THE EFFECT OF MANGANESE OXIDE ON STEEL MAKING SLAGS WITH PARTICULAR REFERENCE TO VISCOSITY.

Thesis Presented

by

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Chapter I.

INTRODUCTION.

The constitution of solid acid open hearth slags is comparatively simple, since they are composed essentially of FeO, MnO and SiO_2 with a small percentage of CaO and still smaller percentages of Al_2O_3 and MgO. While the bases may vary among themselves, it is found that, in general, the ratio of base to acid remains fairly constant. From statistical analysis of 110 acid finishing slags, Hay, Ferguson and White (1) show that this ratio is roughly of the order 40/60, if the CaO, FeO, MnO and SiO_2 only are considered and the small percentage of other elements neglected. This percentage of bases is made up as follows:- 15 to 20 per cent FeO, 12 to 18 per cent MnO and 3 to 5 per cent CaO. Examination of the solid slag reveals primary crystals of silica in a background of either the orthosilicate or metasilicate solid solution series depending on the ratio of FeO to MnO. Up to 7.8 per cent, lime merely enters into solid solution in these silicates/

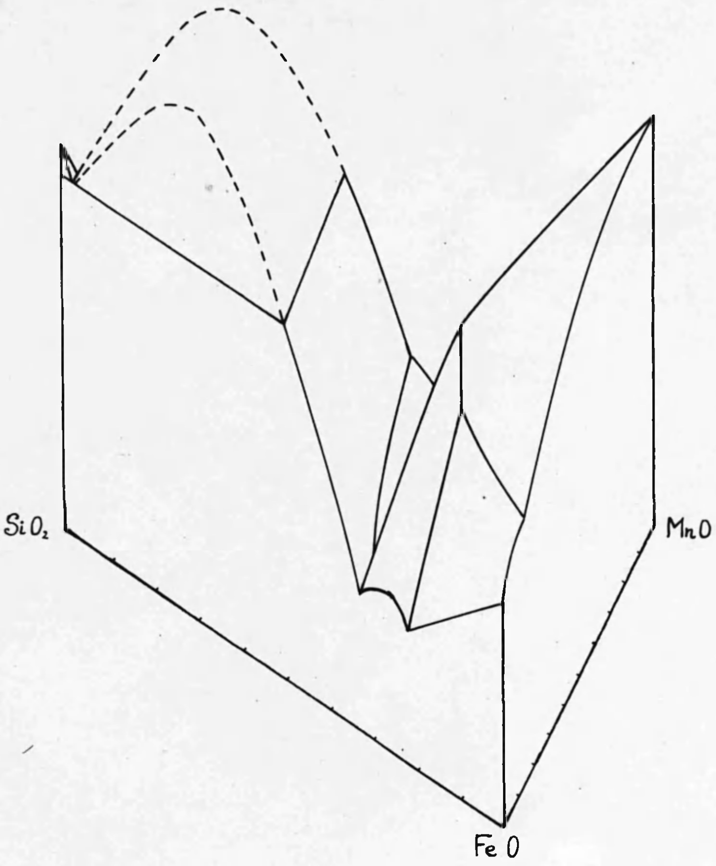


Fig. 1 FeO-MnO-SiO_2 equilibrium diagram.

silicates while above this figure, vogtite appears as a separate phase. From the ternary diagram FeO-MnO-SiO_2 (Fig.1), it will be seen that thesecompositions correspond to the liquidus surface representing saturation with silica. A surprising feature of the analysis mentioned above, is that slags in which the MnO has been increased at the expense of the FeO carry higher percentages of silica, while according to the equilibrium diagram the saturation values of FeO and MnO are about the same. White (2) suggests that this may be due to MnO increasing the fluidity, though there is no evidence to show that the effect of MnO is greater than that of FeO in this respect. This would imply that viscosity, rather than saturation with SiO_2 is the limiting factor in the SiO_2 content of acid slags.

The constitution of the liquid slag is still a matter of controversy, due to insufficient data and the difficulties of investigation but there is evidence to show that compounds can exist in liquid slags. Discontinuties in viscosity curves of liquid silicates have been found by Rait and Hay (3), Rait, McMillan and Hay (4) Preston (5) and Herty (6) and can only be explained by the existence of compounds such as $CaO.SiO_2$and $Na_2O.2SiO_2$ in the liquid state. Chemical evidence is also available in that SiO_2 increases the stability of FeO and CaO increases that of Fe_2O_3, which suggests that ferrous silicates and calcium ferrites are at at least only partially dissociated. Another approach is by consideration of slag-metal relationships , for example, the manganese reaction:-

$$MnO + Fe = FeO + Mn$$

The equilibrium constant of this equation is

$$K = \frac{[Mn] \quad [FeO]}{[MnO] \quad [Fe]}$$

$$= \frac{(FeO) \; L_{FeO} \; [Mn]}{(MnO \; L_{MnO}}$$

where ( ) represent concentration in the slag and [ ] concentration in the metal and L_{FeO}, L_{MnO} the partition coefficients. The partition coefficient for FeO is smaller for acid than for basic slags [Körber (7) and Körber and Oelsen (8)] , showing that part of the FeO must be in combination with SiO_2. The value of K_{Mn} is also smaller for acid slags than for basic slags, not all the difference being accounted for by the variation of L_{FeO}. Some of the MnO must therefore also be combined with SiO_2. Evidence about which silicate is present is more conflicting but White (2) concludes that the meta-silicates $MnO.SiO_2$ and $FeO.SiO_2$ both exist in the liquid state but that the orthosilicates are almost completely dissociated.

There is also the further proposition, as yet unproved, put forward by Martin and Derge (9) and Herasymenko (10) that molten silicates undergo electrolytic dissociation.
This is probably at least partly true and experiments on the electrical conductivity of slags might yield some information on this point.

Chapter II.

The composition and temperature of the liquid slag control the viscosity and it is on the viscosity of the slag that much of the success of the steel making process depends. In general, it may be said that there are three important aspects of steel making in which the viscosity of the slag plays a vital part. These are:-

1. steel refining process
2. attack on refractories
3. formation of non-metallic inclusions in the steel.

1. Steel-refining process

The steel-refining process consists essentially of the oxidation of certain elements in the charge and the transfer of the products to the slag, followed by deoxidation of the metal. In the acid open hearth, the three main elements to be removed are carbon, silicon and manganese, the basicity of the slag being too low to allow of any appreciable removal of sulphur and phosphorus. The slag acts as a medium for the transfer of the necessary oxygen from the atmosphere to the metal and the principal constituent in the slag for this purpose is free FeO. At the surface of the slag, FeO is being continually oxidised to Fe_2O_3, while at the slag-metal interface, Fe_2O_3 is being continually reduced by contact with metallic iron. This may be represented by the following equations.

At the slag surface $2FeO + \frac{1}{2}O_2 = Fe_2O_3$

At the slag-metal interface $Fe_2O_3 + Fe = 3FeO$

The oxidising power of the slag depends on the Fe_2O_3/FeO ratio. In simple iron oxide melts this ratio varies directly with the oxygen pressure and inversely with temperature. In the presence of other oxides, this equilibrium is upset and the Fe_2O_3/FeO ratio increases with lime and decreases with silica, due to the tendency of lime to form ferrites with Fe_2O_3 and of silica to form silicates with FeO. This difference is illustrated in basic slags where, with higher lime content, the Fe_2O_3/FeO equilibrium ratio is higher and gas oxidation proceeds more rapidly.

FeO reacts with the metalloids according to the following equations.

$$C + FeO = CO + Fe$$

$$Si + 2FeO = SiO_2 + 2Fe$$

$$Mn + FeO = MnO + Fe$$

The SiO_2 and MnO so formed dissolve in the slag. The FeO in the metal is thus being constantly reduced and has to be replaced from the slag, where the concentration is kept up by gas and ore oxidation. The actual speed of all the reactions is far greater than the speed with which the reacting substances can be brought together. The speed with which they do take place depends to a large extent on the viscosity of the slag and the degree of agitation. It is well known that the composition of a slag may be favourable for the elimination of a certain element but its viscosity may be too high to allow the reaction to occur. On the other hand, the viscosity of the slag may be increased towards the end of the process simply to slow down the rate of reaction.

The rate of heat transfer to the metal also depends on the viscosity of the slag since heat transfer by convection is more rapid than by conduction. The more fluid the slag, the greater the heat transferred to the bath.

Viscosity varies very rapidly with temperature, the higher the temperature the lower the viscosity. With regard to composition, the viscosity increases with increase in SiO_2 content but here the information is almost entirely qualitative. Thus Herty (11) states that in the simple system MnO-SiO_2, slags containing 10 to 50 per cent SiO_2 are fluid, while with higher SiO_2 content, the viscosity increases rapidly. Similarly in the ternary system, FeO-MnO-SiO_2, increase in the ratio of SiO_2 to (MnO + FeO) increases the viscosity. Control of the viscosity of an acid slag is therefore effected by adjusting the ratio of bases to silica. If the MnO content of the slag is low as may happen with low manganese iron, discreet additions of lime can be added to decrease the viscosity and keep the FeO content low.

(2) Attack on Refractories.

The attack of refractory materials by slags is a complex reaction which depends on many factors, both chemical and physical. This subject has been well reviewed by Rait and Green. (12).

Chemical Factors.

A study of the chemical nature of slagging is greatly facilitated by a knowledge of equilibrium conditions in spite of the fact that such conditions seldom obtain in practice. Equilibrium diagrams of the various components of slags and refractories indicate the reactions most likely to take place and the melting points of the products formed. If the product melts at a temperature higher than that of service there is no serious slagging. If the product is low melting, the extent of the slagging depends on the rate of the reaction. It is sometimes found that even when a slag and refractory can react to form a low melting constituent the rate of reaction is so slow that little corrosion then takes place. In such cases, the acidity and basicity of the slag and refractory are of secondary importance. Temperature greatly influences the rate of reaction and a small increase in temperature may double the rate of reaction.

Physical Factors.

One of the physical factors affecting the rate at which reaction proceeds is the velocity of the slag. The higher the velocity, the greater is the supply of fresh slag to the refractory surface. The flow of the slag may be either streamline or turbulent depending on the velocity and the viscosity.

Turbulent motion is even more effective in presenting fresh slag to the refractory so that it is desirable to keep the velocity low and the viscosity high. High viscosity also decreases the rate of diffusion through the slag and thus decreases the rate at which slagging proceeds.

The degree of actual slag penetration into the refractory depends on the physical nature of both the slag and of the refractory. While slag penetration has not yet been quantitatively correlated with such properties of the refractory as porosity and permeability, it is certain that it does depend on the number, size, type and distribution of the pores. It is generally accepted that if the porosity and permeability are low, slag penetration is low, but high porosity need not be detrimental if the pore size is very small, since the resistance offered to penetration of slag by capillary forces varies inversely with the third power of the radius of the pore. Slag penetration by capillary attraction also varies directly with the surface tension and inversely with the viscosity of the slag and with the contact angle between the slag and the refractory. Decrease in the viscosity of a slag is always associated with increased penetration and attack. If the composition of the slag remains unaltered, the viscosity can only be decreased by an increase in temperature and it is found in practice that the penetration can be greatly increased by a very small rise in temperature.

Thus the viscosity-temperature coefficient of the slag is also important and the depth of penetration is further affected by the temperature gradient through the refractory. If the outer wall be cooled, there is a sharp temperature gradient, a sharp increase in the viscosity of the slag immediately behind the working face and penetration is slowed down. The outer wall may even be cooled sufficiently to render the slag on the surface more viscous and lower the attack there.

In addition to the viscosity of the slag, the viscosity of the liquid product also affects the degree of penetration and attack. After slagging has begun, further attack depends not only on the flow of the slag through the pores but also on diffusion of the slag through the liquid reaction product which tends to fill the pores and on diffusion of that product away from the interface between the slag and the refractory. The lower the viscosity of the product the greater is the rate of diffusion and hence slag attack.

Investigators differ in their estimation of the relative importance of the physical and the chemical effects on slagging but are all agreed that increase in temperature increases all the factors which promote and maintain slag attack. Among these factors the viscosity of the slag and of the reaction product is of primary importance but there is too little data yet available to make quantitative conclusions.

(3) Formation of non-metallic inclusions.

Non-metallic inclusions are formed in steel in many ways but the two most prolific sources are the deoxidation process and the attack of the slag and metal on the refractories with which they come in contact.

Deoxidation involves the addition of manganese, silicon and aluminium to the steel and results in the formation of inclusions of MnO, SiO_2, Al_2O_3 and FeO either separate or in combination with each other. These slag particles can only escape by rising to the surface and the velocity with which they rise is defined by Stokes' equation:-

$$v = \frac{2g}{9\eta} \cdot r^2 (d-d_1)$$

where v = rising velocity

r = radius of slag particle

η = coefficient of viscosity of the molten steel

d = density of steel

d_1 = density of slag

Since the velocity of rise depends on the square of the radius of the particle, any factor which promotes coalescence of small slag particles results in cleaner steel. Two such factors are high surface tension and low viscosity of the liquid inclusion. Surface tension is the more important but little is known as yet about this property of slags.

The viscosity of the slag inclusion is determined by its temperature and composition. The Higher the temperature the lower the viscosity both of the slag and the steel and the easier it is for the particles to coalesce and rise to the surface. The influence of composition on viscosity is illustrated by the behaviour of the different types of inclusions. In the extreme case, simple oxide inclusions such as SiO_2, Al_2O_3 and MnO have melting points above that of steel and hence are usually solid before they can begin to coalesce: their viscosity therefore does not matter.

If the inclusion is rich in silica, due to an over-addition of silicon, it has a high melting point and a high viscosity. Correct adjustment of the proportion of silicon and manganese added, results in the inclusion having a composition in the lowest melting region of the ternary system $FeO-MnO-SiO_2$. It is known qualitatively that this region has also a low viscosity and such inclusions are found in practice to result in cleaner steel.

The other source of non-metallic inclusions is refractory attack by slag and steel. Rait (13) has shown that liquid steel, particularly if the manganese content is high attacks casting-pit refractories to give manganese alumino-silicate inclusions. The reaction take place in two stages:-

(1) The manganese in the steel reacts with the free silica of the firebrick to give manganese oxide and silicon. $2Mn + SiO_2 \rightleftharpoons 2MnO + Si$

(2) The MnO formed reacts with the alumino-silicate refractory to give a manganese alumino-silicate slag.

The composition of these inclusions is closely related to that of the refractory from which they are derived and is quite different from that of an acid open hearth slag. The latter, when carried along with the steel, also attacks casting pit refractories forming inclusions of $MnO-FeO-Al_2O_3-SiO_2$. The degree of attack and therefore the number of inclusions formed, depends on the factors discussed in the previous section.

From a consideration of these three aspects of the steelmaking process, it can be seen that the requirements for slag viscosity are conflicting. In steel refining it is better to have a slag of low viscosity in order to increase the rate of slag-metal reactions and the rate of heat transfer; even here, however, if the viscosity is too low, the slag may be over-oxidised. On the other hand, a slag with a viscosity low enough to be eminently suitable for steelmaking may result in very severe attack on the refractories and an increase in inclusions. The slag inclusion itself is more easily removed when its viscosity is low.

Obviously a compromise between these two opposing influences must be reached. To arrive at op timum conditions, the first essential is quantitative information on the variation of viscosity with composition and temperature of open hearth slags. The present research was undertaken in an effort to fill in this gap in the existing knowledge of the properties of slags. As an initial step in the compilation of viscosity data on acid slags, the effect of MnO on the viscosity was investigated by systematic observations on slags in the binary system MnO-SiO_2.

Chapter III.

The coefficient of viscosity has been defined by Hatschek (14) as the force required per unit area to maintain unit gradient of velocity between two layers of liquid unit distance apart. When the coefficient (η) is expressed in dynes.secs/$_{\mathrm{cm}}2$ the unit of viscosity is the poise. The methods available for measuring the viscosity of liquids at high temperatures are comparatively few and can be classified as follows:-

(1) Capillary flow
(2) Falling sphere
(3) Concentric cylinder
(4) Logarithmic decrement

The classical work on viscosity was carried out by Poiseuille who measured the flow of liquids through capillary tubes and modifications of his method are still the most commonly used for finding the viscosities of liquids at ordinary temperatures. The application of the method to liquids at high temperatures is limited because of experimental difficulties such as the large number of capillary tubes of different bore required,the introduction of the liquid into the tube at high temperatures and the observation of the flow through the tube. The only high temperature viscometer based on the principle of flow is the instrument designed by Herty (6) for use in steel plants. It consists of a split steel mould containing a horizontal channel $\frac{1}{4}$ inch diameter and 10 inches long.

Slag is poured in through a funnel-shaped well at one end and the distance of flow along the tube is taken as a relative measure of viscosity. This instrument is useful as a rough guide in the steel melting shop but is not sufficiently accurate for measurement of absolute viscosities.

The falling sphere method is based on Stokes' Law governing the velocity of a sphere falling freely through a liquid. For high temperature work, the sphere is not allowed to fall freely but is suspended by a fine wire passing over a pulley so that its fall is controlled by counterbalancing weights. This introduces additional errors due to the effect of surface tension on the wire and friction losses at the pulley. To overcome this, the passage of a freely-falling sphere can be recorded by X-ray photographs at definite time intervals and various workers have used this method in determining the viscosity of molten glass. Another alternative is that devised by Hunter (15) who surrounded the crucible containing the liquid by platinum radio coils; as the sphere passed through each coil, a signal was excited, caught by a short wave receiver and recorded on an oscillograph. There is another defect in the falling sphere method in that the well-known Ladenburg correction of Stokes' formula does not hold unless the radius of the crucible is over five times that of the sphere. This condition is difficult to fulfil at high temperatures. A further difficulty lies in the fact that it is necessary to measure the density of the liquid at each temperature. One advantage of the method is that absolute values of viscosity can be obtained without resort to empirical calibration. The range of viscosity is from 40 to 10^5 poises and with the modern refinements mentioned,it has been used successfully for measuring the viscosity of glass. Its range, however, is much too high for very fluid liquids such as blast furnace and open hearth furnace slags.

The concentric cylinder method devised by Margules (16) has been that most commonly used for the determination of absolute viscosities of slags and glasses at high temperatures. It involves the measurement of the torque produced on one of a pair of concentric cylinders when the other is rotated at constant speed, the cylinders being separated with the liquid under test. Whichever cylinder is rotated, the method can be used to obtain absolute values of viscosity. The rotating inner cylinder type has a range of viscosity from 50 to 10^8 poises but its accuracy is very low below about 10 poises,since a large outer cylinder is required to prevent turbulent motion. The size of the outer cylinder is limited by the necessity of maintaining a uniform high temperature throughout the liquid. It has been used successfully for glasses and the more viscous range of blast furnace slags but is not suitable for the more fluid open hearth slags. The rotating outer cylinder type can be used for measuring viscosities in the range of 0.1 to 10^4 poises so that it is suitable for use with blast furnace and open hearth slags. It has the disadvantage that the rotation of the outer cylinder involves a much more complicated mechanism.

