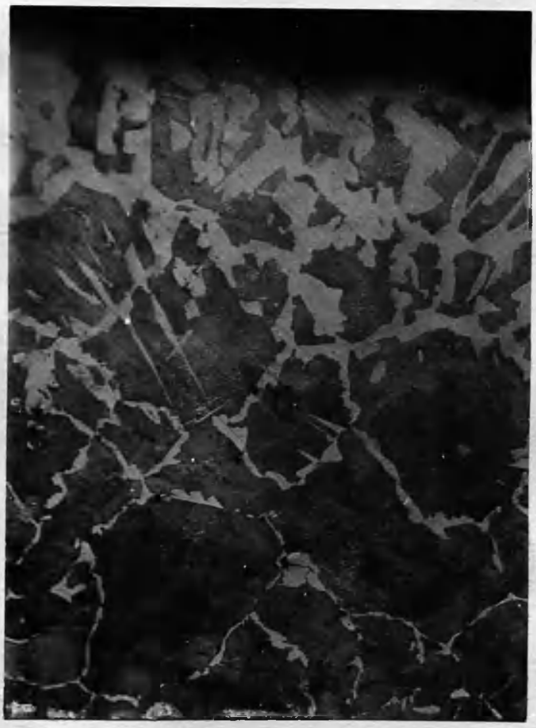
Biaxial interference figure. Obtained from di-calcium ferrite.

Effect of FeO, on steel
at 900°C.

Effect of FeO, on steel
at 1100°C.



Effect of fayalite on steel
at 900°C.



Effect of fayalite on steel
at 1100°C.

Effect of rhodonite on steel at 700°C.

Effect of rhodonite on steel at 900°C.

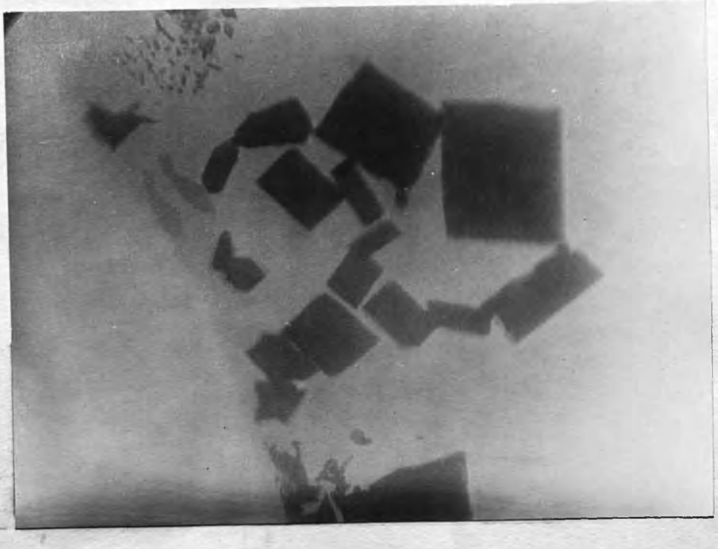
Effect of knebelite on steel at 1100°C.

Effect on MnO on steel
at 900°C.

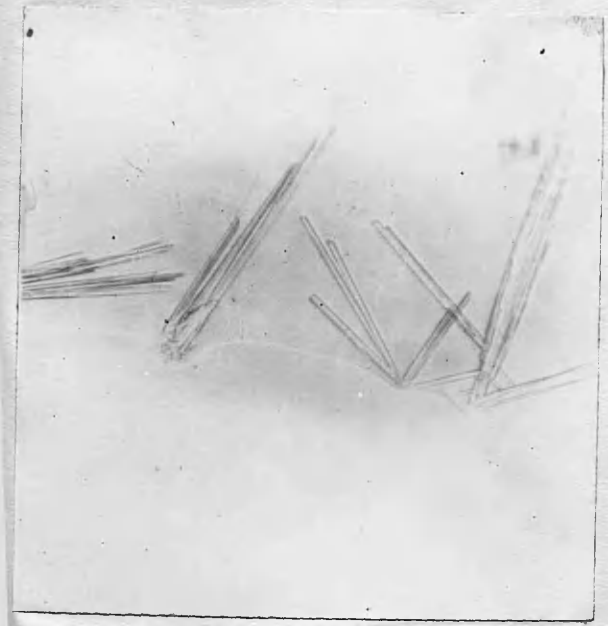
Effect of MnO on steel
at 1100°C.

