The kinetics of the reduction of manganous oxide by graphite

by W. J. RANKIN*, Ph.D., M.S.A.I.M.M. and
J. S. J. VAN DEVENTER†, Hons. B. Ing. (Chem. Ing.) M.S.A.I.M.M.

SYNOPSIS

Mixtures of MnO and graphite were reacted under argon at temperatures ranging from 1200 to 1425°C, and the loss in mass of the mixture was recorded continuously. The results showed that the rate of reduction of MnO increased as the temperature increased and the ratio of MnO to C decreased. The effect of the particle size of MnO and of graphite on the rate of reduction at 1350°C was very small in the range 63 to 250 μm for MnO and 45 to 355 μm for graphite. The rate of reduction at 1350°C was increased markedly by the addition of Na_2CO_3 and K_2CO_3, was slightly increased by the addition of Fe_2O_3, was unaffected by the addition of CaO, MgO, and Al_2O_3, and was decreased by the addition of SiO_2. Some CO_2 was always present in the effluent gas, and this was taken as evidence that the reduction of MnO occurred by way of CO_2 as an intermediate product. The activation energy of the rate-controlling step was 57,5 kcal, and this was similar to the measured activation energy for the gasification of graphite by CO_2, namely, 61,5 kcal per mole of graphite. A simple kinetic model was derived on the assumption that the gasification of graphite was the rate-controlling step, and the results over the temperature range 1200 to 1425°C, when plotted in the appropriate form, yielded straight lines as predicted by the model.

SAMEVATTING

Mengsels van MnO en grafiet is onder argon by temperature van 1200 tot 1425°C laat reageer en die massaverlies van die mengsel is voortdurend geregistreer. Die resultate het getoon dat die reduksietempo van die MnO toegeneem het namate die temperatuur en die verhouding van MnO tot C gestyg het. Die uitwerking van die partikelgrootte van die MnO en die grafiet op die reduksietempo by 1350°C was baie gering. Die partikelgrootte was in die bestek van 63 tot 250 μm vir MnO en 45 tot 355 μm vir grafiet. Die reduksietempo by 1350°C is merkbaar verhoog deur die byvoeging van Na_2CO_3 en K_2CO_3, net effens verhoog deur die byvoeging van Fe_2O_3, glad nie deur die byvoeging van CaO, MgO en Al_2O_3 beïnvloed nie en verlaag deur die byvoeging van SiO_2. Daar was altyd CO_2 in die afvalgas aanwesig en dit is beskou as 'n bewys dat die reduksie van MnO plaasvind met CO_2 as 'n tussenproduk. Die aktiveringsenergie van die tempobeherende stap was 57,5 kcal per mol grafiet en dit stem ooreen met die gemete aktiverengsenergie vir die vergassing van grafiet met CO_2, naamlik 61,5 kcal. Daar is 'n eenvoudige kinetiese model, afgelei met die veronderstelling dat grafietvergassing die tempobeherende stap was en toe die resultate oor die temperatuurbestek van 1200 tot 1425°C in die gepaste vorm gestip is, het hulle reguit lyne gegee soos die model voorspel het.

This work was undertaken to provide fundamental information on the kinetics and mechanism of the reduction of manganous oxide by graphite, and on the effect of the gangue component of ores on the rate of reduction. This information should further the knowledge and understanding of the complex reactions and transformations that occur in the reduction of manganese ores during the production of ferromanganese alloys.

Manganese is present in manganese ores as higher oxides and silicate, and during the early stages of reduction these are reduced to MnO by the reducing atmosphere in the furnace[1]. The reduction of MnO to carbide and metal are the most important reactions in the production of ferromanganese alloys, and can occur by two mechanisms:

(i) reduction in the solid state by carbon, and
(ii) dissolution of MnO in the slag, followed by its reduction from the slag by a solid carbonaceous reducing agent or carbon-saturated alloy.

The latter mechanism has been observed in laboratory-scale experiments[1] and is most probably the major mechanism in the submerged-arc furnace, but whether the former mechanism also occurs to a significant extent is not known. The former mechanism is the subject of the study reported in this paper.

It is generally accepted[2, 3] that, when a metal oxide is reduced by carbon, the reaction occurs by way of

carbon dioxide as a gaseous intermediate product:

$$MO + CO = M + CO_2 \quad \dots \dots \dots \dots \dots \quad (1)$$
$$CO_2 + C = 2CO. \quad \dots \dots \dots \dots \dots \quad (2)$$
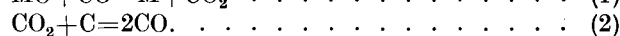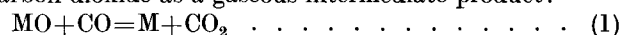
The overall reaction is the sum of equations (1) and (2), and is the same as if reduction had occurred by direct contact of the oxide and carbon:

$$MO + C = M + CO. \quad \dots \dots \dots \dots \dots \quad (3)$$
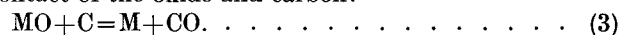
Thermodynamically, there is no difference between equations (1) and (2) on the one hand and equation (3) on the other. If reactions (1) and (2) occur under a certain set of conditions, so can reaction (3). However, equation (3) involves reaction between solids, whereas equations (1) and (2) involve reactions between solids and gases and, from kinetic considerations, reactions (1) and (2) should occur much faster than reaction (3). This is the main argument in favour of the 'gaseous intermediate' mechanism.