The logarithmic decrement method has frequently been used for finding the viscosity of molten metals and its application has recently been extended to slags and glasses. Rait and Hay (3), Endell, Heidtkamp and Hax (17) and McCaffery (18) have all investigated the viscosity of $CaO-SiO_2$ slags by this method and their results show close agreement. A disc or cylinder, suspended by a connecting rod and torsion tape in a liquid contained in an outer concentric cylinder, is made to oscillate about its own axis. The decrement is the ratio of two successive amplitudes and the viscosity of the liquid is proportional to the logarithm of the decrement.

The equation used is

$$\eta = \frac{\sqrt{DI}}{K\pi} \cdot \log_e l$$

where η = coefficient of viscosity of the liquid
D = torque per unit angle of twist of the torsion wire
I = moment of inertia of the oscillating body about the axis of oscillation
l = decrement
K = apparatus constant.

The range of the method depends on the factor $\frac{\sqrt{DI}}{K}$ and can be easily extended to higher viscosities by increasing D and I or decreasing K by altering the dimensions of the cylinders. With such adjustments the range is from 0.1 to about 50 poises and the method is therefore suitable for measuring viscosities of blast furnace and open hearth slags. It is probably the most accurate method available for use at high temperatures over the particular range of viscosity, from 0.1 to 15 poises, expected in open hearth slags. It has the advantage over the only other possible method, the rotating outer cylinder method, that it requires no complicated mechanism in the apparatus. In view of these factors, the logarithmic decrement method was selected for the present work. The underlying theory is developed in Chapter V.

Chapter IV.

Apparatus.

The measurement of the viscosity of open hearth slags is attended by the usual difficulties associated with any experimental work on liquid slags at high temperatures. The selection of a suitable apparatus is made easier by the very fact that the range from which to choose is so narrow. The first essential is a refractory material in which to hold the slag. The refractory must resist slag attack, should be strong, and for most methods of measurement, should have a low coefficient of expansion. Graphite was used by Herty (6), Feild and Royster (19), McCaffery (18) and Rait and Hay (3) in measuring the viscosity of blast furnace slags. It could not be used for open hearth slags, however, because MnO and FeO would be reduced by the carbon at high temperatures, and because an atmosphere of hydrogen is necessary to maintain the graphite, thus accentuating reducing conditions. For measurement of the viscosity of $MnO-SiO_2$ slags, Rait and Hay (3) used molybdenum but again this requires an atmosphere of hydrogen to prevent the formation of molybdenum oxide. Refractory oxides, such as beryllia, magnesia and zirconia have been proved unsuitable either through lack of resistance to slag attack or else through mechanical weakness and low spalling resistance. The most suitable materials as yet are platinum and platinum-rhodium alloys which have been used successfully by English (20) and by Preston (5) for glasses and by Endell (17) for slags. It has also been frequently suggested that the material chosen must be "wetted" by the slag but the significance of this point has been over-emphasized as shown by Adam (21) who points out that there is no such thing as "non-wetting" of a solid by a liquid. The material used in this research was platinum and the angle of contact between open hearth slags and platinum is certainly less than 90°. The furnace in which the measurements are to be carried out must be capable of reaching and maintaining a temperature of at least 1600°C. The most suitable type for this work is a wire-wound resistance furnace and in this case, the wire used was platinum (later platinum-rhodium) which avoided the necessity of using reducing atmospheres, which must be used with molybdenum or tungsten wire. The use of platinum, unfortunately, limits the temperature practically to 1600°C inside the working tube, since the melting point of platinum is only 1773.5°C. Platinum-rhodium wire allows a slight increase in the working temperature.

The original furnace (see figure 2) was contained in a brass cylindrical case, mounted on a base so that the bottom was closed, and fitted with three levelling screws. The furnace tube, which was also the working tube, was wound with platinum wire graded to give a uniform hot zone of 2 inches (the length of the crucible). An outer alundum sleeve protected the winding and the annular space between it and the casing was packed with crushed insulating brick. The bottom

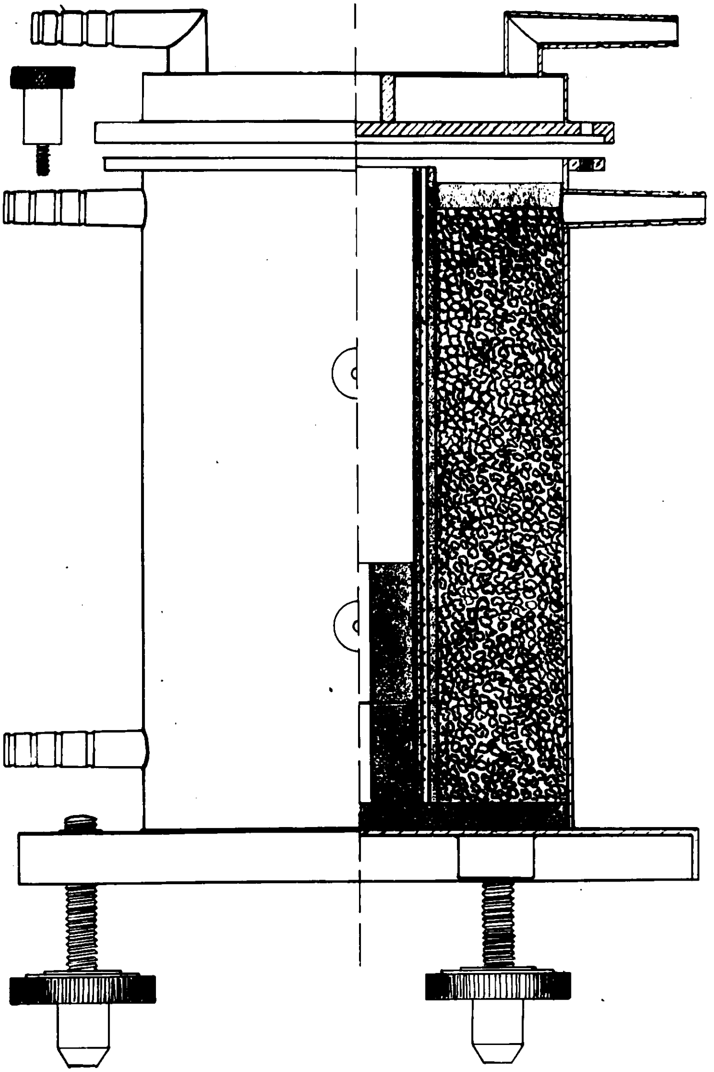


Fig. 2 Section of original viscosity furnace .

plate inside the furnace and the central stools to support the crucible were also made of alundum. The casing had three tubes, two of which could be used for passage of gas if necessary, while the third was used to lead in the thermocouple up through the stools to touch the bottom of the crucible. The furnace was covered with a water cooled lid with a hole in the centre.

The oscillating body (figure 3) of the viscometer was suspended by means of a phosphor bronze torsion tape from an adjustable bracket fixed to the water-cooled top. It consisted of a platinum bob and spindle held by a chuck to a cross bar,on which were two movable weights, the position of which determined the moment of inertia of the system. The small concave mirror above the cross bar reflected the image of a slit of light on to a circular scale and this enabled successive amplitudes to be read off. The platinum crucible, which held the slag and acted as the outer concentric cylinder, was perfectly cylindrical,2 inches high and 1 inch in diameter. The platinum bob already mentioned, was the inner cylinder, 1 inch high x $\frac{1}{4}$ inch diameter.

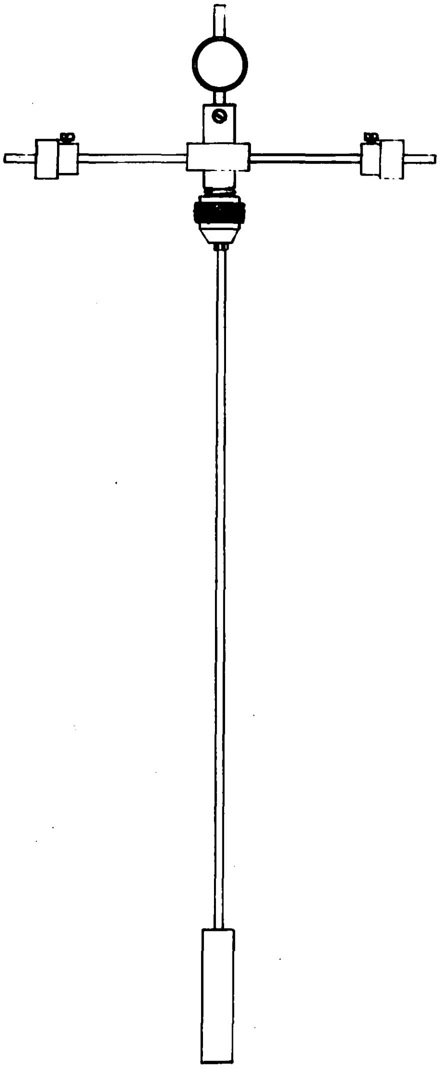


Fig. 3 Oscillating body.

Chapter V.

Theory of the Logarithmic Decrement Method.

In the logarithmic decrement method of measuring viscosities, a cylinder is suspended by a connecting rod and torsion tape and made to oscillate about its own axis in a liquid contained in an outer concentric cylinder. The theory of the method has been developed by Martin (22).

Let a cylinder radius "a" oscillate within a concentric cylinder radius "b", the annular space between being filled with viscous liquid. Consider the motion of an element of liquid.

Let ω = angular velocity of an element of liquid
r = radial distance of the liquid element from the axis of rotation
η = viscosity of the liquid
ρ = density of the liquid
then $\frac{\rho}{\eta} = \nu$ = Kinematic viscosity of the liquid
and $V = \omega r$ = velocity of the liquid element

The basic period differential equation of the motion is

$$\nu \left(\frac{\partial^2 \omega}{\partial r^2} + \frac{3}{r} \cdot \frac{\partial \omega}{\partial r} \right) = \frac{\partial \omega}{\partial t}$$

which can be put in the form

$$\nu \left(\frac{\partial^2 V}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial V}{\partial r} - \frac{V}{r^2} \right) = \frac{\partial V}{\partial t} \quad \text{--------- (1)}$$

neglecting the squares of the velocities.

This equation must first be solved for the case of the inner cylinder rotating at constant speed.

When r = b, V = 0 for all values of t - - - - - - - - (a)

" r = a, V = Vo = constant for all values of t - - - - - -(b)

" t = o, V = 0 for all values of r - - - - - - - - (c)

Let V = RT, where R and T are pure functions of r and t respectively.

Then the basic solution of (1) becomes

$$V = e^{-\nu\lambda^2 t}\left[A_\lambda J_1(\lambda r) + B_\lambda Y_1(\lambda r)\right]$$

where λ is any real constant, aA_λ and B_λ are arbitrary constants and $J_1(\lambda r)$, $Y_1(\lambda r)$ are Bessel Functions of the First Order and of the First and Second Kinds respectively.

If the boundary conditions (a), (b) and (c) be applied to this solution,

$$\text{then } \omega = \frac{V}{r} = \frac{a^2\omega_0}{b^2 - a^2}\left(\frac{b^2}{r^2} - 1\right) + \sum_\lambda a\,\omega_0\, a_\lambda e^{-\nu\lambda^2 t}\frac{1}{r}\left[J_1(\lambda r)Y_1(\lambda b) - J_1(\lambda b)Y_1(\lambda r)\right]$$

$$\text{where} \quad a_\lambda = \frac{2\lambda\left[J_1(\lambda b)\right]^3}{\left[J_1^2(\lambda b) - J_1^2(\lambda a)\right] J_1(\lambda a)}$$

and where the summation is made over the values of λ which are the real positive roots of the equation

$$J_1(\lambda a)\, Y_1(\lambda b) - J_1(\lambda b)\, Y_1(\lambda a) = 0$$

By the application of Duhamel's Theorem, the solution can be obtained for the case in which the angular velocity of the inner cylinder is a function of the time, $\omega(t)$.

This gives

$$\omega = \int_0^t \omega_0'(\tau)\left[\frac{a^2}{b^2 - a^2}\left(\frac{b^2}{r^2} - 1\right) + \sum a\,a_\lambda e^{-\nu\lambda^2(t-\tau)}\frac{1}{r}\left\{J_1(\lambda r)\,Y_1(\lambda b) - J_1(\lambda b)\,Y_1(\lambda r)\right\}\right]_\lambda^{d\tau}$$

The couple K acting on the inner cylinder is given by

$$K = 2\pi\eta a^3 \left(\frac{d\omega}{dr}\right)_{r=a}$$

from which the equation of motion of the cylinder becomes

$$I\frac{d^2\theta}{dt^2} + 4\pi\eta a^2\int_0^t \frac{d^2\theta}{dt^2}(\tau)\left[\frac{b^2}{b^2-a^2} + \sum \frac{J_1^2(\lambda b)}{J_1^2(\lambda b)-J_1^2(\lambda a)} \cdot e^{-\nu\lambda^2(t-\tau)}\right]d\tau + D\theta = 0 \text{----}(2)$$

where $\frac{d\theta}{dt} = \omega$

I = moment of inertia of the cylinder about its axis

and D = constant depending on the torsion tape.

It has so far proved impossible to solve this equation for θ. For the similar case of an oscillating sphere a general solution can be obtained (23) but it is too involved to be of any practical value. Simpler equations of the same type have been considered by Havelock (24) who solved the problem of a flat plate oscillating in a viscous liquid between two parallel planes. In this case, the complete solution for θ contains an infinite series of exponentials with real negative exponents, together with a pair of exponentials with exponents which may be complex, or real and negative. For the case of periodic motion these last two exponents are complex and give a damped oscillation.

If a similar type of solution can be expected for equation (2) then the damping factor in that equation will include a term in which the resistance is proportional to the velocity, together with two exponentials. It has been shown by Verschaffelt (25) that the final state of damped oscillation is reached after a very short time so that the two exponential terms may be neglected. This gives a first approximation to equation (2) of the form

$$I\frac{d^2\theta}{dt^2} + L\frac{d\theta}{dt} + D\theta = 0 \quad ---------- (3)$$

where $L = K\eta$ is the damping factor proportional to the velocity. This equation can now be solved for θ.

The auxiliary equation for the solution of equation (3) is

$$\mu^2 + \frac{L}{I}\mu + \frac{D}{I} = 0$$

$$\therefore \quad \mu = -\frac{L}{2I} \pm i\sqrt{\frac{D}{I} - \left(\frac{L}{2I}\right)^2}$$

$$= -p \pm iq$$

$$\text{where } p = \frac{L}{2I} \text{ and } q = \sqrt{\frac{D}{I} - \left(\frac{L}{2I}\right)^2}$$

Hence solution of equation (3) is

$$\theta = e^{-pt}(A\cos qt + B\sin qt)$$

If zero time taken at θ max ,

$$\theta \text{ max} = A\cos 0 + B\sin 0$$

$$\therefore \theta \text{ max} = A$$

when $\theta = 0$,

$$0 = Ae^{-pt}\cos qt + Be^{-pt}\text{Sin } qt$$

but $t \neq 0 \quad \therefore \text{Sin } qt \neq 0 \quad e^{-pt} \neq 0, \quad \therefore B = 0$

$$\therefore \theta = A^{-pt}\text{Cos } qt$$

$$\text{ie.} \quad \theta = A_e^{-\frac{L}{2I}t}\text{Cos}\left[\sqrt{\frac{D}{I} - \left(\frac{L}{2I}\right)^2}\right]t$$

<u>To find the Period of Oscillation</u>:-

$$\theta = A_e^{-pt}\text{Cos } qt$$

At θ max , $\frac{d\theta}{dt} = 0 = -pAe^{-pt}\cos qt - Ae^{-pt}q\sin qt$

$\therefore -p\cos qt = -q\sin qt$

$\therefore \tan qt = -\frac{p}{q} = n\pi - p/q$

$\therefore t = \frac{1}{q}\left[n\pi + \tan^{-1}(-\frac{p}{q})\right]$

$t_1 = \frac{1}{q}\tan^{-1}(-\frac{p}{q})$

$t_2 = \frac{1}{q}\left[\pi + \tan^{-1}(-\frac{p}{q})\right]$

$t_3 = \frac{1}{q}\left[2\pi + \tan^{-1}(-\frac{p}{q})\right]$

$\therefore t_2 - t_1 = \frac{\pi}{q}$ $\qquad t_3 - t_2 = \frac{\pi}{q}$

$\therefore t_3 - t_1 = \frac{2\pi}{q} = T$ (Period of Oscillation)

And since $q = \sqrt{\frac{D}{I} - \left(\frac{L}{2I}\right)^2}$

$$T = \frac{2\pi}{\sqrt{\frac{D}{I} - \left(\frac{L}{2I}\right)^2}}$$

<u>To find the amplitudes:-</u>

At time t_1 , $\theta_1 = Ae^{-pt_1}\cos qt_1$

" " t_2 , $\theta_2 = Ae^{-pt_2}\cos qt_2$

Now $t_2 = t_1 + \frac{\pi}{q}$

$\therefore \theta = Ae^{-p(t_1 + \frac{\pi}{q})}\cos q(t_1 + \frac{\pi}{q})$

$= Ae^{-pt_1}e^{-p\frac{\pi}{q}}\cos qt_1$

$$\therefore \frac{\theta_2}{\theta_1} = - \frac{Ae^{-pt_1}e^{-p\frac{\pi}{q}}\cos qt_1}{Ae^{-pt_1}\cos qt_1} = - e^{-p\frac{\pi}{q}}$$

$$\frac{\theta_3}{\theta_2} = - e^{-\frac{p\pi}{q}}$$

(Sign is negative since θ_1 and θ_2 are on opposite sides of the zero)

$$\log_e \frac{\theta_2}{\theta_1} = - \frac{p\pi}{q}$$

$$\mathrm{Log}_e \frac{\theta_1}{\theta_3} = \frac{2p\pi}{q}$$

$$\text{i.e.} \quad \log_e \frac{\theta_1}{\theta_3} = \frac{\frac{L\pi}{I}}{\sqrt{\left[\frac{D}{I} - \left(\frac{L}{2I}\right)^2\right]}}$$

Now let $L = K\eta$ and $\log_e \frac{\theta_1}{\theta_3} = \log_e l$

$$\text{Then} \quad (\log_e l)^2 \left[\frac{D}{I} - \left(\frac{K\eta}{2I}\right)^2\right] = \left[\frac{K\eta\pi}{I}\right]^2$$

$$\therefore (\log_e l)^2 \left[DI - \tfrac{1}{4}(K\eta)^2\right] = (K\eta\pi)^2$$

$$K^2\eta^2\left[\tfrac{1}{4}(\log_e l)^2 + \pi^2\right] = (\log_e l)^2 DI$$

$$\therefore \eta = \frac{(\log_e l)\sqrt{DI}}{K\sqrt{1 + \frac{(\log_e l)^2}{4\pi^2}}}$$

$$\text{i.e.} \ \eta = \frac{\sqrt{DI}}{K} \cdot \log_e l \quad (\text{where } \log_e l \text{ is small}) \qquad (4)$$

This relationship is perfectly valid once the oscillation has settled down to a pseudo-steady state and it becomes justifiable to neglect the exponential terms in the derivation of equation (3).