Effect of MnO on steel at 1100°C.
Very much enlarged. 500 diameters.

Photographs showing " α " and " γ " grains on the same specimen of steel.

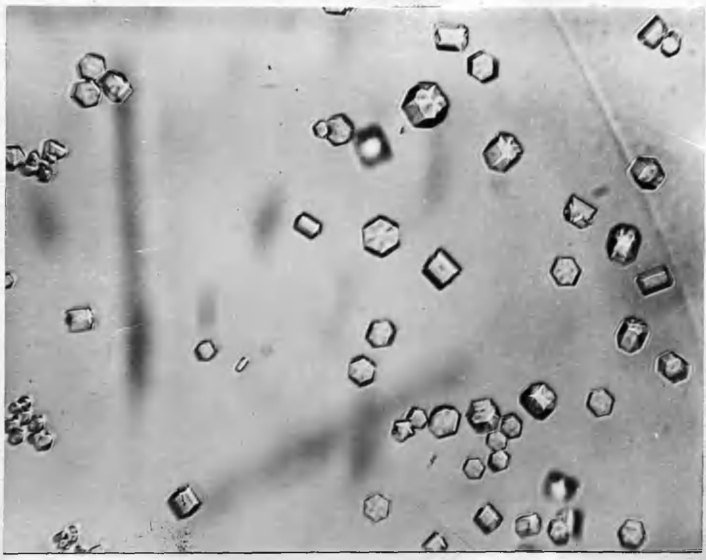


Type of crystals obtained in microchemical test for iron. Magn. 220 diameters.

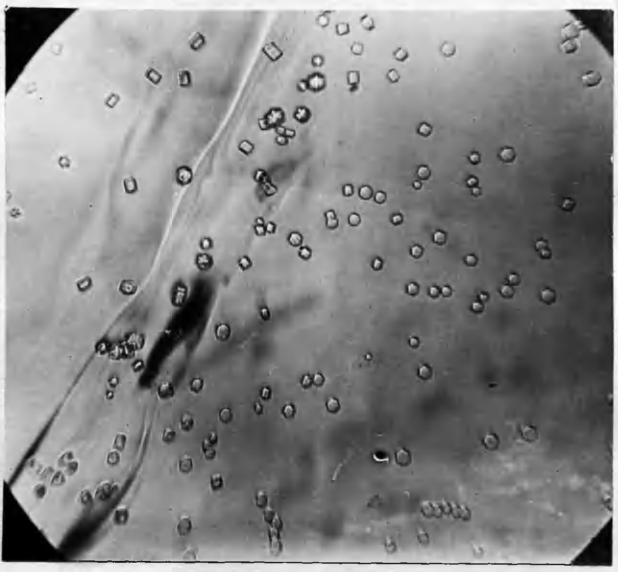


Manganous oxalate crystals, obtained in microchemical test. Magn. 220 diameters.