The rate of reduction of many oxides by graphite is controlled by the rate of gasification of carbon by equation (2), the so-called Boudouard reaction. This reaction is catalysed by small amounts of impurities, particularly alkali-metal oxides and to a lesser extent by metals and other metal oxides[4]. When gangue materials are present, the rate of reduction of MnO by carbon may be increased because of the catalytic effect of the gangue on the Boudouard reaction. The typical composition of a South African Mamatwan manganese ore is given in Table I, from which it is apparent that the major gangue components are CaO, SiO_2, MgO, and iron oxides. The effect of these, as well as of Al_2O_3, Na_2CO_3, and K_2CO_3,

*Comalco Research, Thomastown, Australia; formerly University of Stellenbosch.
†On national service.

on the rate of reduction of MnO was examined in this study.

Thermodynamics of Reduction of MnO by Carbon

For the reduction of MnO by carbon, a system of at least three components, namely, manganese, oxygen, and carbon is necessary. For a two-dimensional representation of the stability fields of the system, two degrees of freedom are possible, and these are most conveniently taken as oxygen potential and temperature. Therefore, from the phase rule, there are three co-existing phases. Since one of these is always a gaseous phase, two condensed phases must be present in each stability field.

Each pair of condensed phases possesses a region of stability in the space between oxygen potential and temperature, and this is determined by the reactions between oxygen and three condensed phases. A curve can be drawn for each combination; on one side of the curve two of the three phases can co-exist, and on the other side another two of the phases can co-exist. In this way, the entire space is divided into regions in each of which only one pair of condensed phases co-exists. A graphical representation of this type is known as a Pourbaix diagram.

The composition of the gas phase in equilibrium can be determined from the reaction between oxygen, the condensed phases, and the gaseous species. When the pressure of the gas species is fixed, a curve can be drawn in the region of the two condensed phases, and by variation of the pressure a surface can likewise be drawn. Each gaseous species has a partial-pressure surface over each pair of condensed phases, the total pressure being the sum of these surfaces.

The Pourbaix diagram constructed by Downing[5] for the Mn–O–C system is shown in Fig. 1. The gaseous phase is composed of CO, CO_2, and manganese vapour, and the total pressure at any point is the sum of the partial pressures of CO, CO_2, and Mn. Lines of constant total pressure are shown in Fig. 1 for values of 1, 10^{-2}, 10^{-4} and 10^{-6} atm (1 atm=101,325 kPa).

At a total pressure of 1 atm, Mn_2O_3 and Mn_3O_4 are unstable in the presence of carbon at all temperatures and react to form MnO. The sequence of reduction of MnO by carbon at atmospheric pressure is shown by the curve for 1 atm of total pressure from 0 °C (line AB in Fig. 1). Initially, the gaseous phase is pure CO_2, but the amount of CO increases with increasing temperature, and
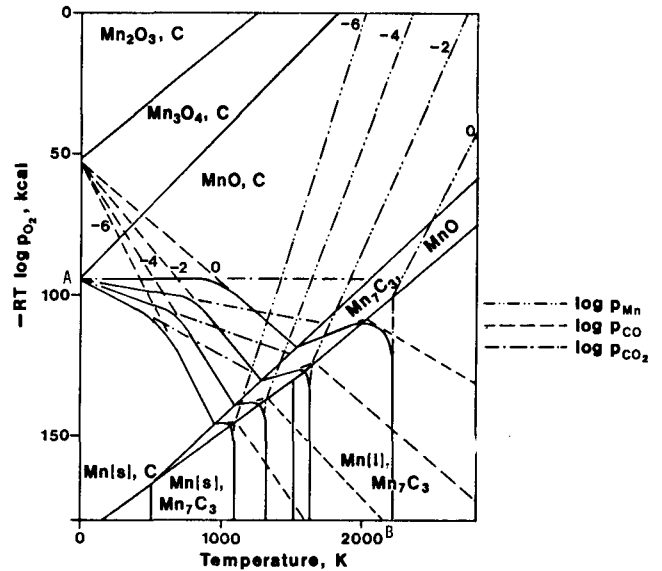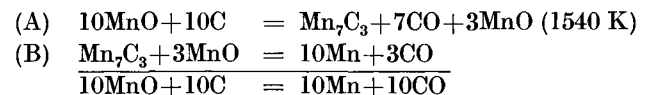

Fig. I—Pourbaix diagram for the Mn–O–C system[5]

above about 1100 K the gas is virtually pure CO. The reduction of MnO starts at about 1540 K to form Mn_7C_3, and this then reacts with excess MnO to form liquid manganese metal at about 2000 K. Pure manganese metal can be prepared by the mixing of MnO and C in equimolar amounts and heating to at least 2000 K (1727 °C):

(A) $10MnO + 10C = Mn_7C_3 + 7CO + 3MnO$ (1540 K)
(B) $\dfrac{Mn_7C_3 + 3MnO = 10Mn + 3CO}{10MnO + 10C = 10Mn + 10CO}$

In step A, the amounts of CO_2 and Mn vapour in the gaseous phase are negligible. In step B, the amount of CO_2 is again negligible but, because of the higher temperature, the vapour pressure of manganese is appreciable and, although low-carbon manganese could be produced by reaction B, the yield would be relatively low.

At lower total pressures, the reduction sequence is the same but the temperatures for the reactions are lower.

Experimental Method

The reduction step to form manganese carbide was investigated in the present study. At a total CO pressure of 1 atm, the minimum temperature required to form carbide is about 1540 K (1267 °C). So that reasonable reaction rates would be obtained, a temperature of 1350 °C was used for most of the experimental work, although temperatures in the range 1200 to 1425 °C were included to show the effect of temperature.