If I, D and K are constant, equation (4) can therefore be written

$$\eta = C \log_e l \text{ - - - - - - - - - - } (5)$$

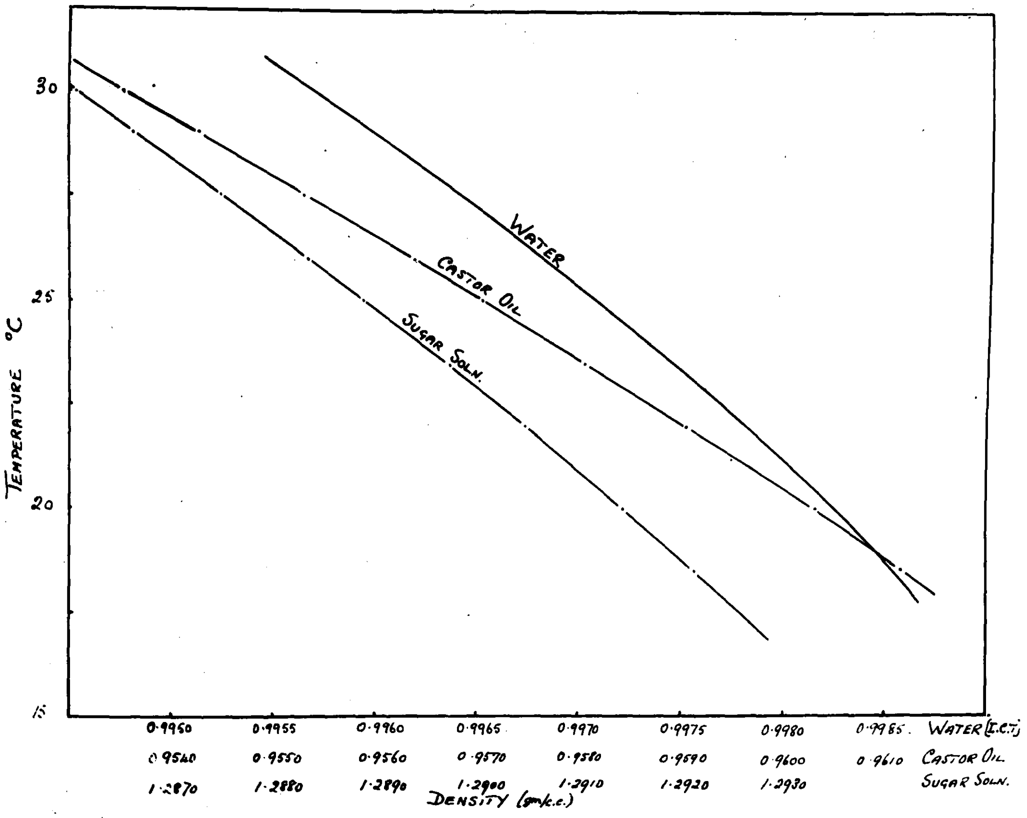


Fig. 4 Variation of density with temperature for various liquids.

Thus η varies directly with $\log_e l$ and by the use of liquids of known viscosity a value for the constant can be found experimentally.

Calibration. The liquids used for calibration were 60% sucrose solution, glycerine/water solution and castor oil. The viscosity of each liquid was determined in capillary viscometers, the instruments used being the Institute of Petroleum Technology Standards No. 3 and No. 4. The density of each liquid was found over a range of temperature and the density/temperature curves obtained are shown in figure 4.

Two viscometers were necessary because the time of flow of castor oil was too long in No. 3 and that of the sucrose solution was too short in No. 4. The No. 3 instrument was calibrated with sucrose solution and the time of flow of the glycerine/water solution was found in No. 3 and also in No. 4 which was the instrument used for castor oil. The glycerine/water solution was used merely as a bridge between the two instruments and determination of its density and viscosity was not necessary. The temperature was kept constant during the experiment by immersion of the instrument in a thermostatic tank. The times of flow for the sucrose and glycerine solutions were found at 25°C only, while that for castor oil was found over a range of temperature.

The following results were obtained:

Density of sucrose solution at 25°C = 1.2865 gms/cc (ρ_s^{25})

Time of flow in No. 3 of sucrose solution at 25°C = 128.0 seconds (S_3^{25})

From the standard tables of the Institute of Petroleum Technology, viscosity of the sucrose solution at 25°C

= 0.4677 poise

Time of flow of glycerine solution in number 3 at 25°C

= 545.9 seconds (G_3^{25})

Time of flow of glycerine solution in number 4 at 25°C

= 92.6 seconds (G_4^{25})

Let density of glycerine solution at 25°C be ρ_g^{25}

Then $\eta_g^{25} = \eta_s^{25} \dfrac{\rho_g^{25} \times G_3^{25}}{\rho_s^{25} \times S_3^{25}}$ where η_g^{25} = viscosity of glycerine at 25°C.

and $\eta_c^T = \eta_g^{25} \dfrac{\rho_c^T \times C_4^T}{\rho_g^{25} \times G_4^{25}}$ and η_c^T = viscosity of caster oil at T °C.

Substituting for η_g^{25}

$$\eta_c^T = \frac{\eta_s^{25}\, \rho_g^{25} \times G_3^{25}}{\rho_s^{25} \times S_3^{25}} \cdot \frac{\rho_c^T \times C_4^T}{\rho_g^{25} \times G_4^{25}}$$

$$= \frac{\eta_s^{25} \times G_3^{25}}{\rho_s^{25} \times S_3^{25} \times G_4^{25}} \left(\rho_c^T \times C_4^T \right)$$

The viscosity of castor oil at different temperatures could thus be calculated .

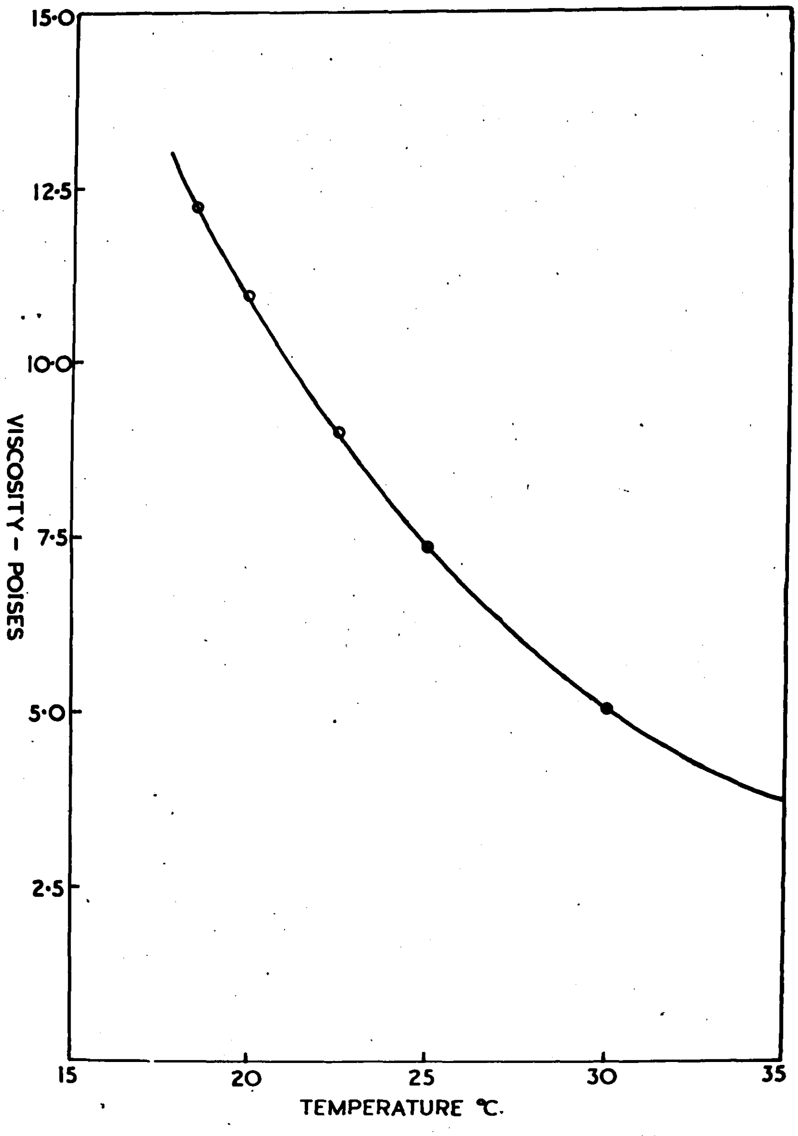


Fig. 5 Variation in viscosity of castor oil with temperature.

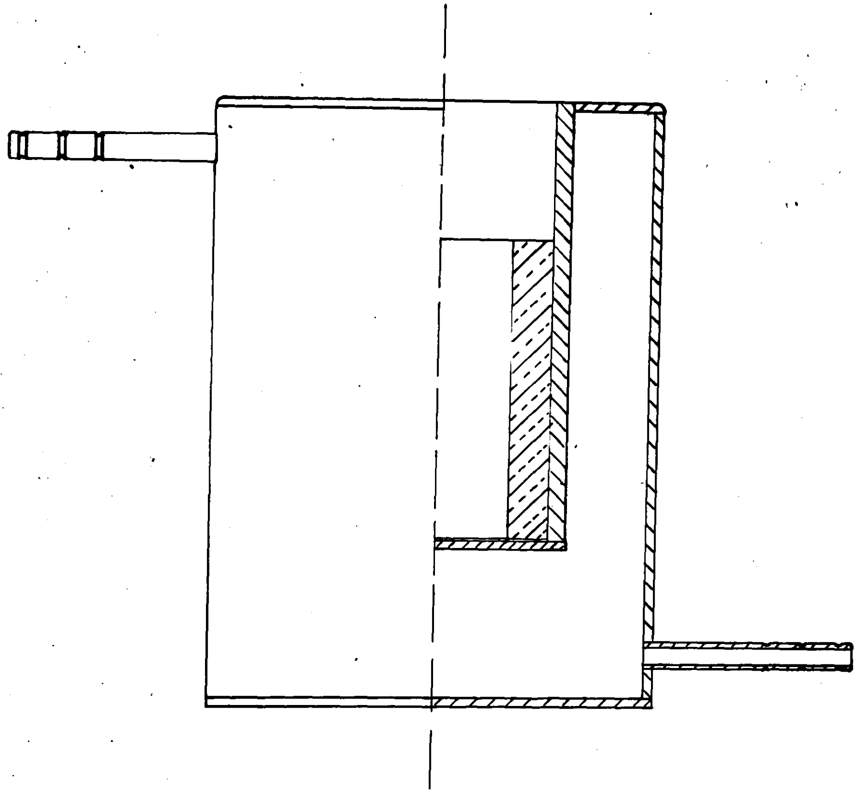


Fig. 6.. Water jacket .

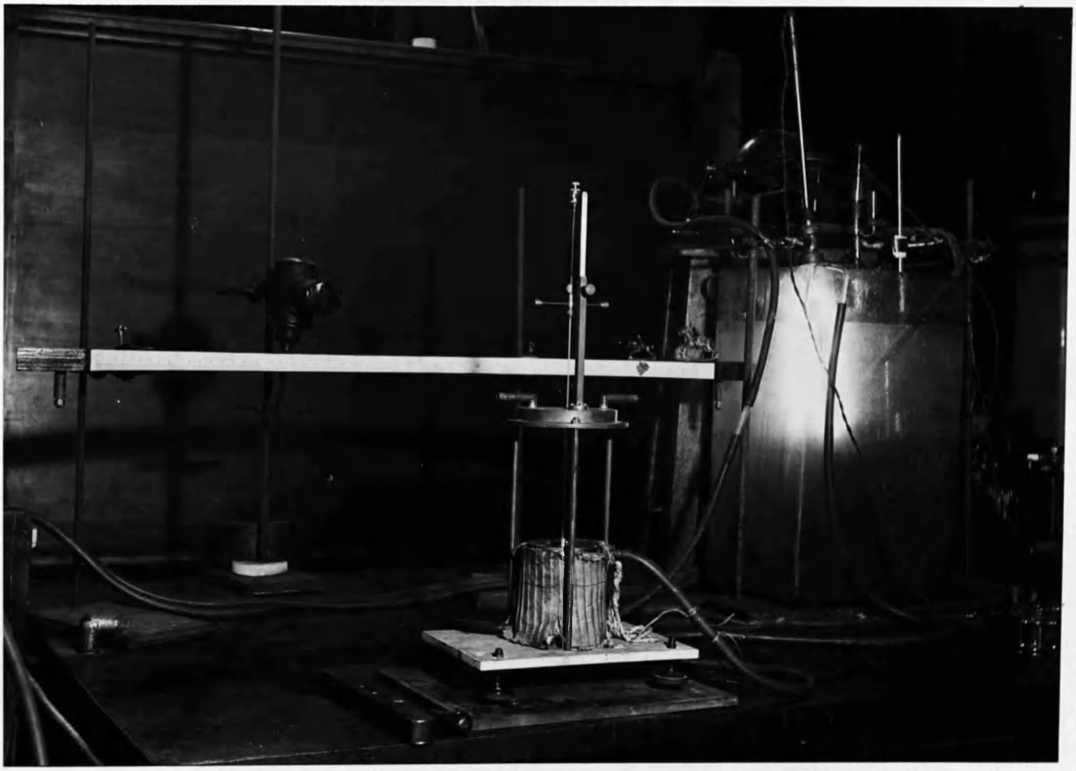


Fig. 7. Arrangement of viscometer for calibration.

Temperature °C	Density gms/cc.	Time of Flow Seconds	Viscosity Poises.
18.5	0.9612	760	12.23
20	0.9602	681	10.95
22.5	0.9587	561	9.01
25	0.9570	459	7.35
30	0.9535	314	5.01

Figure 5 shows the viscosity/temperature curve for castor oil obtained by plotting these values.

The castor oil was now used in the calibration of the logarithmic decrement apparatus. The crucible was held in the water jacket shown in figure 6 through which was pumped water from the thermostatic tank. The temperature of the castor oil was always measured immediately after taking readings to avoid any error due to a lag between the temperature in the crucible and that of the tank. The rest of the viscometer was set-up as shown in figure 7.

The crucible was filled to a certain height with castor oil, the spindle lowered to a standard depth, the beam of light focussed on the scale and the zero position noted. The spindle was then set oscillating and successive readings read off from the graduated scale. For each temperature, measurements were made at three values of the moment of inertia of the oscillating cylinder. At each temperature and for each value of the moment of inertia several readings were taken and an average value used. A typical set of results was as follows :-

Castor Oil.

Temperature	Zero	Scale Readings			Amplitudes		$\log_e l$
					a_1	a_3	
29.1°C	50.2	10.2	24.4	33.7	40	16.3	0.448
		1.3	19.1	30.5	48.9	19.7	0.450
		17.3	29.3	36.9	32.9	13.3	0.453
		7.4	23.0	32.6	42.8	17.6	0.444
		.3	16.0	29.6	50.5	20.6	0.448
		8.3	23.5	33.0	41.9	17.2	0.443
						Average	0.448

Using the η values from the viscosity-temperature curve for castor oil (figure 3) a graph was drawn relating $\log_e l$ to viscosity for three values of the moment of inertia. This is shown in figure 8 in which the gradient of each curve gives the value of the constant C in equation (5) for the corresponding moment of inertia I.

The equation then becomes

$$\eta = 12.00 \log_e l \qquad (\text{I large})$$

$$\eta = 6.58 \log_e l \qquad (\text{I intermediate})$$

$$\eta = 4.43 \log_e l \qquad (\text{I small})$$

An investigation was also made of the effect of end clearance and of height of liquid in the crucible on the determined value of the logarithmic decrement.

(1) Effect of end clearance.

If the end clearance, that is, the distance between the bottom of the outer cylinder and that of the inner cylinder, be small there will be an additional damping effect on the

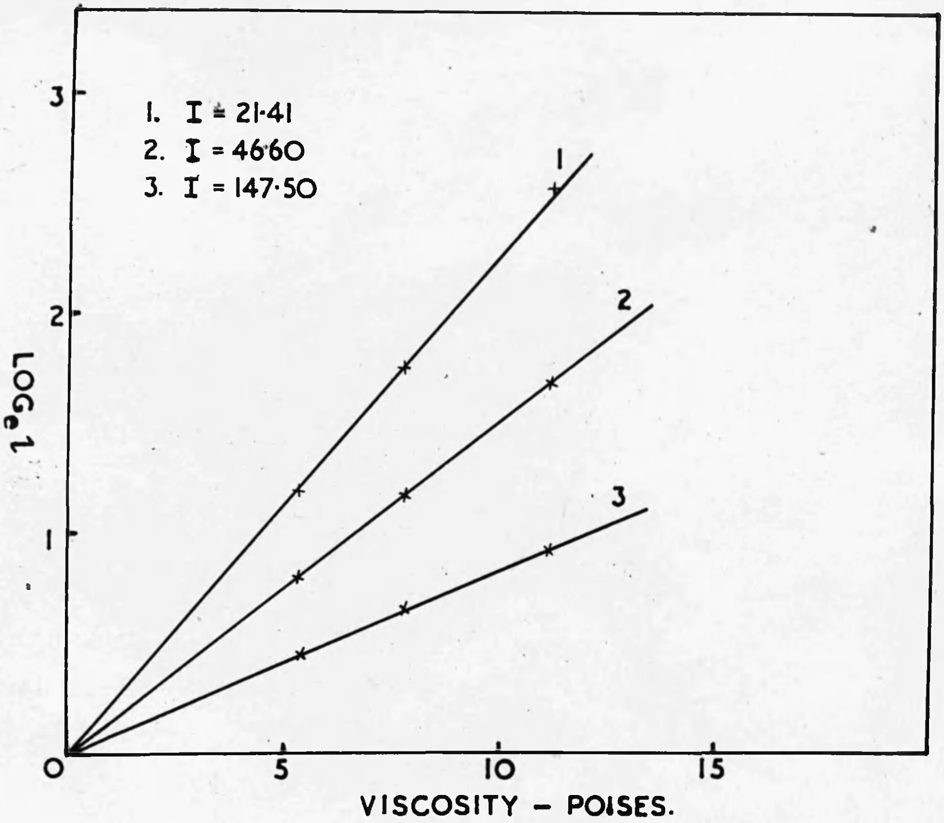


Fig. 8. Calibration graph. Variation of logarithmic decrement with viscosity.

motion of the inner cylinder. The end clearance at which this effect became negligible was found by experiment. The temperature and the volume of castor oil in the crucible were kept constant and the logarithmic decrement determined for different values of end clearance. The variation of $\log_e l$ with end clearance is shown in figure 9 from which it can be seen that the end effect on the logarithmic decrement is negligible when the end clearance is greater than 0.4 cm. It was therefore decided to work with an end clearance of 0.6 cm.

(2) Effect of height of liquid.

The inner cylinder is suspended from the torsion tape by means of a thin spindle which is, in effect, an additional inner cylinder, but of radius so small that it would be expected to have little effect on the motion. This was corroborated by determining the logarithmic decrement in castor oil with the temperature and end clearance constant and varying the height of liquid in the crucible. A different length of spindle was thus immersed at each determination. In figure 10 values of the logarithmic decrement are plotted against the length of cylinder + spindle immersed in the liquid. The curve shows that when the inner cylinder is totally immersed, further increase in the height of liquid has little effect and the logarithmic decrement remains practically constant. The spindle has thus a negligible effect on the motion. The working level selected is shown on the graph and is equivalent to a height of liquid 1 cm. below the top of the crucible.