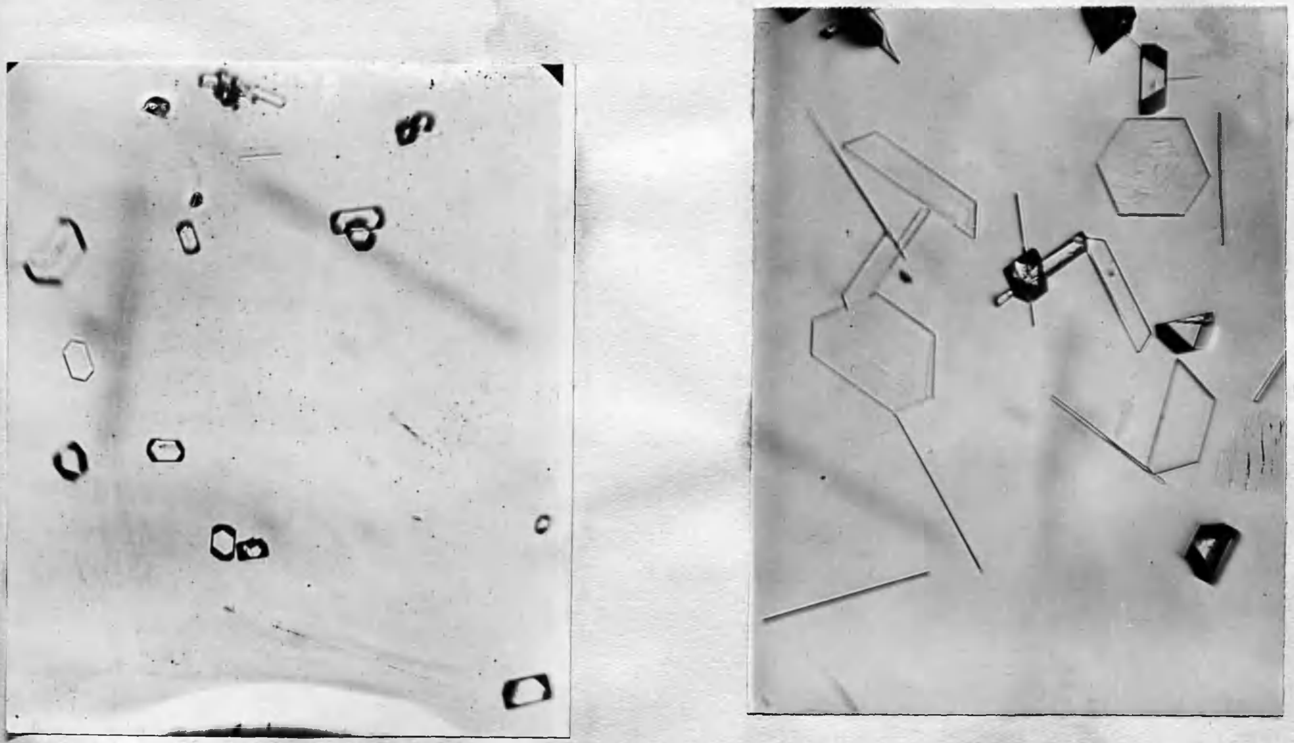
Manganous oxalate crystals under dark field illumination. Magn 220.



Crystals obatained in the microchemical test for SiO_2. Magn. 175. diameters.



The same crystals at a magnification of 100 diameters.



Types of crystals obtained in the microchemical test for calcium. Magn. 175. Diameters.

Specimen of an inclusion in Wrought Iron. The ring is for identifying the inclusion after etching, Magn. 100.

The same specimen etched in HCl. Note the iron also etched. Magn. 100.

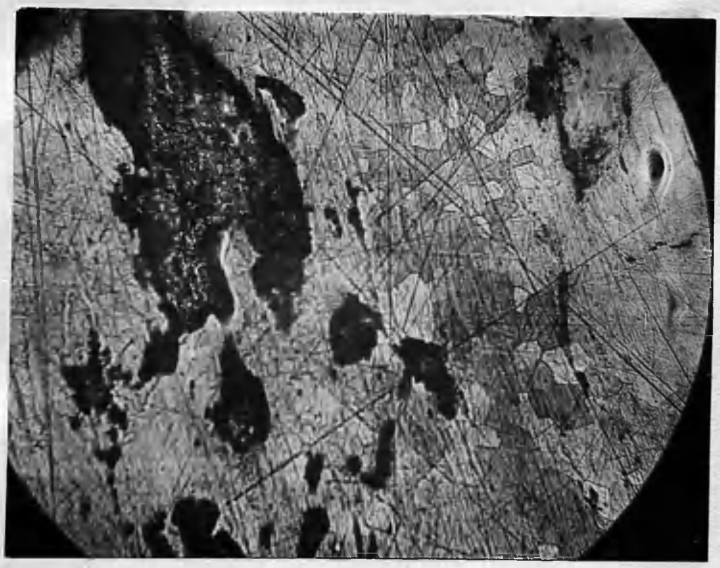
Inclusion in wrought iron. Polished so as to inhibit etching of the iron. Magn. 100.