Equimolar amounts of MnO (2 g) and graphite (0,34 g) were mixed intimately, with or without the addition of one of the following: CaO, MgO, SiO_2, K_2CO_3, Na_2CO_3, Fe_2O_3, and Al_2O_3. The mixture was placed in a small recrystallized-alumina crucible. A continuous weighing and recording electronic balance was mounted above a tube furnace of 50 mm internal diameter, which was heated by six silicon carbide elements and maintained at constant temperature by a Eurotherm on–off controller. The furnace assembly is shown in Fig. 2. The crucible,

TABLE I

TYPICAL ANALYSIS OF MAMATWAN ORE

Constituent	Mass %
MgO	3,10
Al_2O_3	< 0,10
SiO_2	4,27
CaO	12,96
Mn_2O_3	55,90*
Fe_2O_3	5,99
Cr_2O_3	0,36
P_2O_5	0,17
K_2O	0,21
CO_2	14,91
H_2O	0,54

* This is the total manganese content of the ore expressed as Mn_2O_3

with a Pt-13%Rh support wire, was introduced into the bottom of the tube, which was then sealed and flushed with argon. Over a period of 30 seconds, the crucible was raised to a predetermined position and was supported from the balance, which had automatic taring. During a run, the tube was flushed with argon at the rate of 630 ml/min and the loss in mass of the crucible was recorded continuously. The temperature of the crucible was also recorded continuously as a check that it remained constant during the run. After the reaction, the crucible was lowered into the water-cooled quenching chamber at the bottom and was allowed to cool.

The MnO was prepared from manganese dioxide of analytical-reagent grade, which was heated for 5 hours in a large magnesia crucible at 1100 °C under a hydrogen atmosphere. The X-ray-diffraction pattern of the product revealed only MnO. The size distribution of the MnO is given in Table II. For most runs, the MnO was unsized and the distribution of particle sizes in a sample then corresponded to that given in Table II. However, so that the effect of particle size on the rate of reduction could be investigated, several different size fractions were prepared.

The graphite was Ellor 7, a high-purity form with a maximum impurity level of 0,06 per cent, and it was milled and separated into several size fractions. The most frequently used size fraction was 120 to 180 μm and, unless otherwise stated, this size fraction was used in all the runs. In some instances, the phases present in the products of reaction were examined by X-ray diffraction. A Pillips diffractometer with a graphite monochromator was used, the radiation being Cu Kα.

Results and Discussion

The data on loss in mass were converted to fractional reaction on the assumption that the loss in mass of the sample was due entirely to the evolution of CO. This permitted the calculation of the mass of oxygen removed from the MnO and hence the fractional reaction (x):

$$x = \frac{\text{mass of oxygen removed}}{\text{total mass of removable oxygen}}. \quad . \quad . \ (4)$$

For the case of 2 g of MnO and 0,34 g of graphite,

$$x = \frac{70,94\ m}{2 \times 28,01} = 1,26\ m, \quad . \ . \ . \ . \ . \ . \ . \ (5)$$

where m is the measured loss in mass. When Fe_2O_3 was added, the oxygen content of the Fe_2O_3 was included as removable oxygen. The rate of reduction of MnO is defined as dx/dt and is equal to the slope of the curve for fractional reaction versus time.

TABLE II

SIZE DISTRIBUTION OF THE MnO USED IN THE REDUCTION TESTS

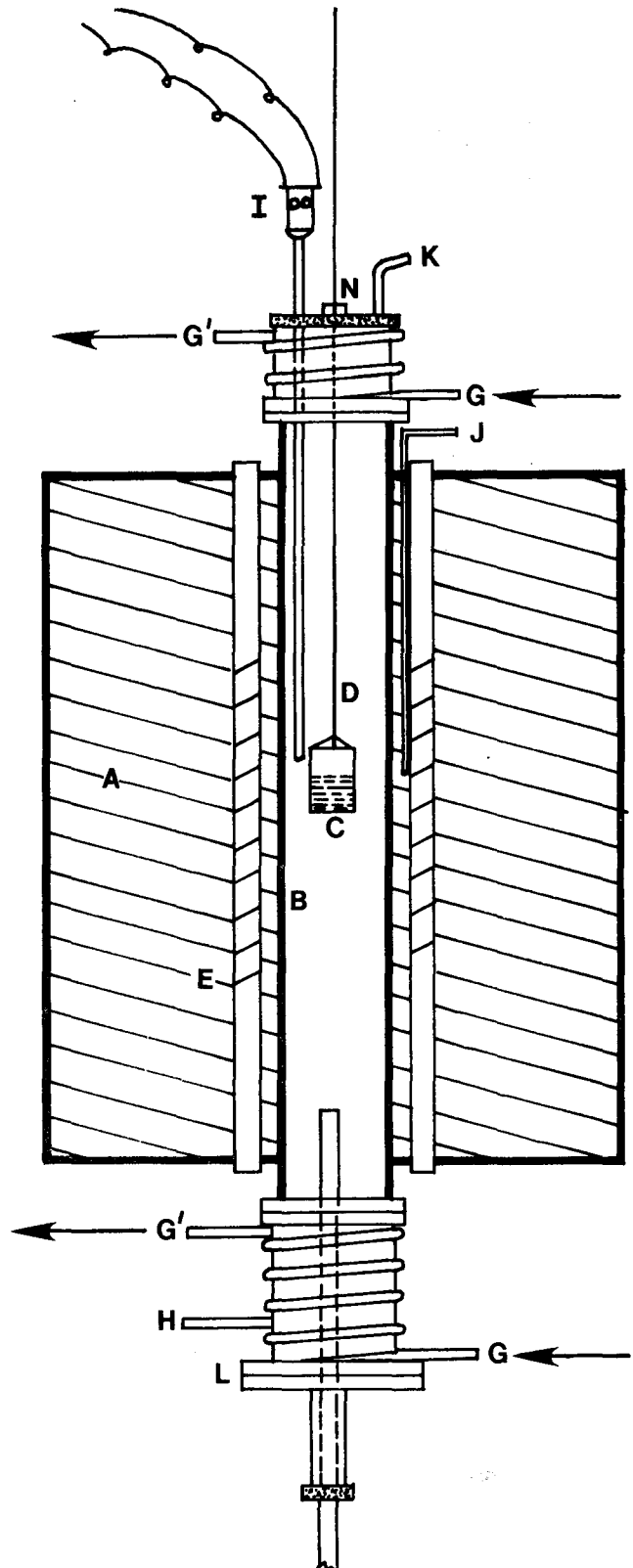| Size fraction, μm	Mass, %
< 45	1,9
45 to 63	0,5
63 to 75	0,8
75 to 90	1,7
90 to 125	3,7
125 to 180	27,9
180 to 250	58,1
250 to 355	2,0
> 355	3,2