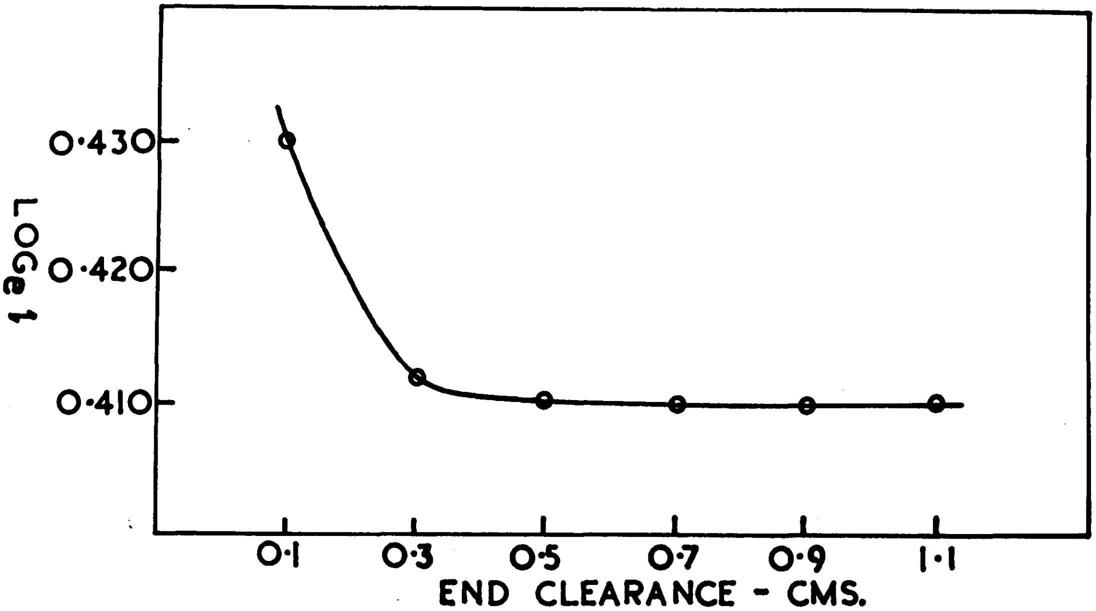


Fig.9. Variation of logarithmic decrement with end clearance.

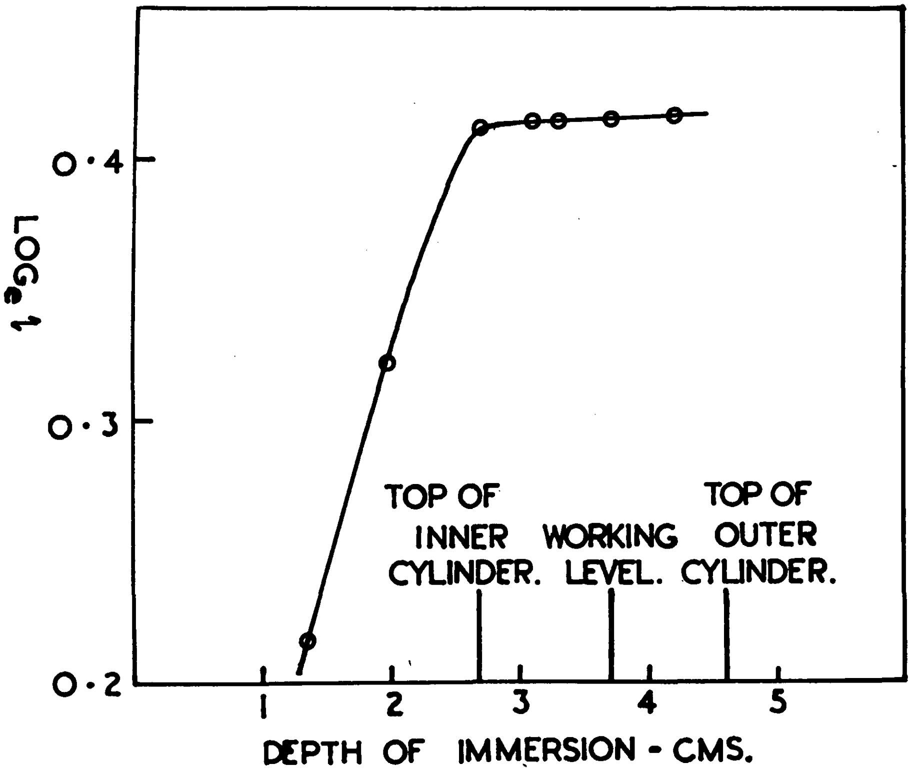


Fig.10. Variation of logarithmic decrement with depth of immersion of inner cylinder.

By selecting working values of end clearance and of height of liquid from the horizontal part of these two curves, any slight error in measurement arising from the immersion of the inner cylinder would have a negligible effect on the logarithmic decrement.

This empirical calibration served as a useful basis from which to begin the measurement of slag viscosities. A direct method of calculating η is to be preferred, however, if a solution of the equation of motion can be found.

Consider equation (4)

$$\eta = \frac{\sqrt{DI}}{K\pi} \log_e l$$

It is evident that in order to calculate the coefficient of viscosity it is necessary to evaluate D, I and K

$$D = \frac{NJ}{l}$$

where N = modulus of elasticity of the torsion tape

J = moment of inertia of the torsion tape

l = length of the torsion tape

J could be calculated from the mass and dimensions of the tape but N could not be measured directly and only an approximate value could be obtained from tables. D was therefore determined experimentally. A brass cylinder of radius 0.4743 cm. and mass 49.8070 gms was suspended vertically from the torsion tape and the period of oscillation (T_s) found.

T_s is related to the constant D and moment of inertia I_s of the cylinder by the equation

$$T_s = 2\pi\sqrt{\frac{I_s}{D}}$$

$$\text{i.e. } D = \frac{4\pi^2 I_s}{T_s^2}$$

$$I_s = \tfrac{1}{2} Mr^2 = 5.6$$

The time taken for 50 oscillations was found to be 58 seconds.

$$\therefore T_s = \frac{58}{50} = 1.16 \text{ seconds}$$

Substituting for I_s and T_s

$$D = 164.5$$

Again, the moment of inertia I of the oscillating body could not be calculated directly from the mass ~~and dimensions~~ of the latter, because it was made up of too many components. The moment of inertia was therefore obtained from the periods of oscillation of the body and the brass cylinder used in the above calculation of D.

If the period of oscillation be T

$$\text{then } \frac{T}{T_s} = \sqrt{\frac{I}{I_s}}$$

$$\therefore I = \frac{T^2 I_s}{T_s^2}$$

The time taken for 50 oscillations was found to be 297.5 seconds.

$$\therefore T = \frac{297.5}{50} = 5.95 \text{ seconds}$$

$$T_s = 1.16 \text{ seconds} \quad I_s = 5.6$$

$$\therefore I = 147.5$$

Substituting these values for I and D, equation (4) now becomes

$$\eta = \frac{164.5 \times 147.5}{\pi} \cdot \frac{\log_e 1}{K}$$

$$\text{i.e. } \eta = \frac{49.6}{K} \log_e 1 \text{ - - - - - - - - - - - - - - - } (6)$$

The term K is the factor proportional to the velocity in equation (2) and it has been stated that a rigid solution of this equation is impossible. Rait (26), however, has published a private communication from Andrade concerning this problem.

Andrade states: "What is required is a full solution of the problem of an oscillating cylinder surrounded by a concentric cylindrical vessel, the interface being filled with viscous liquid~~s~~. It is impossible to solve this problem mathematically for the general case. A general solution is possible for the sphere and for very viscous liquids, a simple solution can be obtained if certain conditions are obeyed. It seems highly probable that these conditions can be extended to the cylinder.

If the differential equation of the oscillating body is

$$I \frac{d^2\theta}{dt^2} + L \frac{d\theta}{dt} + D\theta = 0$$

it can be shown that, if there is no phase difference between the oscillating shells of liquid, the following expressions hold.

For a sphere of radius "a" inside a sphere of radius "b"

$$L = 8\pi\eta a^3 \frac{b^3}{b^3 - a^3}$$

For a cylinder of radius "a" inside a cylinder of radius "b", where h is height of cylinder

$$L = 4\pi\eta h \frac{a^2 b^2}{b^2 - a^2}$$

in deducing this for the sphere we have to assume that the real part of c^2d^2 and also of all powers of c^2d^2 is small compared with unity, where

$$d = b - a \quad \text{and} \quad c^2 = \frac{\rho}{\eta}\left[-\frac{\log_e l}{T} + i\frac{2\pi}{T}\right]$$

ρ = density of liquid
η = viscosity of liquid
$\log_e l$ = logarithmic decrement
T = period of oscillation

If we extend this result for the sphere to the case of the cylinder we conclude that the approximation is justified if

(1) $(b - a)$ is small and also "a" fairly small
(2) $\frac{\log_e l}{T}$ which represents the damping, is small
(3) $\frac{2\pi}{T}$ is small
(4) $\frac{\rho}{\eta}$ is small "

The expression proposed by Andrade for L, where $L = K\eta$ is

$$L = 4\pi h\eta \frac{a^2 b^2}{b^2 - a^2}$$

This expression is derived from a consideration of steady motion. If a cylinder of radius "a" is rotating with uniform angular velocity ω_0 in a liquid bounded externally by a coaxial cylinder radius "b", the frictional couple on the inner cylinder is

$$-4\pi h\eta \frac{a^2b^2}{b^2 - a^2} \cdot \omega_0 .$$

Andrade has applied the expression obtaining for steady motion to the case of oscillatory motion. The application must be limited, because in oscillatory motion ω_0 is continually changing and the frictional couple on the inner cylinder is proportional not to ω_0 but to $\frac{d\omega}{dr}$, where ω and r are the angular velocity and radius respectively of an element of liquid.

If equation (2)

$$I\frac{d^2\theta}{dt^2} + 4\pi\eta a^2\int_0^t \frac{d^2\theta}{dt^2}(\tau)\left[\frac{b^2}{b^2-a^2} + \sum \frac{J_1^2(\lambda b)}{J_1^2(\lambda b) - J_1^2(\lambda a)} \cdot e^{-\nu\lambda^2(t-\tau)}\right]d\tau + D\theta = 0$$

were capable of solution, it can be seen that the expression proposed by Andrade would be the first term in the factor proportional to the velocity and may therefore be a good first approximation. The more nearly the oscillatory motion approaches steady motion, the closer the approximation will be to the truth.

Realisation of the complete set of conditions stipulated by Andrade for the approximation to hold good seems to be impossible. Conditions (1) and (2) are incompatible in practice for when the annulus between the inner and outer cylinders, that is (b - a), is small, the damping effect $\frac{\log_e 1}{T}$

must

be large. The period of oscillation T can be increased by increasing the moment of inertia I within the limits of the apparatus. The logarithmic decrement will then be as small as possible but it will still increase as (b - a) decreases. There is also a practical limitation to the fulfilment of condition (1) in that when the cylinders are very close together, i.e. (b - a) very small, it is difficult to overcome the surface tension effect tending to draw the inner cylinder away from its central position and causing it to adhere to the outer cylinder.

Condition (3), that is $\frac{2\pi}{T}$ small, can be fulfilled in conjunction with any of the other conditions if the moment of inertia is large enough. Condition (4), i.e. ρ/η small, is outwith control since ρ/η is a physical property of the liquid. This condition is incompatible with condition (2) for, when the viscosity η of the liquid is high so that ρ/η is small and condition (4) fulfilled, the logarithmic decrement is large and condition (2) is vitiated. This can be partly overcome by increasing T and so decreasing the damping effect $\frac{\log_e l}{T}$. The moment of inertia of the oscillating cylinder, however, cannot be increased indefinitely and if the viscosity is high, the damping effect will be large. It is thus impossible to satisfy all the conditions at the same time.

Andrade derives these individual conditions from the original requirement that the real part of c^2d^2 and of all powers of c^2d^2

be small,

where $d = (b - a)$ and $c^2 = \frac{\rho}{\eta}\left[-\frac{\log_e l}{T} + i\cdot\frac{2\pi}{T}\right]$

It coes not necessaril y follow, however, that both c^2 and d^2 must be small, since if either factor be sufficiently small, the product will also be small. It appears that Andrade has laid down sufficient conditions, so that if they were all fulfilled, his approximation would definitely be justified. In practice it is impossible to satisfy all these conditions but if they were reduced to the minimum necessary, the approximation should still hold good.

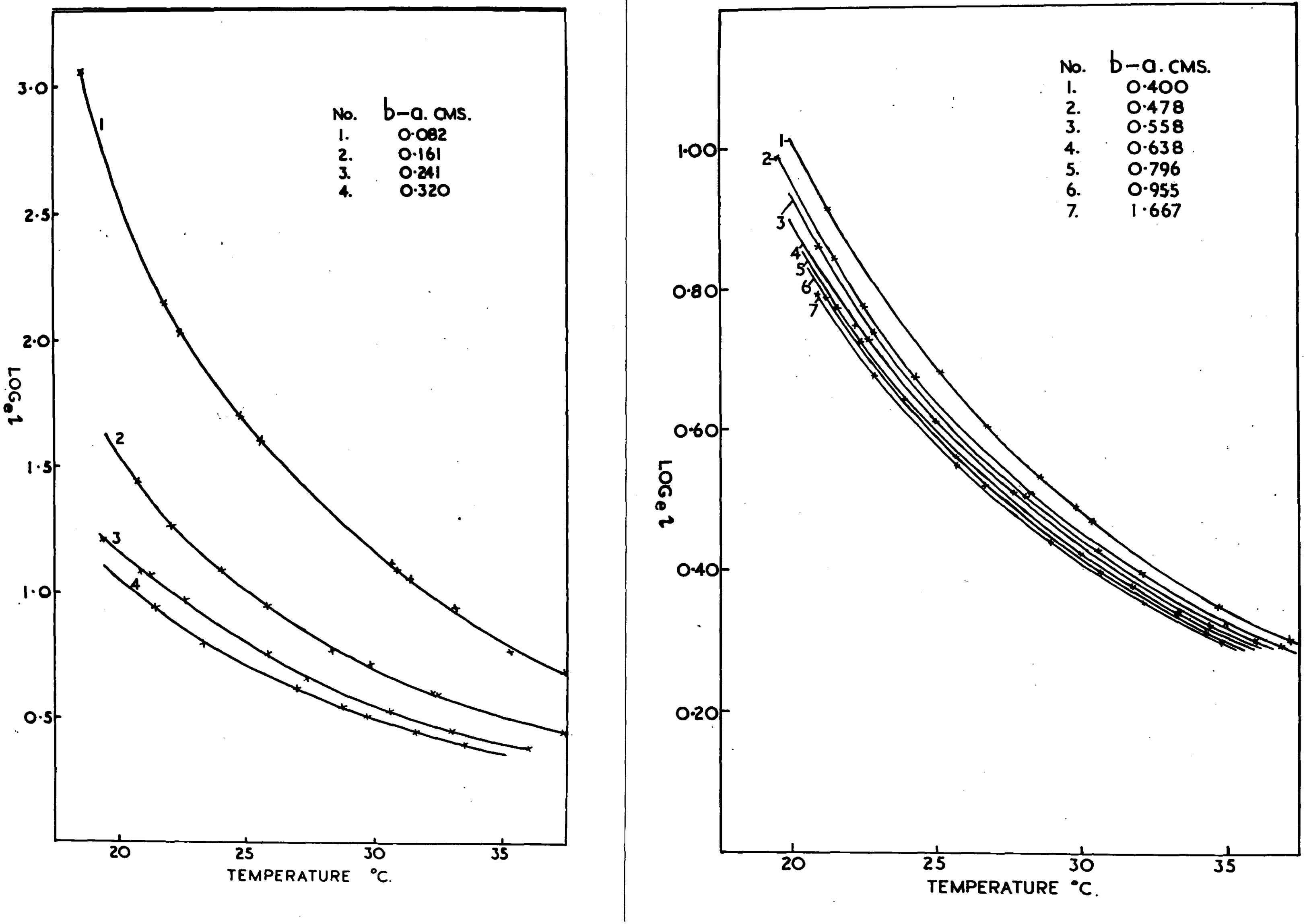
To summarise, $\frac{\rho}{\eta}$ is fixed by the liquid investigated; the moment of inertia and hence the period of oscillation can be fairly large independently of amy of the other conditions so that $\frac{2\pi}{T}$ is small; but $\log_e l$ is almost certainly large when $(b - a)$ is very small and conversely, in order that $\log_e l$ should be small, $(b - a)$ should be large. It therefore remained to be found which set of conditions, if either, would fit the Andrade approximation, $(b - a)$ small but $\log_e l$ large or $(b - a)$ large and $\log_e l$ small.

Experiments were undertaken to find the effect of $(b - a)$ and therefore of $\log_e l$ on the validity of the approximation. A series of determinations of η for castor oil was made and variation in $(b - a)$ was effected by altering the radius of the outer cylinder. The radius of the inner cylinder was kept constant, 0.315 cm as an alteration in its dimensions would have involved a redetermination of the moment of inertia. Initially, the radius of the outer cylinder was 0.397 cm so that (b - a) was 0.082 cm which was as small as was practicable. Values of logarithmic decrement were determined over a range of temperature from 20°C to 35°C. The radius of the outer cylinder was then increased by 0.08 cm and the logarithmic decrement again measured. This was repeated until the radius of the outer cylinder was 1.27 cm which was the radius of the crucible in the high temperature apparatus. The effect of a larger radius was found by using the water jacket itself as the outer cylinder. The variation of logarithmic decrement ($\log_e l$) with temperature for different values of (b - a) is shown in figures 11 and 12. The curves in figure 13 were then derived showing the variation in $\log_e l$ with (b - a) at four temperatures, that is, at four values of viscosity. When (b - a) is small, $\log_e l$ is large but as (b - a) increases, $\log_e l$ tends to a constant value.

Considering equation (6)

$$\eta = \frac{49.6}{K} \log_e l$$

it is evident that, at constant viscosity $\log_e l$ should vary directly with K and the graph of $\log_e l$ against K should be a straight line through the origin, If Andrade's value for K i.e. $K = 4\pi h \frac{a^2 b^2}{b^2 - a^2}$ be plotted against $\log_e l$ as in figure 14, it can be seen that the straight line relationship is only true when K is small, that is, when (b - a) is large, and $\log_e l$ small. When K is large and therefore (b - a) small, the determined values of $\log_e l$ lie above the straight line.



Figs. 11 and 12. Variation of logarithmic decrement with temperature in castor oil at different values of (b- a).