Same inclusion etched in HCl. The iron shows no sign of etch. Magn. 100.

Inclusion in Wrought Iron. Polished so as to inhibit etching of the iron

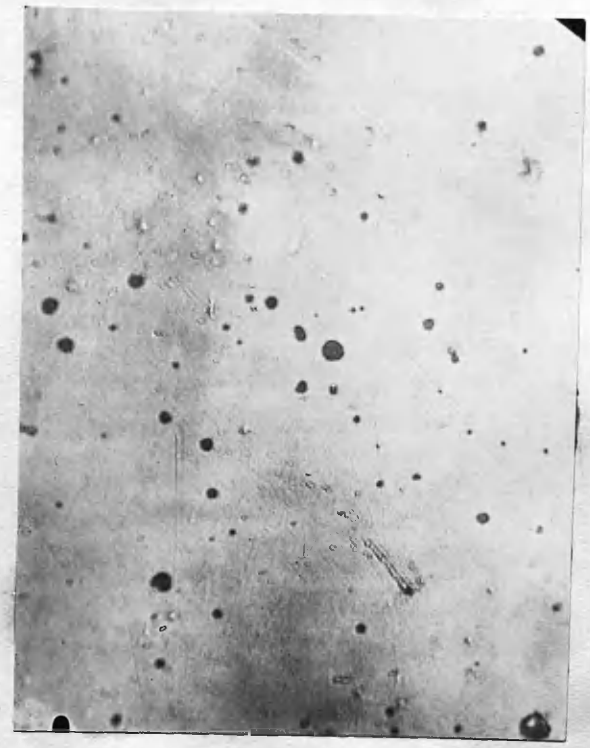
Magn. 100.

Inclusion as opposite, etched in HCl. No sign of attack of the iron. Magn. 100.



Same inclusion in Wrought Iron, as above. The iron was polished in the normal way, and the etching was done with HCl. Magn. 125.

Section of small ingot containing FeO as inclusion. Actual size.

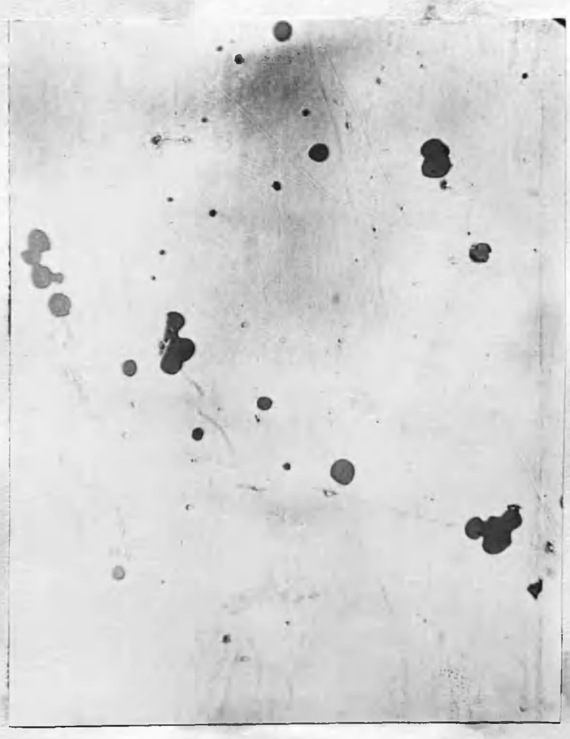


Shape of FeO inclusions in small ingot. Magn. 200.

Section of small ingot containing MnO as inclusion. Actual size.

Shape of MnO inclusion in small ingot. Magn. 200.

Section of small ingot containing FeO 50%. MnO 50% as inclusion. Actual size.



Shape of the inclusions of composition FeO 50% MnO 50%. Magn. 200.

Section of small ingot containing CaO. SiO_2. as inclusion. Actual size.

Shape of CaO. SiO_2 inclusions. Magn. 200.

Section of small ingot containing $CaO.\ Al_2O_3$. as inclusion. Actual size.

Section of small ingot which was thoroughly deoxidised. Actual size. Note size of pipe.