Fig. 2—Furnace assembly for the MnO-graphite reduction tests

A Insulating bricks
B Pythagoras work tube
C Alumina reaction crucible
D Pt-13%Rh support wire
E Silicon carbide element
F Pushrod
G Water for cooling
H Argon inlet (during run)
I Pt/Pt-13%Rh indicating thermocouple
J Pt/Pt-13%Rh control thermocouple
K Argon inlet (for flushing)
L Removable plate for insertion and removal of crucible

The results for runs in which no gangue components were added are shown in Figs. 3 to 6. These show the effects of temperature, ratio of MnO to C, and particle sizes of graphite and MnO. In all the tests, the rate of reduction was greatest at the start of the reduction, remained fairly constant until most of the reaction was complete, and then decreased rapidly to zero. Wherever the fractional reaction was less than 1, X-ray diffraction revealed unreacted MnO but no graphite. This shows that the slowing down and eventual cessation of the reaction was due to depletion of graphite.

The product of reaction was identified by X-ray diffraction as Mn_5C_2 (and not Mn_7C_3, as expected from the Pourbaix diagram), and it appears that Mn_5C_2 is
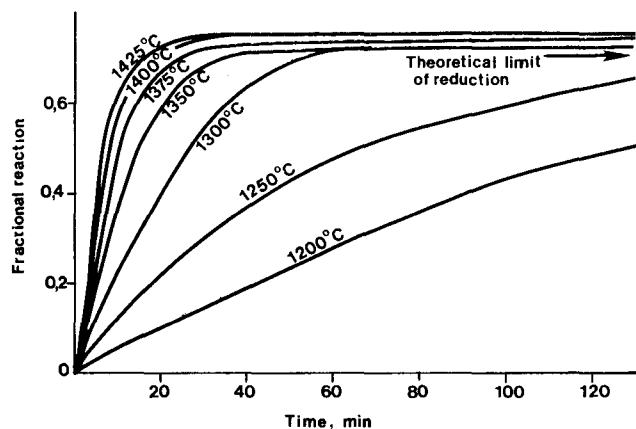
Fig. 3—The effect of temperature on the reduction of MnO by graphite

the stable carbide of manganese under the experimental conditions.

The effect of increased temperature is an increase in the rate of reduction of MnO as shown by the slopes of the first portion of the fractional reaction curves in Fig. 3. According to stoichiometric calculations, the maximum fractional reaction if all the oxygen is removed as CO is 0,72 for equimolar mixtures of MnO and graphite. The calculated fractional reactions in Fig. 3 are from 0,74 to 0,77, which are slightly greater than the theoretical value.

The reason for the slightly higher values of fractional reaction is most probably that a small amount of CO_2 escaped from the reaction mixture. Since CO_2 carries twice as much oxygen per mole of carbon as does CO, the presence of CO_2 in the gas raises the apparent fractional reaction. Calculations show, for example, that, if all the oxygen were removed as CO_2, there would be more than enough carbon in an equimolar mixture of MnO and graphite to entirely reduce the manganese to Mn_5C_2.

Thermodynamically, the existence of an appreciable amount of CO_2 in the presence of graphite is not possible at temperatures above about 1000 °C. However, during reduction, non-equilibrium conditions exist in the mixture and considerable amounts of CO_2 are formed:

$$5MnO + 9CO = Mn_5C_2 + 7CO_2. \qquad \text{(6)}$$
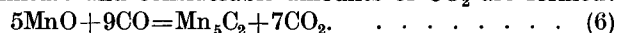
If only CO were evolved from the mixture, all the CO_2 formed by reaction (6) would react with graphite to reform CO. It is most likely that the greatest proportion of CO_2 will be evolved at the stage when the curves for fractional reaction begin to flatten out, because this is the stage at which carbon is becoming deficient and the diffusion of CO and CO_2 between the MnO grains and
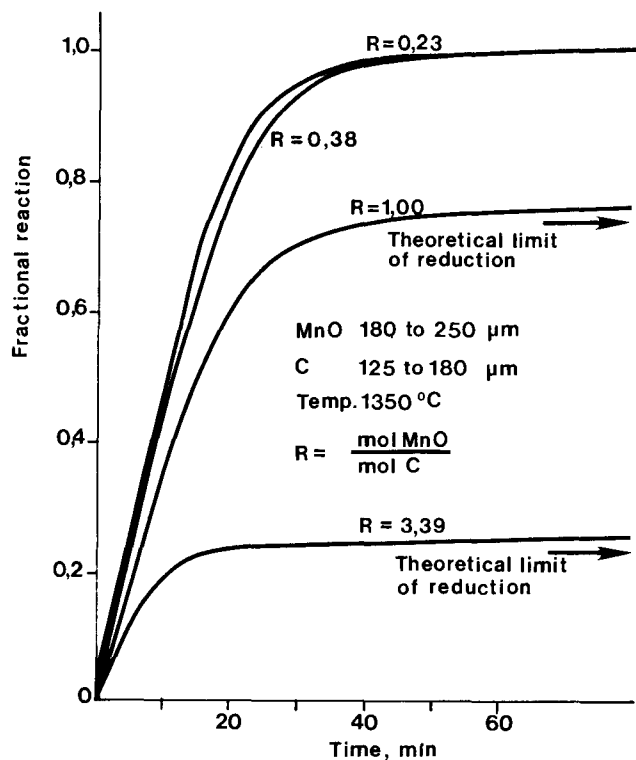

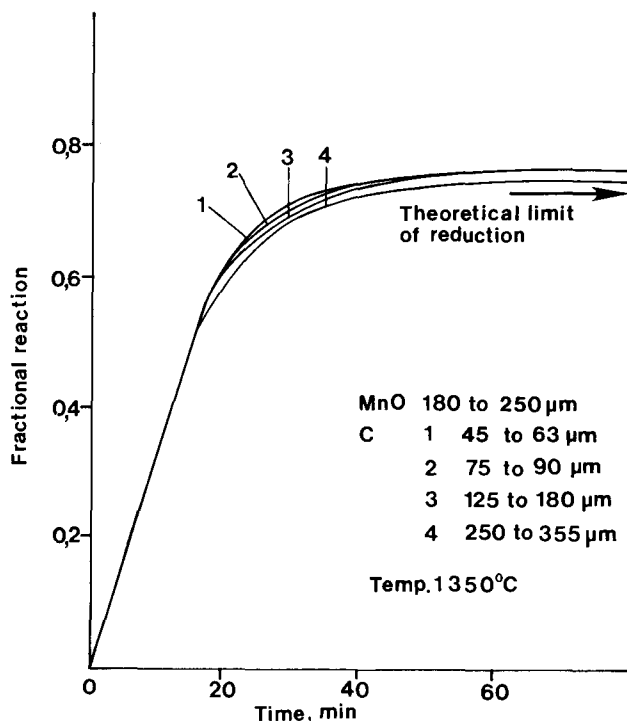Fig. 4—The effect of MnO-to-C ratio on the reduction of MnO by graphite

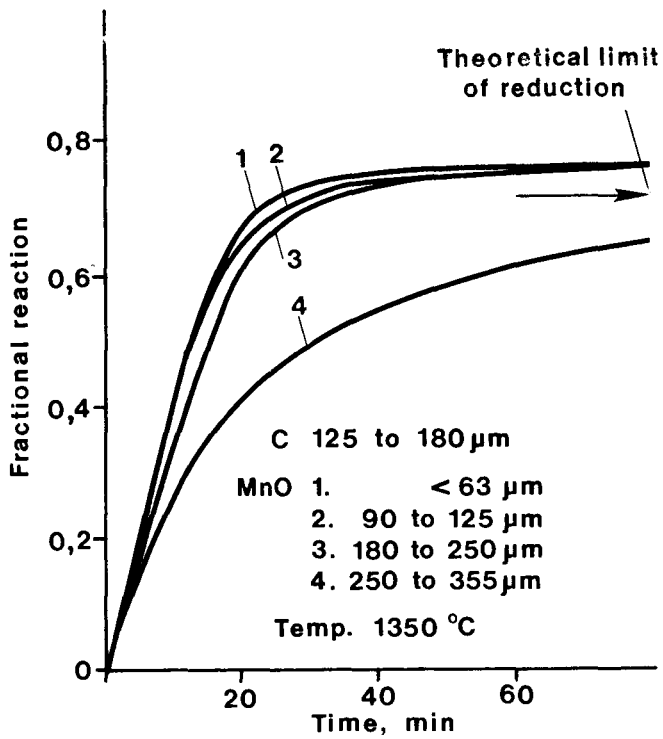Fig. 5—The effect of the particle size of graphite on the reduction of MnO by graphite

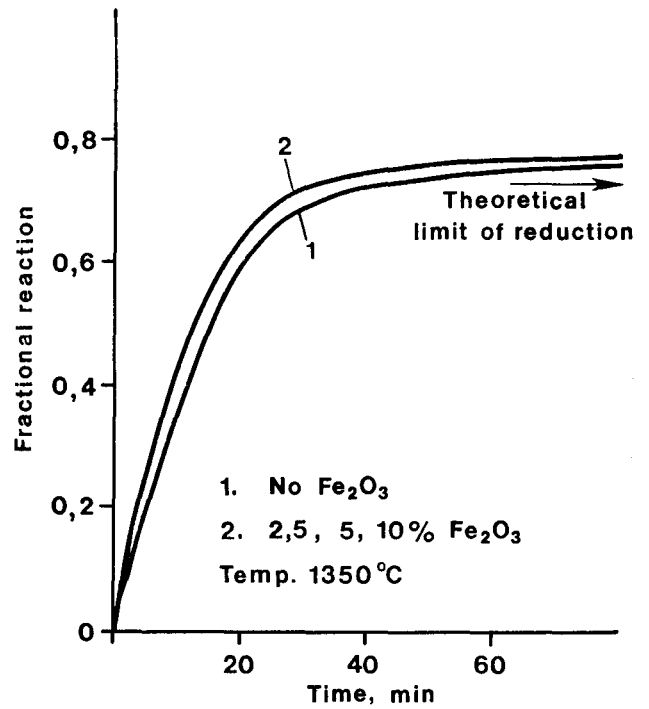Fig. 6—The effect of the particle size of MnO on the reduction of MnO by graphite