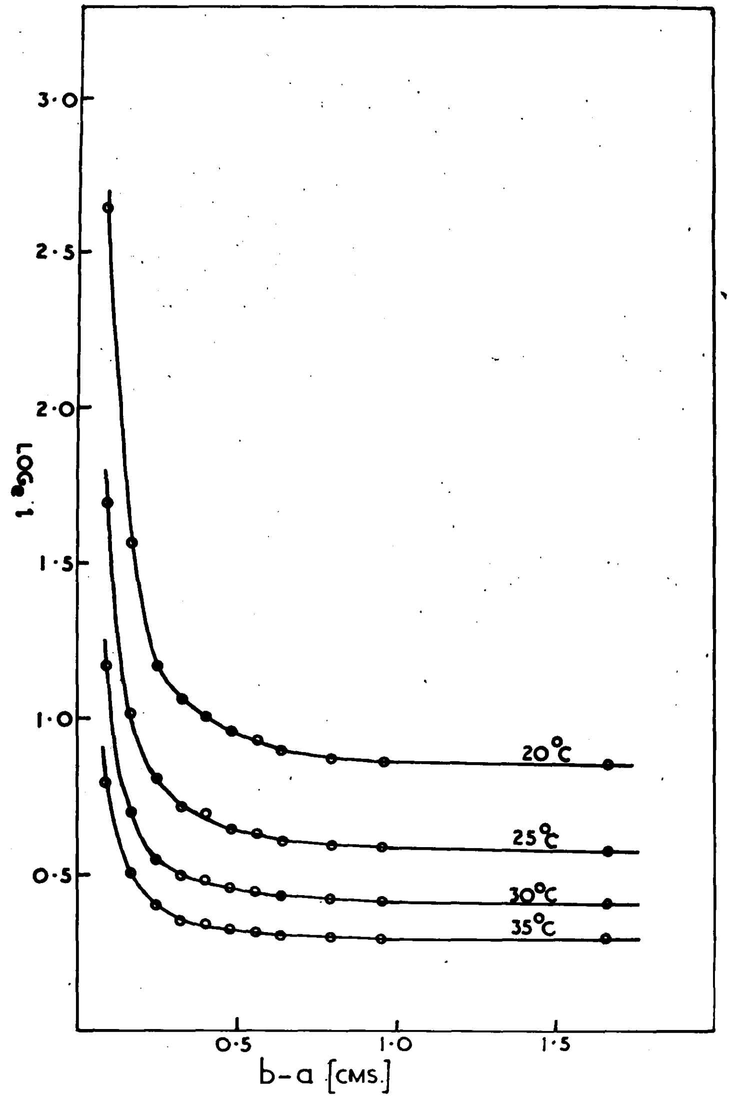


Fig. 13. Variation of logarithmic decrement with (b− a)[annulus between inner and outer cylinders] at different temperatures, that is, at different values of viscosity.

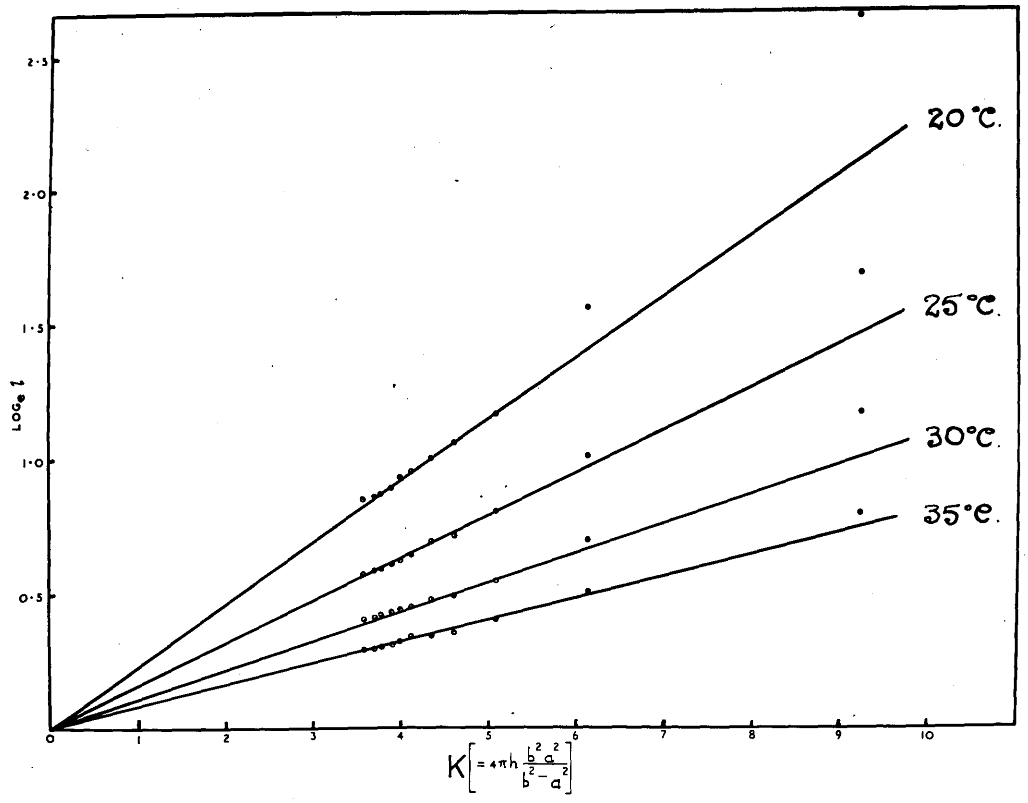


Fig. 14. Variation of logarithmic decrement with " K " at different values of viscosity.

In these determinations the moment of inertia of the oscillating cylinder was as large as possible within the limits of experimental method so that $\log_e 1$ was a minimum. With smaller values of the moment of inertia it is probable that the straight line relationship would be true over an even narrower range.

Taking the value of $\frac{\log_e 1}{K}$ from the curves in figure 14 and substituting in equation (6) the following values of the viscosity of castor oil are obtained, shown for comparison with those obtained by the capillarity method.

Temperature	η (Logarithmic Decrement)	η (Capillarity)
20°C	11.39	10.95
25°C	7.83	7.35
30°C	5.35	5.02
35°C	3.99	3.75

It has already been shown that it is impossible to satisfy Andrade's conditions completely and that a choice has to be made between the two alternative (a) (b - a) small and $\log_e 1$ large or (b) $\log_e 1$ small and (b - a) large, the other conditions being fulfilled by keeping T large.

The experimental results show that the second alternative meets the necessary conditions. The dimensions of the cylinders in the apparatus for measuring slag viscosities are such that (b - a) is large and $\log_e 1$ small , the necessary conditions are satisfied and the use of Andrade's approximation is justified. By the use of this approximation and the experimental values for D and I the results obtained by the logarithmic decrement method are within 6 per cent of the results obtained by the capillarity method. In view of the many other experimental difficulties associated with the determination of slag viscosity, this variation can be considered to be quite good agreement.

Chapter VI.

While the investigation of the logarithmic decrement method was proceeding, as described in Chapter V, a few preliminary trial measurements were made of the viscosities of slags to ascertain if there were any unforeseen experimental difficulties which might necessitate a modification in the design of the apparatus. It was desirable to make a trial run with a slag of known viscosity. A blast furnace slag, 10 per cent Al_2O_3, 45 per cent CaO, 45 per cent SiO_2, was selected because its viscosity, as determined by Rait and Hay (3), was known to be low and of the order expected for open hearth slags. Part of the $CaO-Al_2O_3-SiO_2$ diagram is shown in figure 15 and point A indicates the composition of the slag under examination which should consist of gehlenite, anorthite and calcium bisilicate. The crucible could not contain the required quantity of powdered slag so that after the first melting it had to be cooled and refilled. Unfortunately, the slag dusted during cooling, showing that equilibrium cannot have been attained and that the orthosilicate must have been present. While the crucible did not burst, it was sufficiently distorted to be useless for viscosity measurements.

When a new crucible was obtained, it was decided not to try another lime-alumina-silica slag but to embark immediately on to the manganese silicate system, part of which had been previously investigated by Rait and Hay (3) using molybdenum crucibles.

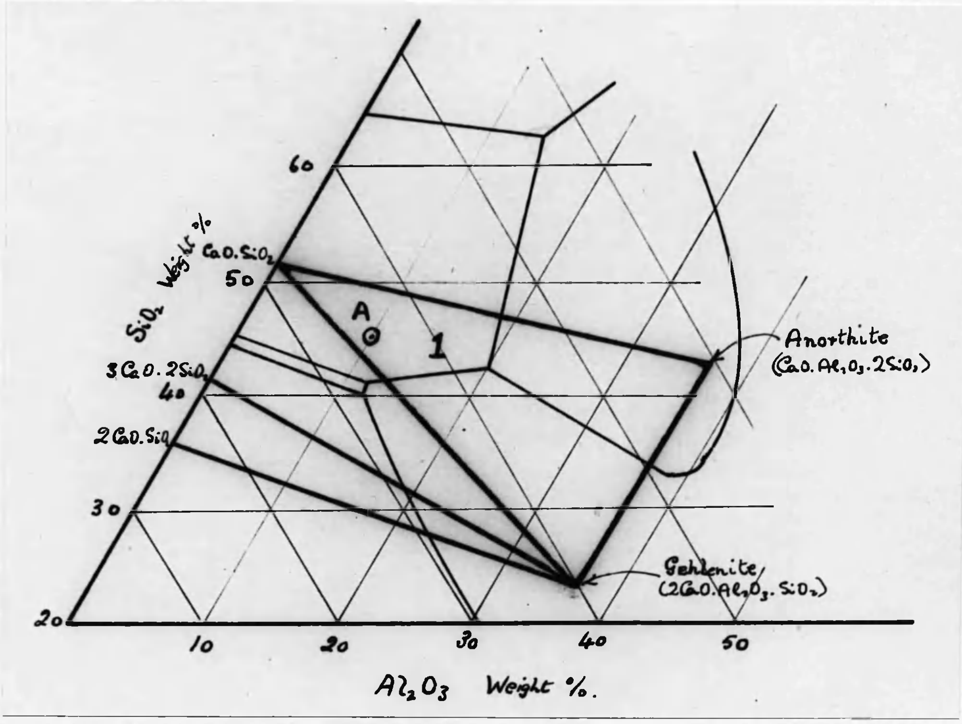


Fig.15. CaO-Al_2O_3-SiO_2 equilibrium diagram.

MnO was prepared by heating manganese oxalate to 1000°C in an atmosphere of nitrogen and hydrogen. This gave a light green product which was stable in air and gave on analysis 98.7 per cent MnO. It may be of interest to record that one particular batch of manganese oxalate would not yield MnO under such treatment and caused considerable trouble. The product was always dark brown in colour and obviously contained higher oxides of manganese. After repeated washing with water, this oxalate was made to yield MnO. Very little information as to the cause of this behaviour was obtained from ordinary quantitative analysis but a spectrographic analysis showed the presence of the following elements:-

Mg, Al, Ca, Na, Pb and traces of Fe, Ni, K, Si.

The approximate concentration of these impurities was as follows:-

Mg = 0.5%, Al = 0.1%, Ca $>$ 0.1%, Pb $<$ 0.01%, Na $<$ 0.1%.

None of these elements appears particularly harmful with the possible exception of calcium. It may be that lime acts on manganese oxides in the same way as on iron oxides, that is, tending to stabilise the higher oxide by forming calcium manganite, analagous to calcium ferrite. Fortunately, further supplies of manganese oxalate from a different manufacturer were purer, and no more trouble was encountered. Two sources of silica were used at different times because of difficulties in obtaining material of satisfactory quality.

1. finely crushed acid washed silica sand
and
2. pure precipitated silica

A slag containing 62 per cent MnO, 38 per cent SiO_2 (i.e. eutectic composition see figure 16) was weighed out and the crucible filled. This slag foamed violently during melting and rose out of the crucible and up the tube, ruining the furnace completely. As several disadvantages of this furnace had been discovered by this time, it was rebuilt to a new design. The principal fault lay in the diameter of the case which was so small that the furnace could not be properly insulated and the outside became much too hot, after even a short time at the high temperature. Another feature was the closed bottom which, while excellent from the point of view of controlled atmospheres, greatly reduced the accessibility of the crucible, thermocouple, etcr, if any trouble was encountered. Further, there was no room for an inner working tube so that the furnace tube itself was exposed to too many dangers. These handicaps were overcome in the design of the new furnace which had a larger diameter casing and adequate insulation. It was open at both ends and contained an inner refractory tube passing right through the furnace. The working atmosphere was thus independent of the furnace winding. The water-cooled top fitted into a recess cut in the asbestos plate in the top of the furnace and the actual viscosity apparatus was practically unchanged, with the exception that a longer spindle was required because of the increased length of the furnace. The empirical calibration and the investigation of the method described in the previous chapter were carried out using the longer spindle.

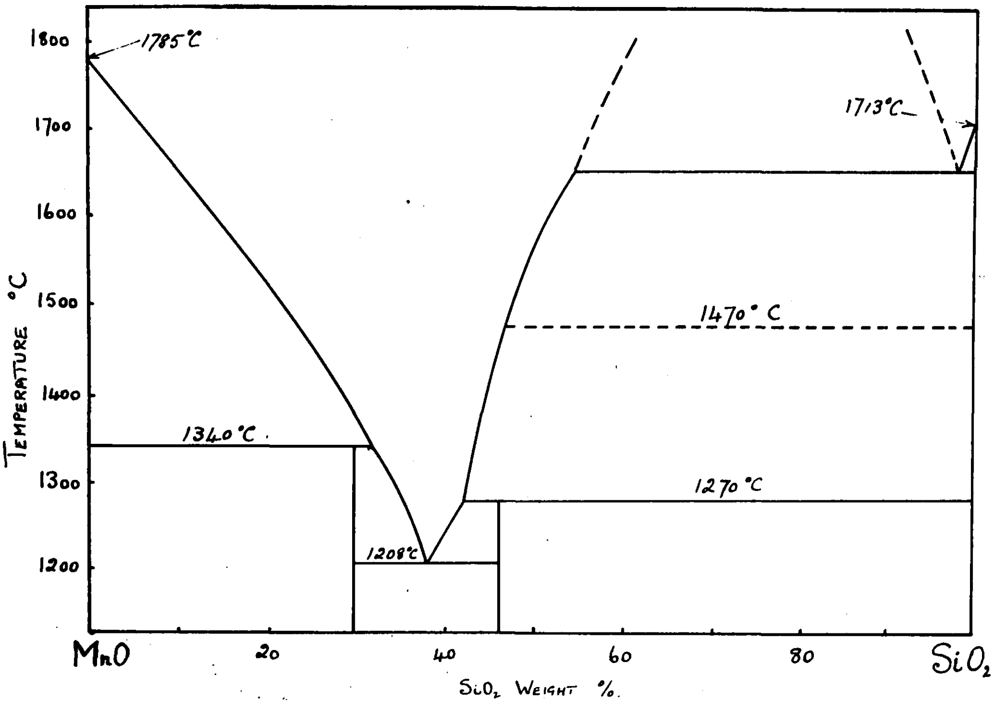


Fig. 16. MnO-SiO_2 equilibrium diagram.

The circular scale was fixed to the furnace itself at the correct distance by two arms screwed on to the asbestos cover. A photograph of the furnace is given in figure 17 and a sectional drawing in figure 18.

In view of the difficulties caused by the foaming of the eutectic slag in the previous attempt, it was decided to use a different slag and as a further precaution, to melt it externally. The slag chosen was Tephroite $2MnO.SiO_2$ and the weighed constituents were thoroughly mixed and put in an iron crucible. This crucible was made of dead soft mild steel tube 6 inches long X 1 3/4 inches in diameter with a ¼ inch bottom of similar steel welded on. The slag was melted in a molybdenum wound furnace capable of reaching temperatures of over 1600°C, in an atmosphere of nitrogen and hydrogen obtained from ammonia by means of a cracking train. This atmosphere is necessary round the molybdenum winding to preserve it from oxidation and it was led into the working part of the furnace simply by having two refractory tubes entering from the top and bottom with a small gap in the middle. The gases could thus penetrate through the porous alundum furnace tube and surround the crucible. After the melting operation, the crucible was sawn up and the slag removed and crushed. It was then remelted in the platinum crucible in the viscosity furnace. The spindle was then screwed into position above the level of the slag, centred and carefully lowered into the slag. The correct depth of immersion was found by lowering the spindle until it touched the bottom and then raising it by 0.6 cm. Later

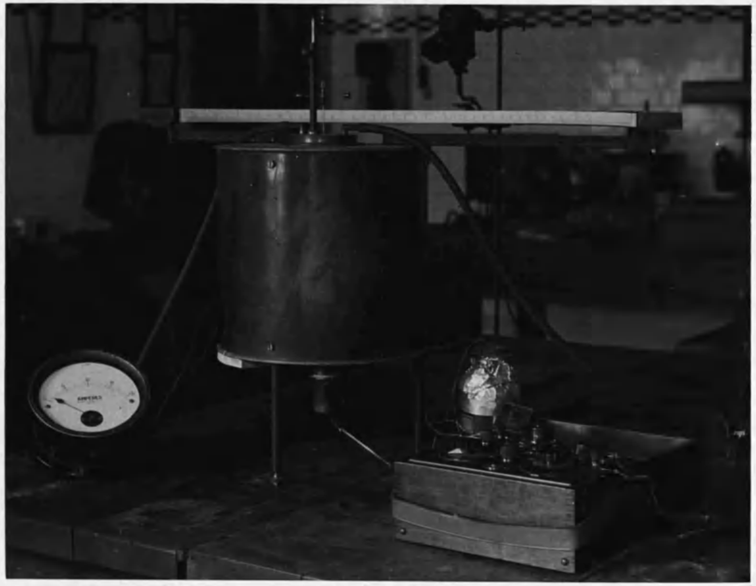


Fig. 17. Final viscosity apparatus.

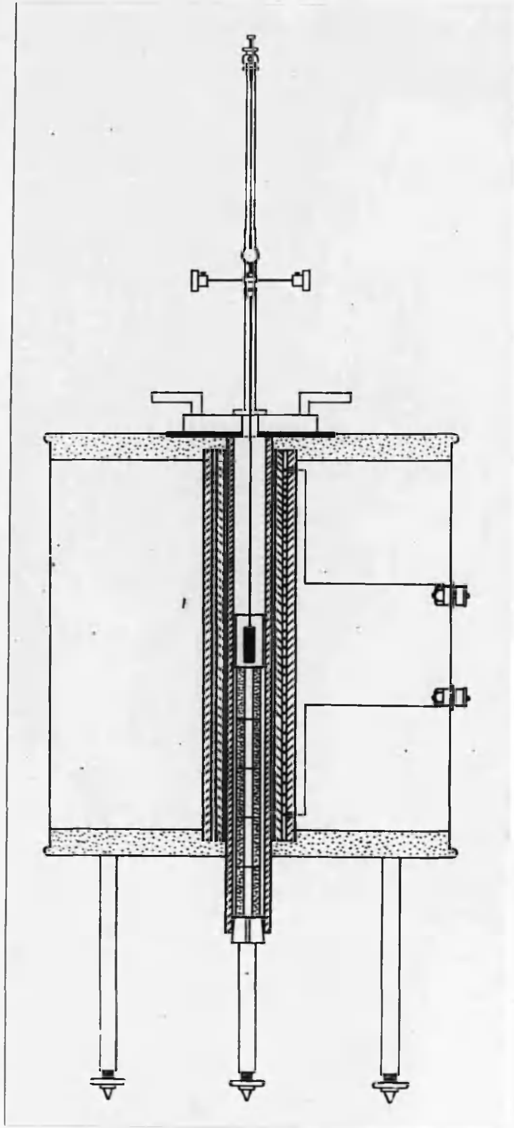


Fig. 18. Sectional view of viscometer in Fig.17

operations proved that this method was risky, as the spindle was liable to stick to the bottom of the crucible. The temperature was then raised to 1600°c, the highest temperature to be used, and held there for at least fifteen minutes. It was subsequently found that variations in temperature affected the viscosity of the slag to a remarkable degree, but that fifteen minutes at the required temperature were more than sufficient to obtain constant results. The light having been previously adjusted so that the reflection from the mirror fell on a suitable part of the scale, the zero reading with the spindle at rest was noted. The spindle was then set in motion and once it had settled down to a steady oscillation, readings of successive amplitudes were taken. This procedure was repeated at various temperatures down to 1450°C, about six determinations being made at each temperature and an average taken.