Fig. 8—The effect of additions of Fe₂O₃ on the reduction oi MnO by graphite
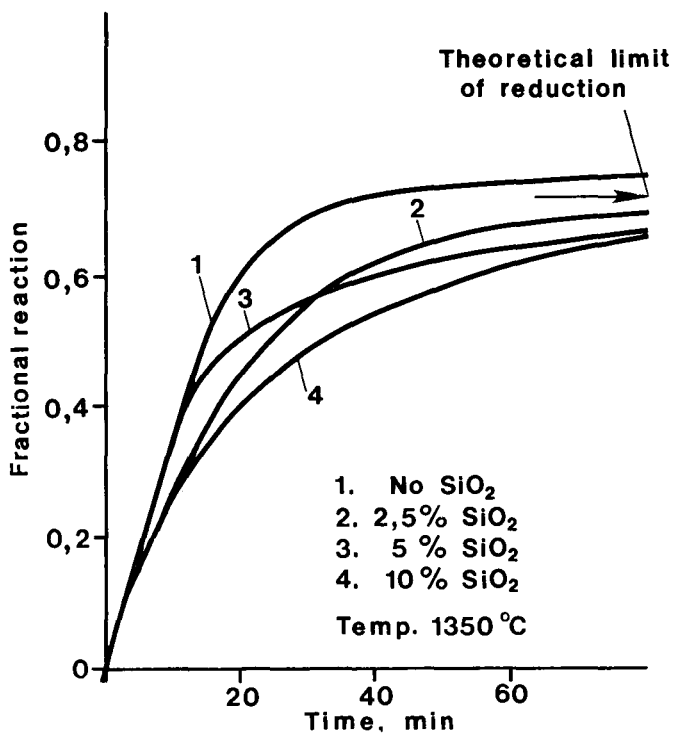

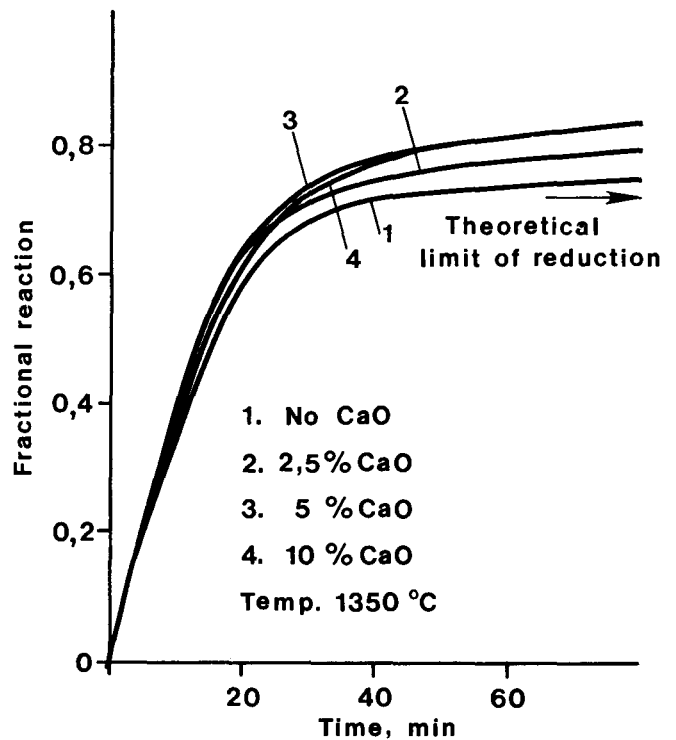Fig. 7—The effect of additions of SiO₂ on the reduction by graphite

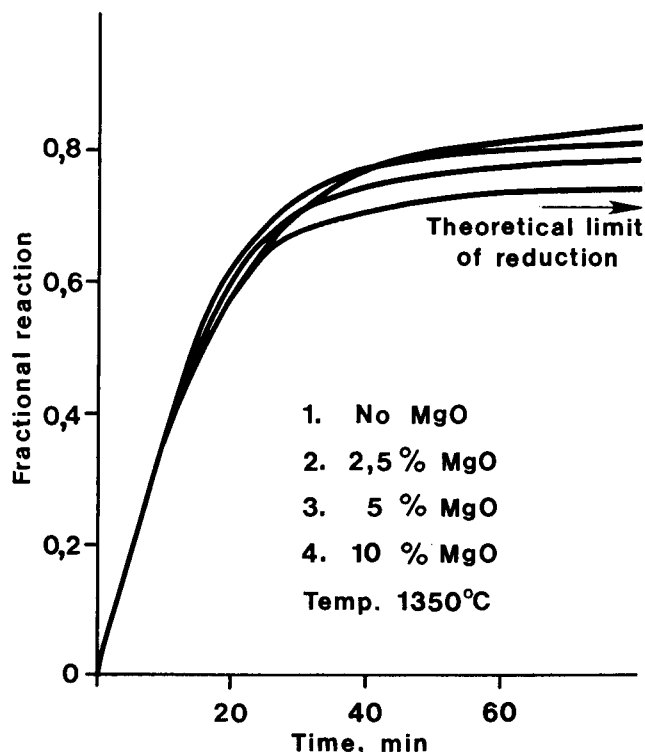Fig. 9—The effect of additions of CaO on the reduction of MnO by graphite

Fig. 10—The effect of additions of MgO on the reduction of MnO by graphite

graphite grains is the rate-controlling step. At this stage it is possible for part of the CO_2 formed by reaction (4) to escape from the mixture before it encounters sufficient graphite to reduce it to CO.