The composition of the slag was then altered by the addition of a weighed amount of silica and the whole remelted. This raised the level of the slag very slightly but the calibration had shown that there was a large tolerance in the depth with no change in viscosity. Readings were taken as before and it was found that addition of silica had caused an increase in viscosity.

Again the composition of the slag was altered by a further addition of silica, sufficient to make the slag of eutectic composition. In this case however, a solid crust formed

formed on top and as this melted, the slag began to foam. As usual with a foaming slag, it happened very quickly and the slag rose to within an inch of the top of the inner working tube. The foaming was probably caused by higher oxides of manganese giving off oxygen below the highly viscous siliceous layer, but it may be significant that it was again the slag of eutectic composition which foamed.

The crucible was cleaned out by pouring off as much slag as possible, fusing with sodium and potassium carbonates and boiling with dilute hydrochloric acid. It was then refilled with a slag of rhodonite composition, $MnO \cdot SiO_2$. This slag was made as before in an iron crucible, then finely ground and analysed for iron to find how much was introduced by this method. Analysis showed 0.5 per cent Fe. The platinum crucible was filled to the correct level, the spindle centred and lowered. Unfortunately, as it was lowered, it swayed to one side, stuck firmly to the crucible and could not be dislodged. The current was switched off, in case there might be a field of attraction caused by the furnace winding but this proved useless and the slag was poured out. During cleaning, it was found that the crucible was adhering so firmly to the bob that it had to be machined off.

A new crucible was therefore filled with the rhodonite slag and additional guides used to prevent the spindle swaying as it was lowered into the crucible. This slag was found to be much more viscous than tephroite. Readings were recorded at different temperatures and the slag cooled. A weighed quantity of MnO was then added, a little at a time, the slag being remelted and allowed to solidify between each addition. There was considerable effervescence on melting each time but the melt was always tranquil by 1600°C. This slag was found to be more fluid than rhodonite. When the spindle was being withdrawn after the measurements were completed, it again stuck to the side of the crucible. Subsequent repeated fusions with sodium carbonate separated them with no damage either to the crucible or the bob. This problem has been encountered again and again in subsequent work on slags using platinum apparatus. Whenever two pieces of platinum come into contact in the presence of liquid slag at temperatures above 1400°C they adhere so firmly that they cannot be separated without cooling and cleaning. Any apparatus, therefore, used to find the physical properties of molten slags using platinum must be very finely adjusted to eliminate this danger as far as possible.

Since the previous slag had had to be poured out to remove the spindle another fresh slag was made up of eutectic composition. No foaming occurred in this case and viscosity measurements were made successfully. Once again the spindle stuck on being withdrawn. When measurements were being made on the next slag (60/40 MnO/SiO_2), another method was used to introduce the spindle into the liquid.

The crucible was lowered the height of itself, the spindle lowered to its correct depth and stabilised and the crucible carefully raised into position. This method was found to be more successful and was used thereafter.

When the results obtained were plotted as viscosity/composition curves, it was found that there was an abnormally high value at the eutectic composition which interrupted an otherwise smooth curve As the silica used in this instancehad been different, it was felt that there may have been some difference in the composition which would account for the discrepancy. Analysis showed that the silica had been very high in alumina and to a lesser extent in Fe_2O_3. Another melt was therefore made up using the normal silica, acid-washed to remove as much impurity as possible. In this case, the viscosity was lower but still showed a slight break from the normal curve. The results for the system $MnO-SiO_2$ as far as it has been completed are shown in figures 19 and 20.

The viscosities of an acid and a basic open hearth furnace slag were also measured and are shown in figure 21. Both had relatively high melting points and it was only possible to measure the viscosity over a comparatively short range of temperature. The acid slag foamed badly at the first attempt to melt it but the second attempt was quite successful. The sudden increase in the viscosity of the basic slag as the temperature fell from 1450°C to 1440°C indicates that the liquidus lies within this range.

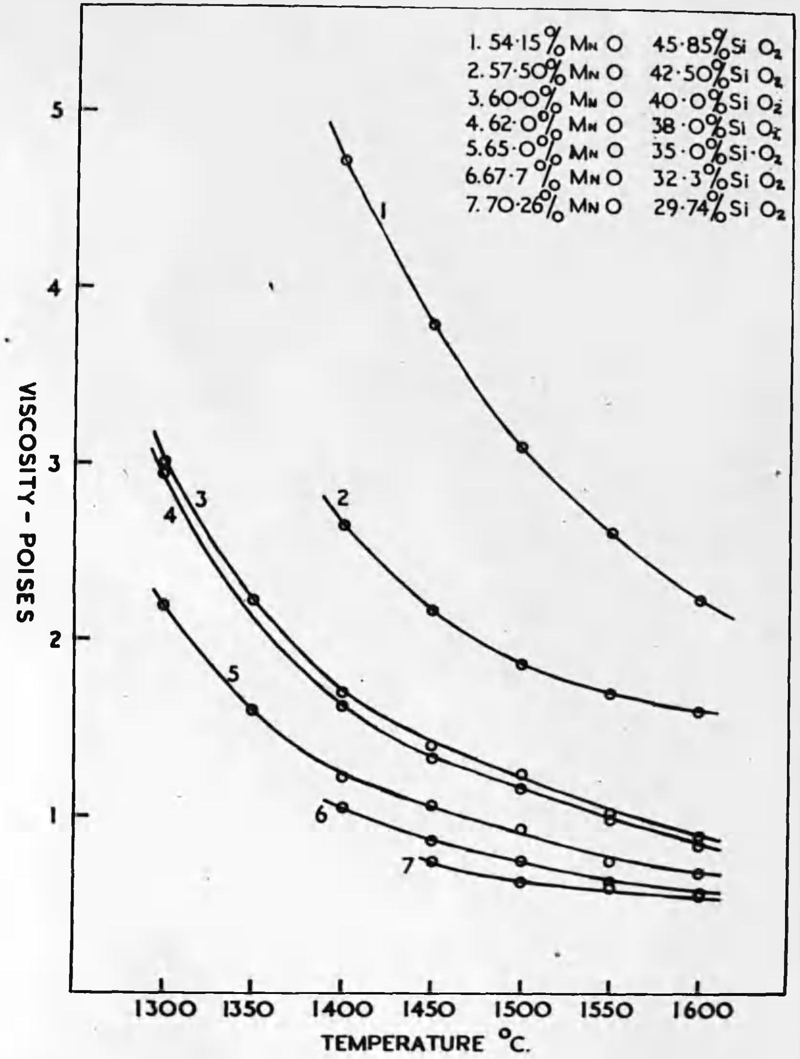


Fig. 19. Variation of viscosity with temperature in various MnO-SiO_2 slags.

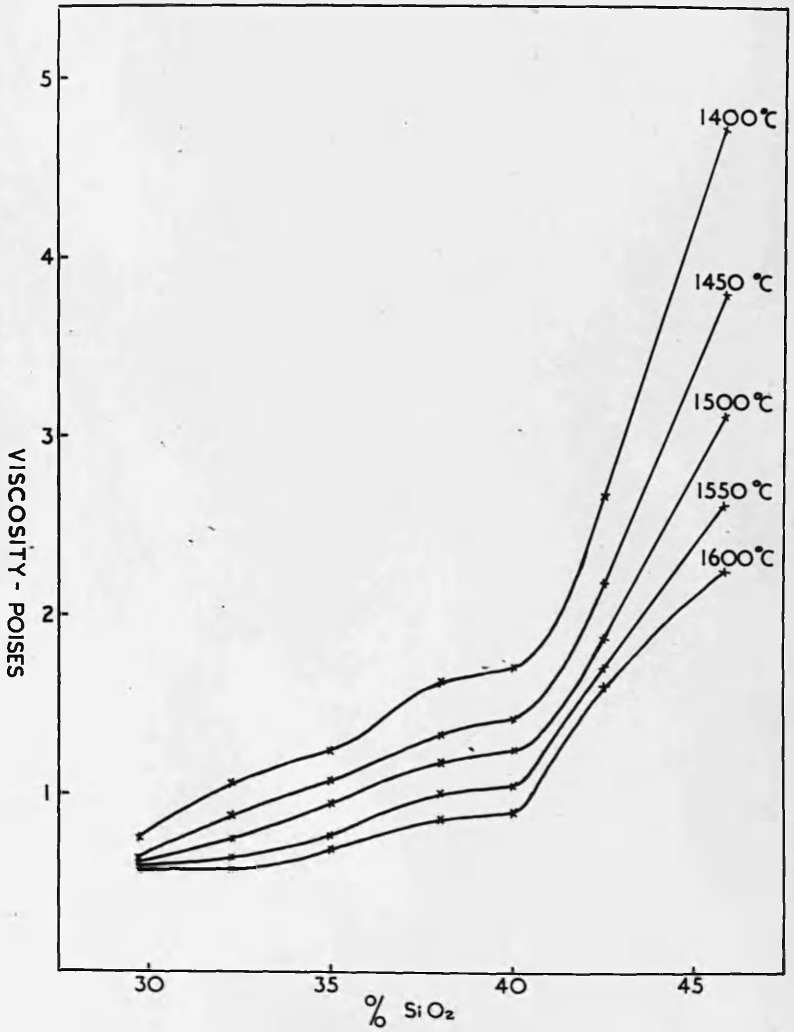


Fig.20. Variation of viscosity with composition of MnO-SiO_2 slags at different temperatures.

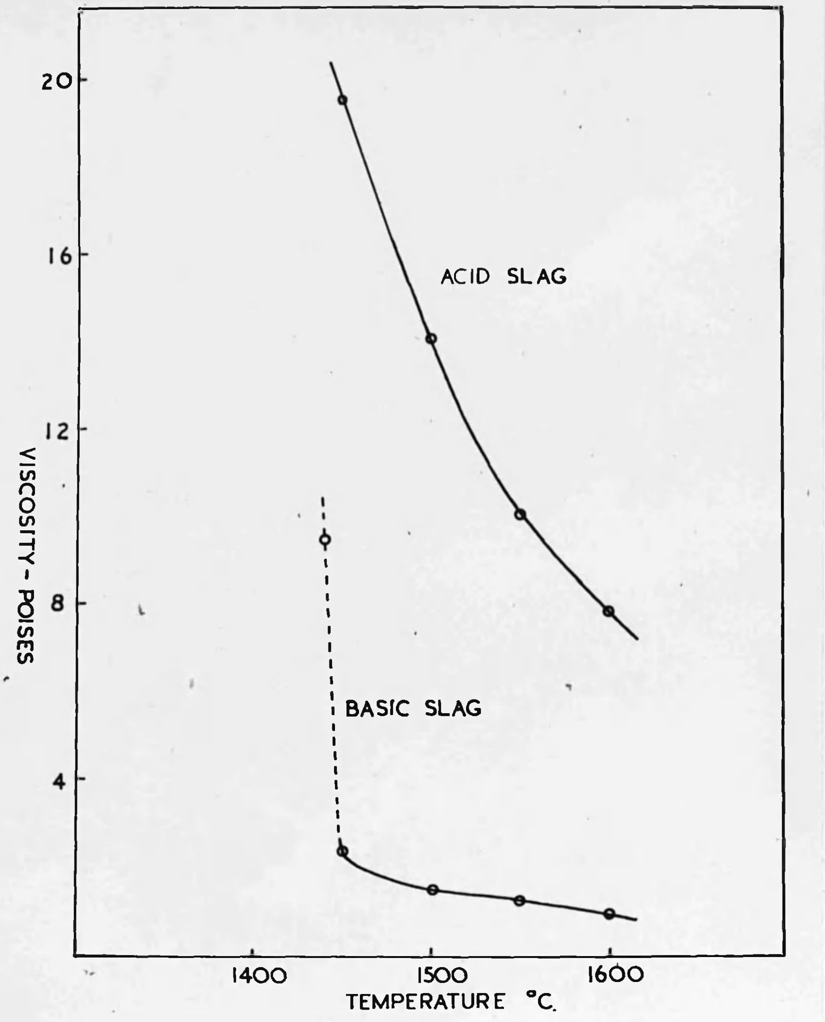


Fig.21. Variation of viscosity with temperature in (a) an acid open hearth slag and (b) a basic open hearth slag.

Chapter VII.

In view of the effect of impurities and in particular, of alumina on the viscosity of the eutectic slag in the $MnO-SiO_2$ system, it was decided to obtain some further data. Acid open hearth slags contain varying amounts of alumina but the precise effect on the viscosity has not been investigated. The procedure adopted was to select a slag with a particular MnO/SiO_2 ratio and add increasing amounts of alumina. The eutectic composition of the binary system was chosen as the starting point, that is, MnO/SiO_2 ratio 62/38. To this was added 5 per cent Al_2O_3, the mixture melted as before in an iron crucible in a reducing atmosphere, cooled and extracted. The melt was uniformly grey in colour and consisted of large well-formed crystals which appeared to be orthorhombic. The slag was remelted in platinum and the viscosity determined. To a slag with the same MnO/SiO_2 ratio, i.e.62/38, 10 per cent Al_2O_3 was added, melted as before and the viscosity measured. Similarly, a slag containing 15 per cent Al_2O_3 with the same MnO/SiO_2 ratio was made and investigated. This slag had the highest melting point, solidifying just below 1400°C and had also the lowest viscosity in this series. The results are plotted in figures 22 and 23 and show a slight maximum in the viscosity at 10 per cent Al_2O_3.

A new MnO/SiO_2 ratio was then selected, the starting point in the binary systen being rhodonite, that is 54.15 per

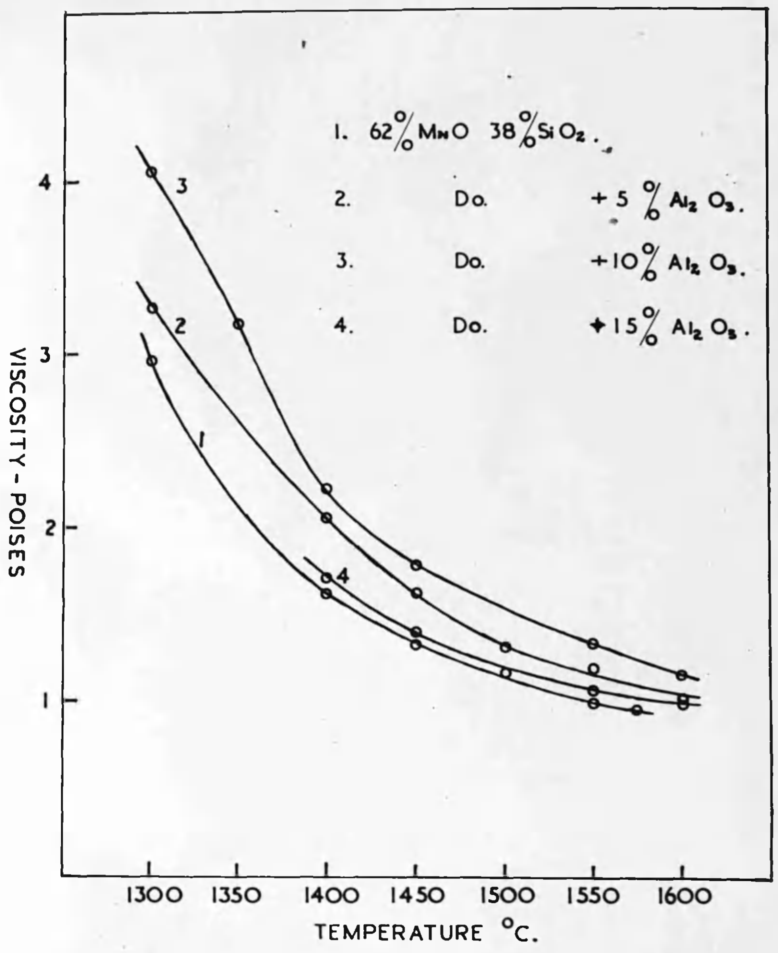


Fig. 22. Variation of viscosity with temperature in various $MnO-Al_2O_3-SiO_2$ slags. (MnO/SiO_2 ratio 62/38 by weight)

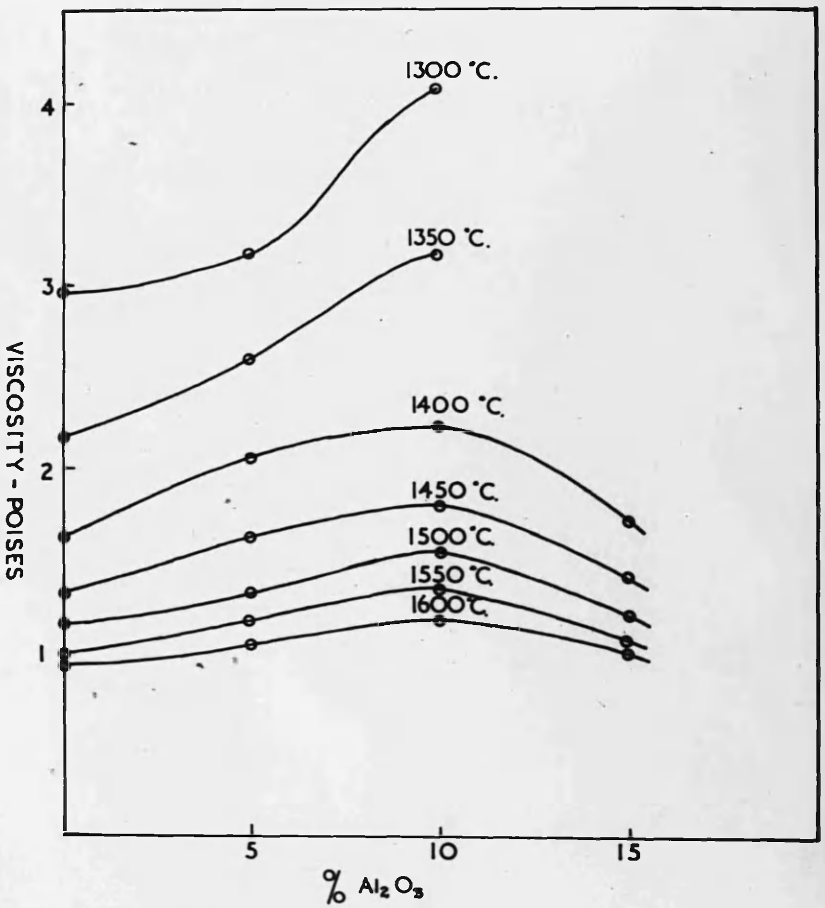


Fig.23. Variation of viscosity with addition of Al_2O_3 to $MnO-SiO_2$slags at different temperatures. (MnO/SiO_2 ratio 62/38 by weight)

cent MnO and 45.85 per cent SiO_2 by weight. The first slag of the new series contained 51.44 per cent MnO, 43.56 per cent SiO_2 and 5 per cent Al_2O_3. As before, 200 gms of the mixed oxides were melted in an iron crucible in a reducing atmosphere but when the melt was extracted, it was found to consist of two layers in about equal proportions, the top half being brownish-pink and the bottom half grey. A photograph of this slag is shown in figure 24. This result being unexpected, the slag was crushed and remelted under the same conditions; this produced the same result, except that the ratio of grey to pink was slightly higher. Since the solid slag was obviously not homogeneous, more precautions were taken in the measurement of the viscosity. Several methods were attempted but the most successful consisted of melting in an iron crucible the exact weight required to fill the platinum crucible to the correct depth. This was then entirely transferred to the platinum crucible and the viscosity determined, the figure obtained being actually slightly lower than for rhodonite without Al_2O_3 present. A slag containing 10 per cent Al_2O_3 was then made up (MnO 48.74 per cent. SiO_2 41.26 per cent), melted as before and found to consist of two layers, the top half being a glass and the bottom half grey. This slag was crushed and remelted in the iron crucible and it was found that after being held liquid for 9 hours in all, a uniformly grey melt was obtained. The viscosity of this melt was then determined.