The evolution of CO_2 from the reaction mixture is evidence that reduction occured by way of CO_2 as an intermediate product. The alternative mechanism, reduction of MnO by solid graphite at points of contact, would produce no detectable amount of CO_2 at temperatures above about 1000°C.

The effect of the MnO-to-C ratio on the rate of reduction is shown in Fig. 4. The rate of reduction is increased as the MnO-to-C ratio decreases. The final values for fractional reaction are slightly higher than the theoretical values at MnO-to-C molar ratios of 3,39 and 1,0, indicating the evolution of a small amount of CO_2. At ratios of 0,38 and 0,23, the final fractional reaction is 1, which is the theoretical value since there is an excess of graphite, thus indicating that only CO was evolved in these instances; there was sufficient graphite throughout the reaction for the reduction of CO_2 to CO.

The particle size of the graphite (Fig. 5) has no effect on the reaction rate. As shown in Fig.6, the rate of reduction is also almost independent of MnO particle size in the size range 63 to 250 μm. However, there is a large decrease in reaction rate when the MnO size is increased to between 250 and 355 μm. The reason for this is not certain, but it is probably due to a change in the rate-controlling step from the rate of gasification of graphite to the rate of reaction of the MnO.

The Effect of Gangue Components

The effect of SiO_2 on the rate of reduction of MnO is shown in Fig. 7. Although there is some crossing of the curves, it is evident that SiO_2 causes an appreciable

decrease in the rate of reduction. The most likely explanation of this is that MnO and SiO_2 react to form a slag. There is insufficient SiO_2 to flux anything but a fraction of the MnO, and the reduced rate of reduction is probably due to a coating of slag on the MnO particles that reduces the area of contact between the MnO grains and the reducing atmosphere. The presence of β-$MnSiO_3$ was detected in the reaction products by X-ray diffraction, and this supports the above argument.

The effect of Fe_2O_3 is shown in Fig. 8. Since Fe_2O_3, as well as MnO, is reduced, the oxygen content of the Fe_2O_3 was included in the calculation of the fractional reaction. The addition of Fe_2O_3 increases the rate of reduction slightly, and this may be due to two factors.

(i) Fe_2O_3 is much easier to reduce than MnO, and hence the rate of reduction of a mixture of the two is higher than that of MnO. However, the amount of Fe_2O_3 present is too small for this effect to be appreciable.

(ii) Metallic iron and iron carbide, when present even in very small amounts, catalyse the Boudouard reaction[6-8]. If the rate of gasification of graphite is the rate-controlling step, the reduction of Fe_2O_3 very early in the reaction leads to an increase in the overall rate of reduction.

The effect of CaO, MgO, and Al_2O_3 is shown in Figs.9 to 11, and it is evident that the effect on the rate of reduction is very small, if not negligible, indicating that CaO, MgO, and Al_2O_3 do not catalyse the Boudouard reaction. However, for each mixture, the final fractional reduction was raised, showing that a greater amount of CO_2 evolved than when there were no additions. The reason for this is not certain, but it may be due to the diluting effect of the additions on the graphite in the mixture, which
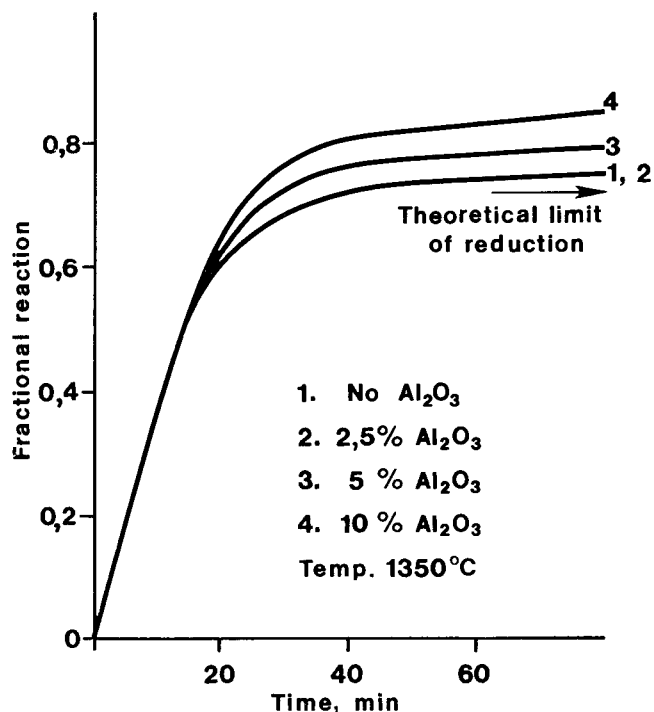