Fig.24. Rhodonite + 5% Al_2O_3 Melt extracted from iron crucible. Top: pink. Bottom: grey.

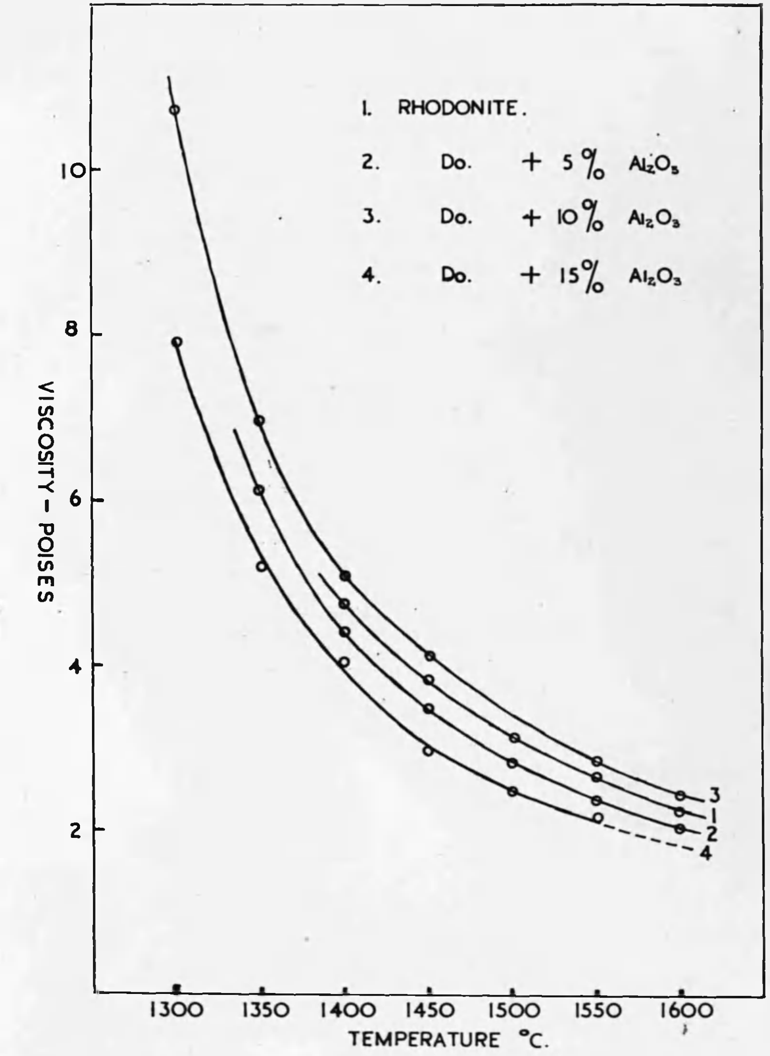


Fig.25. Variation of viscosity with temperature in various $MnO-Al_2O_3-SiO_2$ slags. (MnO/SiO_2 ratio 54.15/45.85 by weight)

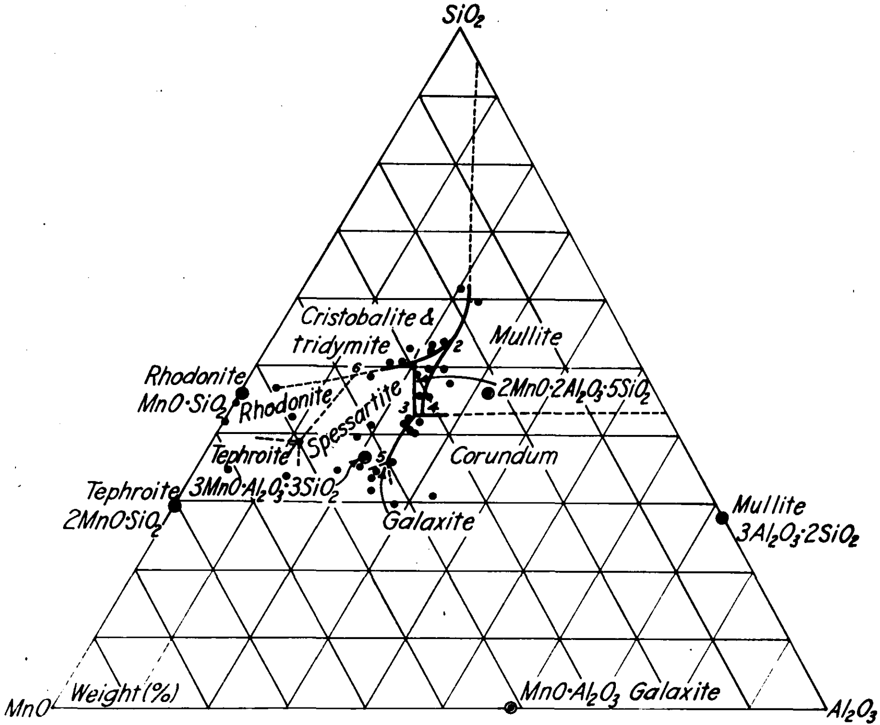
A slag containing 15 per cent Al_2O_3 with the same MnO/SiO_2 ratio giving the composition 46 per cent MnO, 39 per cent SiO_2, 15 per cent Al_2O_3, was found to behave in a similar fashion. On first being melted, the slag consisted of two layers, an upper glass and a lower grey crystalline layer. After being molten for 9 hours, the slag became uniformly grey and it was on this grey slag that the viscosity determinations were carried out. The viscosity results for this series are shown in figure 25 and again the 10 per cent Al_2O_3 slag has the highest viscosity.

Chapter VIII

The behaviour of the second series of slags obtained by adding increasing amounts of Al_2O_3 to rhodonite, was peculiar in the light of the ternary diagram MnO-Al_2O_3-SiO_2 (figure 26). Further viscosity determinations were therefore temporarily suspended in order that some information regarding these ternary slags might be obtained.

The three slags being studied had one feature in common. When first melted, each consisted of two quite distinct layers, the 5 per cent Al_2O_3 slag having the top layer crystalline and pink in colour, and the bottom layer also crystalline but grey in colour. Both the 10 per cent Al_2O_3 slag and the 15 per cent Al_2O_3 slag were made up of brown glass on top of a grey crystalline layer. After prolonged soaking (9 hours) in the liquid state, each slag was found to be uniformly grey and crystalline.

The chemical analyses of each layer and each of the uniform melts are shown in Table I. The silica used in the preparation of the slags contained 97.6 per cent SiO_2, 1.7 per cent Al_2O_3, 0.7 per cent FeO, which was the purest obtainable at the time. As a result of this impurity, the alumina figure is rather high. The amount of FeO picked up by the slag was surprising and the small percentage in the silica was not sufficient to account for it. The only other source from which it could be introduced was therefore the iron crucible. From Table I, it can be seen that the percentage of FeO in the slag increases (a) with the length of time of contact between the



-Equilibrium diagram of part of system $MnO-Al_2O_3-SiO_2$.

Fig. 26. $MnO-Al_2O_3-SiO_2$ equilibrium diagram (Snow).

liquid slag and the crucible and (b) with the percentage of Al_2O_3 in the slag. Previously, the various slags of the binary system $MnO-SiO_2$ had only been melted in contact with the iron crucible for a very short period of time and had never been found to contain more than 1 per cent FeO. While the presence of even 1 per cent of FeO was undesirable, it was considered that constitutionally it would not have much effect, since both a metasilicate and an orthosilicate solid solution series occur in the $FeO-MnO-SiO_2$ system (figure 1). The FeO would therefore be expected to go into solution and the total MnO equival ent was obtained by adding the FeO and MnO figures together. This has been done in Table I in order to obtain a clearer idea of the basicity of the slag.

The exact mechanism behind the conversion of the iron of the crucible into the FeO in the slag is not clear. Part of the FeO might be introduced at the expense of the MnO, which would necessitate an increase in the manganese content of the iron. Part of the crucible was therefore analysed and the manganese content was found to have increased from 0.034 per cent up to 0.55 per cent near the surface in contact with the slag. This surface also showed an increase in hardness noticeable even during the sawing of the crucible. But since the basicity of the slag had been increased, all the FeO could not be accounted for by this reaction. The remainder of the FeO may have entered the slag at the expense of the SiO_2.

TABLE I.

SLAG ANALYSES.

		Alumina added.	MnO	FeO	MnO + FeO	SiO_2	Al_2O_3
1A	Pink	5%	45·5	2·4	47·9	46·5	6·2
1B	Grey		53·0	3·8	56·8	36·0	6·8
1C	Uniform		49·0	5·0	54·0	38·4	6·8
2A	Glass	10%	44·9	3·1	48·0	39·8	11·9
2B	Grey		50·0	2·4	52·4	36·4	10·2
2C	Uniform		42·4	6·3	48·7	39·3	11·1
3A	Glass	15%	44·6	2·2	46·8	36·7	16·2
3B	Grey		50·1	3·0	53·1	31·9	14·6
3C	Uniform		40·1	8·9	49·0	33·9	16·1

The analysis figures show that in every case, the top layer is siliceous, the bottom layer basic, and the final uniform melt intermediate between the two but more basic than the original mixture. Both the Al_2O_3 and the FeO are almost equally distributed between the two layers.

The most recent work on the MnO-Al_2O_3-SiO_2 system is that by Snow (27) and figure 26 shows that part of the liquidus surface which he has worked out. If the analysis of the 5 per cent Al_2O_3 slag be considered in relation to this diagram, rhodonite should be the primary phase in the top layer, and tephroite in the bottom layer and in the uniform melt. Repeated experiments in melting and holding this slag at different temperatures always indicated that two layers were formed until sufficient FeO was picked up to alter the composition so that rhodonite was no longer the primary phase.

Identification of the phases present in these slags was then attempted by X-ray analysis. The only method feasible was by comparison with standard photographs. This is caused by

(1) the inherent weakness of the powder method of giving all the possible diffraction lines in the same photograph,

(2) the difficulties involved in indexing the diffraction lines given by crystals of a low order of symmetry,

(3) the weakness of the lines obtained from artificially prepared specimens, particularly of rhodonite and

(4) the similarity of the diffraction patterns of rhodonite and tephroite.

Standard X-ray photographs were therefore prepared of MnO, α and γ Al_2O_3, all modifications of SiO_2, rhodonite, tephroite and spessartite. According to Gossner and Brückl (28), the structure of rhodonite is triclinic with

$a = 7.77 \qquad \alpha = 85^\circ10'$

$b = 12.45 \qquad \beta = 94^\circ4'$

$c = 6.74 \qquad \gamma = 111^\circ29'$

this data being obtained from the naturally-occurring rhodonite mineral containing some impurities. To obtain a standard photograph of rhodonite two specimens were prepared by melting

(a) in an iron crucible
and
(b) in a molybdenum crucible

followed by annealing in nitrogen at 1050°C for twelve hours. Each of these specimens was identified as rhodonite by comparison with the data given above. A standard photograph of tephroite was prepared from a specimen made in an iron crucible and compared with data obtained by Rinne (29) who gives the structure as orthorhombic with axial ratio a: b: c: 0.4648; 1 : 0.5857. A standard photograph of spessartite similarly prepared was compared with data given by Menzer (30) who cites the structure as cubic with a = 11.6Å. The results obtained from X-ray analysis are given in Table II.

Evidence of the presence of free oxides was not obtained, thus indicating that the slags were properly melted.

TABLE II. X-RAY ANALYSIS.

Rhodonite.			Tephroite.			Spessartite.		
Angle of reflection	Intensity		Angle of reflection	Intensity		Angle of reflection	Intensity	
14° 45′	S		12° 6′	M		15° 00′	M	
15° 40′	M		13° 45′	VW		16° 51′	S	
16° 45′	M		15° 9′	M		23° 39′	M	
20° 00′	VW		17° 6′	S		26° 36′	M	
22° 15′	W		19° 45′	W		28° 00′	M	
31° 24′	W		24° 45′	S		29° 00′	M	
31° 45′	W		29° 15′	M		35° 30′	M	
32° 45′	W		31° 15′	VW		36° 30′	W	

1A (Pink)			2A (Glass)			3A (Glass)		
Angle of reflection	Intensity	Compound	Angle of reflection	Intensity	Compound	Angle of reflection	Intensity	Compound
14° 45′	M	R	14° 45′	S	R	12° 15′	M	T
15° 36′	S	R	16° 36′	M	R	13° 48′	M	T
16° 36′	M	R				16° 51′	S	Sp
18° 21′	VW	?				18° 30′	VW	?
20° 00′	VW	R	The other lines are very broad and weak.			23° 30′	VVW	Sp
22° 15′	W	R				24° 45′	M	T
31° 24′	W	R				28° 00′	VVW	Sp
31° 45′	W	R				29° 15′	M	T and Sp
32° 45′	W	R				35° 30′	VVW	Sp

1B (Grey)			2B (Grey)			3B (Grey)		
Angle of reflection	Intensity	Compound	Angle of reflection	Intensity	Compound	Angle of reflection	Intensity	Compound
12° 9′	W	T	12° 9′	M	T	12° 00′	M	T
15° 9′	M	T	13° 45′	M	T	13° 45′	M	T
17° 12′	S	T	15° 9′	M	T	15° 9′	M	T
24° 45′	M	T	17° 6′	S	T	17° 6′	S	T
29° 15′	W	T	24° 45′	M	T	24° 45′	M	T
31° 36′	VVW	T	29° 15′	M	T	29° 15′	W	T
						31° 36′	VW	T

1C (Uniform)			2C (Uniform)			3C (Uniform)		
Angle of reflection	Intensity	Compound	Angle of reflection	Intensity	Compound	Angle of reflection	Intensity	Compound
12° 9′	VW	T	12° 00′	VW	T	12° 9′	M	T
15° 9′	MS	T and Sp	15° 9′	M	T and Sp	14° 00′	M	?
17° 00′	S	T and Sp	16° 57′	S	T and Sp	15° 9′	M	T and Sp
24° 45′	M	T	23° 30′	VVW	Sp	17° 00′	S	T and Sp
29° 00′	W	T and Sp	24° 45′	M	T	24° 45′	M	T
			28° 15′	VVW	Sp	29° 15′	M	T and Sp
			29° 15′	M	T and Sp	31° 36′	VW	T
			31° 36′	VVW	T			

R = Rhodonite. Sp = Spessartite. T = Tephroite. S = Strong. W = Weak. M = Medium.

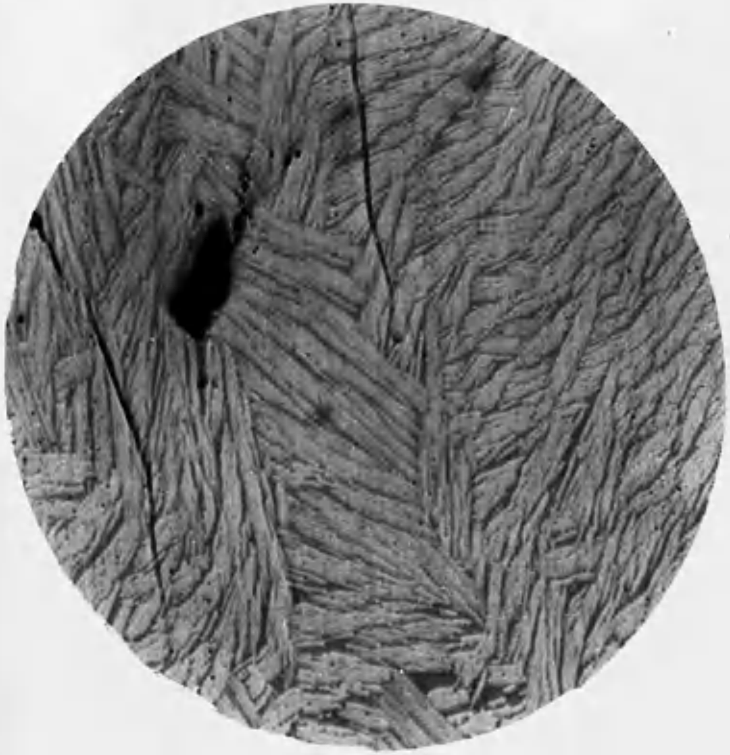


Fig.27. Micro-section of slag IA.
Top (pink) layer. (x180)

Fig. 28. Micro-section of slag 1B.
Top of bottom (grey) layer. (x180)

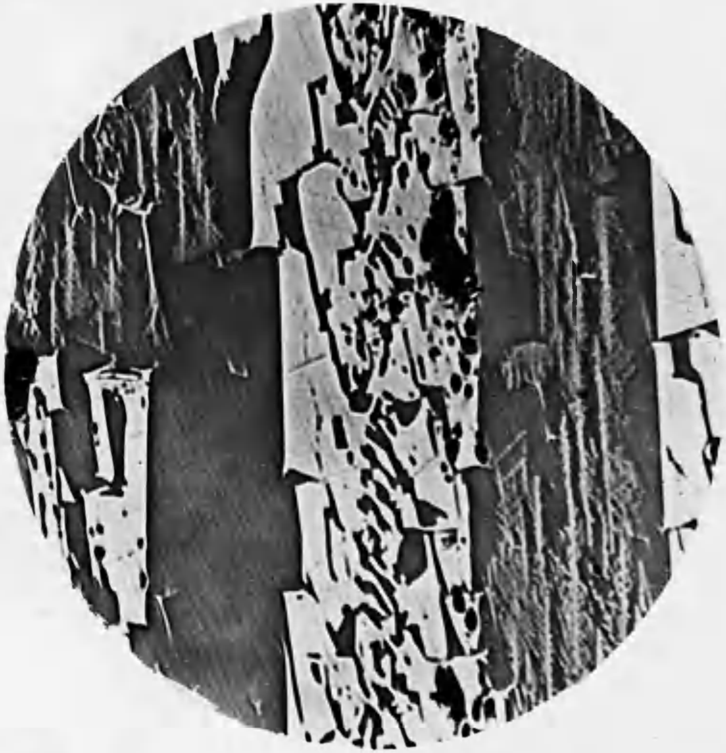


Fig. 29. Micro-section of slag 1B.
Bottom of bottom (grey) layer. (x180)

Fig.30. Micro-section of slag 1C.
Uniform grey melt. (x180)

Fig.31. Micro-section of slag 2B.
Bottom (grey) layer. (x180)

Fig. 32. Micro-section of slag 3C.
Uniform grey melt. (x180)

Fig. 33. Micro-section of spessartite.
(X180)

The top (pink) layer of the 5 per cent Al_2O_3 slag showed mainly a well-developed rhodonite structure while the top layer (glass) of the 10 per cent al_2O_3 slag gave a similar but much fainter structure. This confirmed that rhodonite was the primary phase in the top layer in each case. The top layer of the 15 per cent Al_2O_3 slag showed crystals of tephroite with some spessartite. The absence of diffraction lines of rhodonite did not necessarily mean that it was not present in the slag. Even after prolonged annealing, rhodonite gives such weak diffuse diffraction lines that even the strongest of them are always weaker than the medium-weak lines of tephroite and spessartite. The grey layers of each slag showed tephroite while each of the uniform melts showed principally tephroite with some spessartite.

Further identification of the phases was attempted by examination of the microsections, photographs of which are shown in figures 27 to 33. In the 5 per cent Al_2O_3 slag,(figure 27) the top (pink) layer consisted mainly of laths of rhodonite with a small amount of glassy phase between the laths, probably spessartite. The bottom (grey) layer (figures 28 and 29) consisted of long white crystals of tephroite with a glassy-grey background containing a eutectic structure, the crystals being larger at the bottom of this layer than at the top. The uniformly grey melt (figure 30) showed the same type of structure, with a third more angular phase in some fields. The glassy layers of the 10 per cent and 15 per cent Al_2O_3 slags, while microcrystalline in that they gave diffraction lines on an X-ray powder photograph, showed nothing under the microscope. The grey layers of these slags have the same type of long white tephroite crystals already described but with much more glass present. This glass is probably spessartite which always solidified from the liquid as a glass and had to be annealed at 1000°C before it would crystallise. Great care had to be exercised in the polishing of these specimens, because with inferior polishing scarcely any structure was revealed at all. They were all examined unetched, because no suitable etching reagent was found. Experiments were made using molten potassium pyrosulphate as etching reagent with distinctly hopeful results but further work would need to be done.

In an attempt to find out what was happening in the liquid state, small 1 gm melts of the 5 per cent Al_2O_3 slag were held for definite periods of time up to 8 hours, at various temperatures in iron crucibles in an atmosphere of nitrogen and examined through a quartz window with a low power microscope. The slag was entirely molten by 1330°C and a reaction appeared to be taking place at that temperature. After being held for a short time at this temperature, the top layer was pink and the bottom grey, but after eight hours soaking, the slag was entirely grey. At 1400°C and 1470°C, much shorter times were required to make the slag uniformly grey showing that the rate of iron pick-up increased with temperature. These melts were also sectioned, polished and examined microscopically and found to be in complete agreement with those obtained from the 200 gm melts previously described.

As the examination of all these melts involved the destruction of the crucible each time, it was economically impossible to use platinum and thus avoid the effect of iron. One melt of 10 gms was made in a platinum crucible and soaked in vacuum for 30 hours, in six five hourly periods. Each time the surface of the slag was partly pink and partly grey and showed no signs of going uniformly grey. The melt was given a final soaking in an atmosphere of nitrogen before the crucible was sectioned in order to examine the structure of the slag. There were still two layers present but the microstructure was extremely fine, probably due to the more rapid cooling in the thin-walled platinum crucible. The top layers was practically structureless, while the bottom layer showed the same white crystals of tephroite as before, only very much smaller. The slag was ground down, 6 per cent FeO added and the mixture remelted in platinum for half an hour. This was sufficient to make the slag uniformly grey.

Quenching experiments were then tried in order to find if the two layers existed in the liquid state. The crucible containing the molten 5 per cent Al_2O_3 slag was quenched in water from a temperature of 1420°C and one side ground away to reveal the nature of the contents. The glass obtained was light brown in colour at the top, and dark at the bottom. On annealing for 6 hours at 1050°C the top turned pink and the bottom grey, indicating that there had been two layers in the liquid state. In this connection, an interesting mishap occurred which supported this view. A tapered thin walled iron crucible with a welded bottom containing some of this 5 per cent Al_2O_3 slag was suspended in a furnace at 1350 °C. While at this temperature, the crucible developed a slight annular leak at the bottom. When the crucible was removed it was found that there was a large globule of grey slag hanging from the bottom, while the remaining slag inside the crucible was entirely pink. It appeared that the grey slag had been much more fluid than the pink and had managed to leak out through the tiny annular space. This seemed to be a further indication that there had been two liquid layers in the crucible.

As the pink layer was always found on top of the grey layers, density determinations were made on the 5 per cent Al_2O_3 slag to ascertain if there was any marked difference between the two layers. At room temperatures the densities were as follows:-

Average value for top layer = 3.327 at 20°C

Average value for bottom layer = 3.518 at 20°C

Average value for uniform melt = 3.444 at 20°C

At high temperatures the density was determined by means of a chemical balance capable of weighing to 0.00005 gms, from one arm of which a platinum sinker was suspended in the molten slag. A sample of the 5 per cent Al_2O_3 slag containing both pink and grey layers was remelted in a platinum crucible in a furnace placed below the balance. The latter was protected from the heat by a water cooled plate and an asbestos shield. The furnace could be raised or lowered by a specified amount by means of a screw (figure 34). The sinker, suspended by a fine

Fig. 34. Apparatus used for density determinations.

platinum wire, was lowered into the hot zone and weighed, then immersed just below the surface and weighed again. The whole furnace was then raised 0.14 cm (pitch of the screw) and the sinker was weighed again. This was repeated every 0.14 cm until the sinker touched the bottom of the crucible. The determinations were then repeated by lowering the furnace through the same steps.

The graphs of density against depth of immersion for different temperatures are shown in figures 35 to 37. These graphs have not been corrected for

(a) increased volume of wire immersed

(b) buoyancy errors

(c) expansion of the platinum wire and sinker

(d) surface tension and

(e) interfacial tension

The effect of (a), (b) and (c) is practically negligible and the effect of surface tension is such that the true values of density are larger than the figures given but for each layer the effect is constant.

While the density continually increases from the top to the bottom of the slag, in every case there is a distinct break in the middle of the curve. The extent of this break corresponds to the height of the sinker. This discontinuity can only be accounted for by the presence of two liquids but the fact that the density increases in each layer suggests that neither layer is in itself uniform. The gradient of the curves is different at each temperature as a result of varying lengths of time of soaking, becoming less steep with increasing time and temperature which

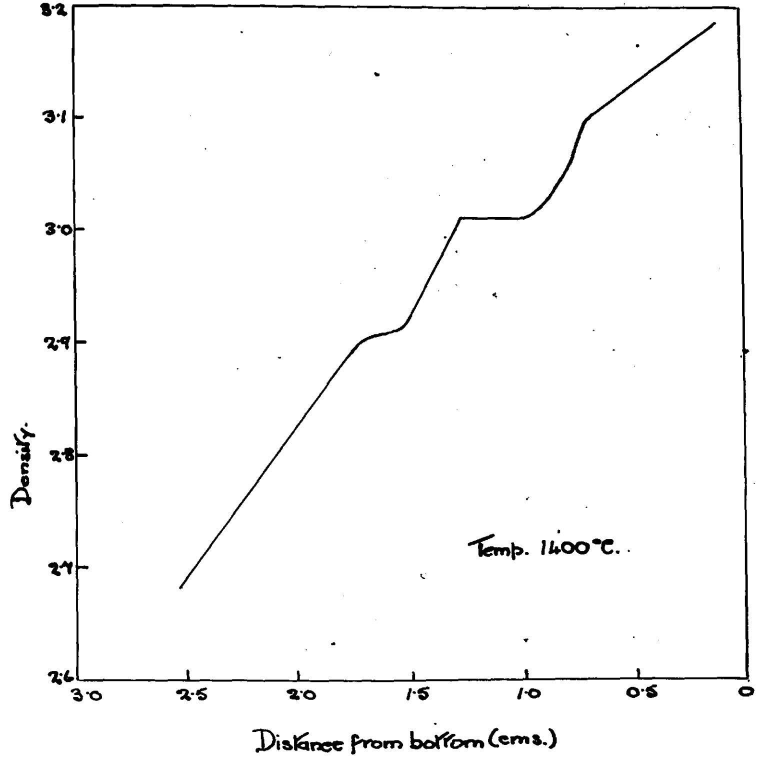


Fig.35. Variation of density from top to bottom of slag at 1400°C. (Rhodonite 5 per cent Al_2O_3).

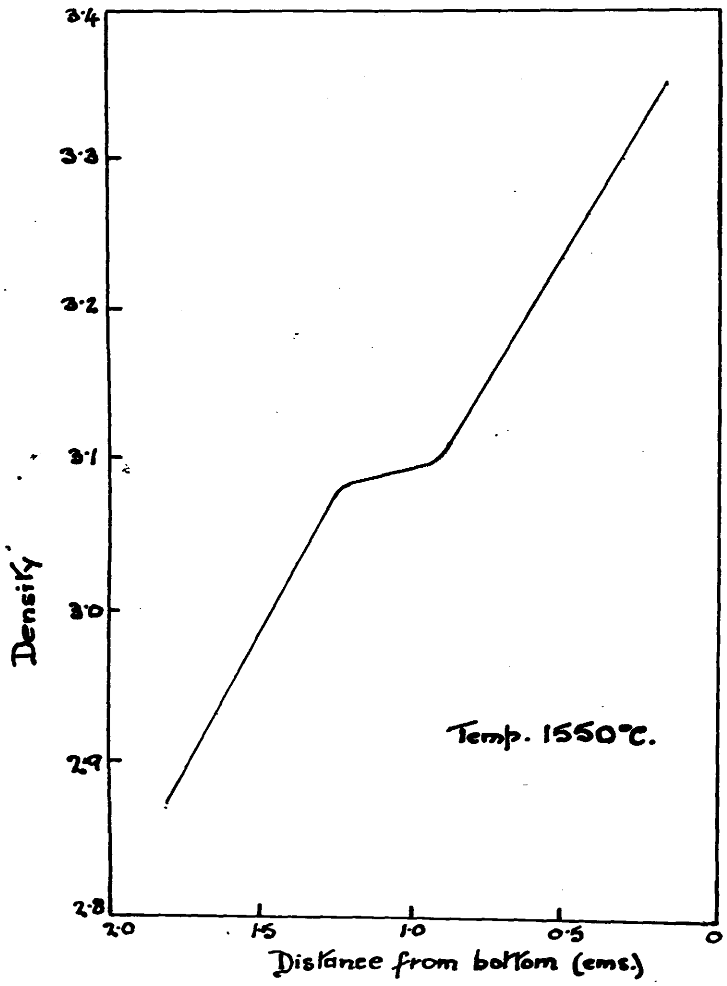


Fig.36. Variation of density from top to bottom of slag at 1550°C. (Rhodonite 5 per cent Al_2O_3).

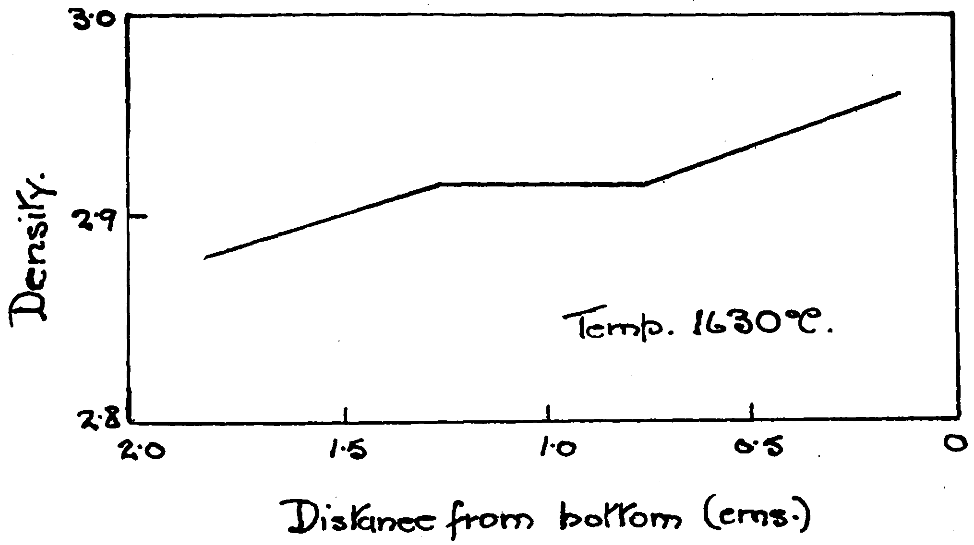


Fig.37. Variation of density from top to bottom of slag at 1630°C. (Rhodonite 5 per cent Al_2O_3).

seems to indicate that each layer is becoming more homogeneous. For comparison the same method was used with various liquids at room temperatures. The graph obtained for two immiscible liquids such as water and bromoform, was similar except that in each layer the density was constant and the break was more distinct. This would be expected from the vast difference in chemical and physical properties of these two liquids, whereas with silicates these properties are much more similar.

These experiments carried out on the 5 per cent Al_2O_3 slag, while by no means conclusive, indicate the presence of two phases in the liquid state near the rhodonite composition in the ternary system $MnO-Al_2O_3-SiO_2$. One of these liquids is rich in SiO_2 and the other rich in MnO. The slag cannot be rendered homogeneous with time up to 30 hours at a temperature just above the melting point but the density curves for higher temperatures suggest that the difference between the two liquids is less and the immiscibility is smaller. Addition of FeO either directly or through reaction with the crucible alters the slag so that its composition lies outside the range of immiscibility.

Chapter IX

Conclusions.

The logarithmic decrement apparatus is suitable for measuring the viscosities of open hearth slags and values of viscosity can be calculated to an accuracy of 6 per cent without resort to empirical calibration, if the dimensions of the cylinders are suitably chosen as discussed in Chapter V.

The results for slags in the binary system $MnO-SiO_2$ confirm qualitative knowledge. Slags with over 60 per cent MnO are extremely fluid, the highest viscosity in this composition range being 1.6 poises at 1400°C for the slag containing 60 per cent MnO,40 per cent SiO_2. As the silica content is increased above 40 per cent the viscosity increases very rapidly The only previous quantitative investigation of viscosities in this system is that by Rait,~~and~~ McMillan and Hay (4), who published values for three compositions on the tephroite side of the eutectic. Two of their values are in agreement with the present results but their value for the eutectic slag is much higher, 3.8 poises at 1400°C compared with the present value of 1.63 poises. As they made no determinations of slags with silica contents higher than 38 per cent, their results are too meagre to allow conclusions to be drawn. Even the present value for the eutectic slag seems rather high and gives rise to a slight break in the smooth curve relating viscosity and composition. The discrepancy, however, is within the range of experimental error. It would be worth while measuring the viscosities of one or two slags with higher silica content than rhodonite, as this range of composition approximates to that of acid open hearth furnace slags and the viscosity appears to be increasing rapidly with increase in silica content. Unfortunately, the slope of the liquidus is so steep, that very few measurements will be possible below 1600°C which is practically the temperature limit of the apparatus. A systematic investigation of the viscosities of FeO-MnO-SiO_2 slags should also be carried out.

The actual acid open hearth slag which was measured had a relatively high viscosity, 7poises at 1600°C and in addition the viscosity increased rapidly with fall in temperature to 17 poises at 1450°C. The basic slag was much more fluid, the viscosity at 1600°C being less than 1 poise. The sudden increase in viscosity between 1450°C and 1440°C indicates the beginning of crystallisation in this basic slag.

In the ternary system MnO-Al_2O_3-SiO_2, two series of results were obtained. In the first series of slags with MnO/SiO_2 ratio of 62/38 by weight, there is a slight maximum in the viscosity at 10 per cent Al_2O_3 but it is not sufficiently pronounced to indicate the presence of a compound in the liquid. Additions of Al_2O_3 up to 10 per cent increase the viscosity from 1.5 poises to 2.0 poises but with 15 per cent Al_2O_3 the viscosity falls again to 1.5 poises. In the other series with the MnO/SiO_2 ratio 1/1(54.15/45.85 by weight) , the results are obscured by the changes in composition taking place during melting. At first sight, there appears to be a maximum viscosity at 10 per cent alumina but the analysis of this slag shows that the ratio of silica to bases (FeO + MnO) is higher than in the slag containing 15 per cent Al_2O_3 slag and therefore the viscosity would be expected to be higher. The basicity of the 10 per cent Al_2O_3 slag, however, is higher than that of the slag without Al_2O_3; the viscosity would therefore be expected to be lower, but it is found to have increased from 3.24 poises to 3.64 poises at 1450°C. Thus additions of Al_2O_3 up to 10 per cent increase the viscosity in this series also. As far as can be judged from the narrow range of slags investigated, the presence of small amounts of Al_2O_3 tends to increase the viscosity of acid open-hearth slags.

The anomalous behaviour of the second series of $MnO-Al_2O_3-SiO_2$ slags has not yet been cleared up but the evidence available indicates that there is a range of liquid immiscibility in the system near the rhodonite composition. Addition of FeO acts in the same way as addition of MnO, that is, it increases the basicity until the slag composition is outside the immiscibility range. It was also noticed that pure rhodonite melts tended to form pink and grey layers and this in conjunction with other small points such as discrepancies in melting point temperatures and micro-structures has raised doubts about the accuracy of the published $MnO-SiO_2$ equilibrium diagram. These may be quite unjustified but it may be worth while to check the diagram by some method other than that of differential heating and cooling curves by which it was originally obtained by White, Howat and Hay (31).

One minor point was discovered with respect to rhodonite. A recalescence at just over 1000°C was observed in a small sample of rhodonite cooling from 1600°C. Heating and cooling curves of a sample were taken and pronounced arrests were recorded at 1070°C on heating and at 1050°C and 1020°C on cooling. The reason for the double arrest on cooling was not apparent but it seems quite definite that rhodonite undergoes transformation at this temperature. This was further confirmed by experiments on the specific heat and heat content of rhodonite. Values of heat content fell on a smooth curve up to 233 calories at 1000°C but between 1000°C and 1100°C very erratic figures were recorded including an exceptionally high value of 455 calories at 1020°C.

It is surprising that this has not been observed before, since similar inversions occur in other metasilicates. $MgO.SiO_2$ exists as monoclinic clino-enstatite above 1145°C and as orthorhombic enstatite below that temperature, while $CaO.SiO_2$ exists as monoclinic pseudo-wollastonite above 1125°C and triclinic wollastonite below. $MnO.SiO_2$ exists in the triclinic form at room temperatures and it is possible that it changes to a monoclinic form above 1050°C. It is hoped that X-ray analysis may yield some further information about this transformation.

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