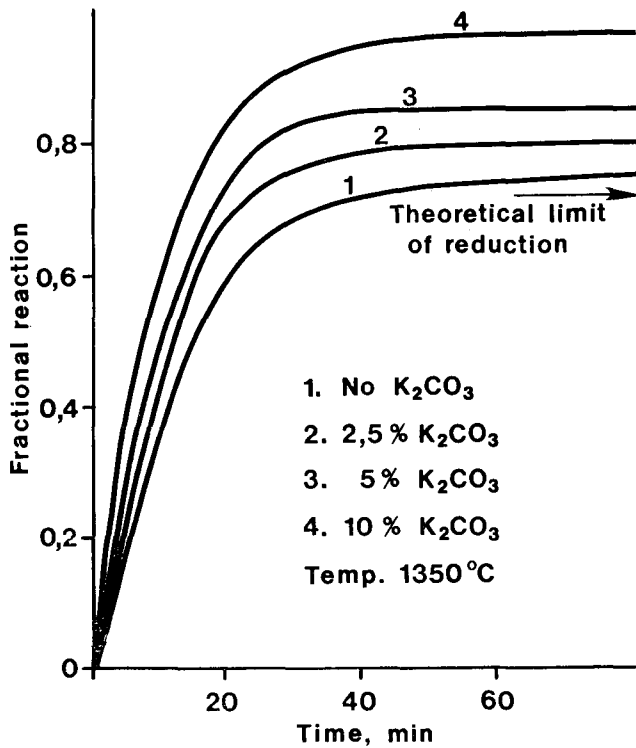**Fig. 11—The effect of additions of Al_2O_3 on the reduction of MnO by graphite**

Fig. 12—The effect of additions of K_2CO_3 on the reduction of MnO by graphite

1. No K_2CO_3
2. 2,5 % K_2CO_3
3. 5 % K_2CO_3
4. 10 % K_2CO_3

Temp. 1350 °C

reduced the chance of CO_2 encountering graphite particles for reaction. No reaction between MnO and the additives was indicated by the X-ray-diffraction patterns of the reacted mixtures.

The effect of K_2CO_3 and Na_2CO_3 is shown in Figs. 12 and 13, from which it can be seen that there is a marked increase in the rate of reduction of MnO when K_2CO_3 or Na_2CO_3 is present. Also, the final value of fractional reduction is greatly increased owing to the evolution of CO_2 but, as before, the reason for this is not clear. The explanation for the marked increase in the rate of reduction is almost certainly that K_2CO_3 and Na_2CO_3 catalyse the gasification of graphite.

Activation Energy for the Reduction of MnO by Graphite
According to the Arrhenius equation,

$$\text{Rate} = Ae^{-E/RT}, \qquad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (7)$$

where A is a constant, R is the universal gas constant, T the absolute temperature, and E the activation energy, and the relation between the logarithm of the rate of reaction and the reciprocal of the absolute temperature is linear with a slope equal to $-E/R$.

The rate of reduction of MnO at the start of the reduction was determined from the curves in Fig. 3. As shown in Fig. 14, the relation is linear, as expected, and is described by the following equation obtained by linear regression:

$$\ln \frac{dx}{dt} \bigg|_{t=0} = -28\,950/T + 14{,}54. \qquad \ldots \ldots \ldots (8)$$

Hence, the activation energy is 57,5 kcal.

The value corresponds to the activation energy of the rate-controlling reaction, which was suggested earlier to be the Boudouard reaction. The activation energy of the

Boudouard reaction has been the subject of several laboratory investigations, and the results have been reviewed by Rao[4]. The values obtained vary from 59 to 97 kcal per mole of graphite, and appear to depend on the form of the carbon and probably also on the impurities in the carbon. For this reason, the activation energy of the Boudouard reaction was determined again, this time from the graphite with which the MnO reduction study was conducted.

Samples of powdered graphite of 2 g each were reacted with carbon dioxide at a flowrate of 1500ml/min in the same apparatus as that used for the tests on the reduction of MnO. The curves for fractional reaction were linear at temperatures below 1100 °C but curved slightly at higher
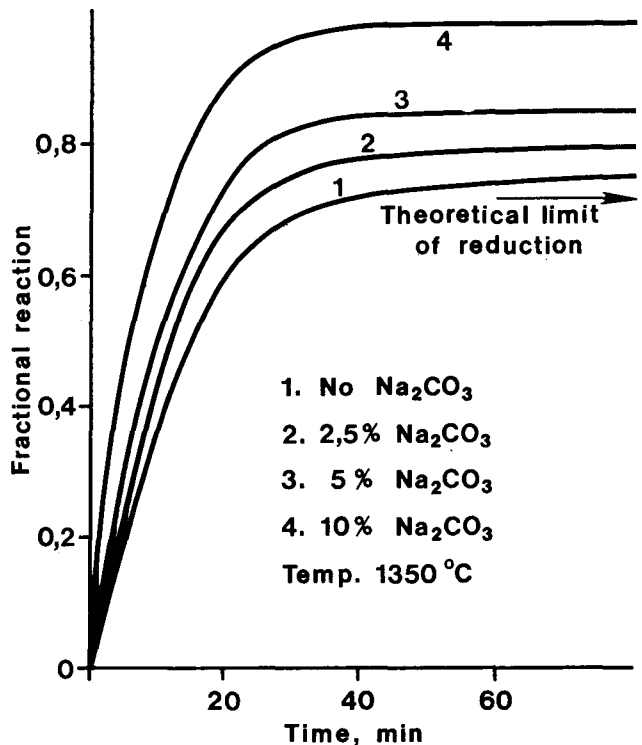

Fig. 13—The effect of additions of Na_2CO_3 on the reduction of MnO by graphite

1. No Na_2CO_3
2. 2,5% Na_2CO_3
3. 5 % Na_2CO_3
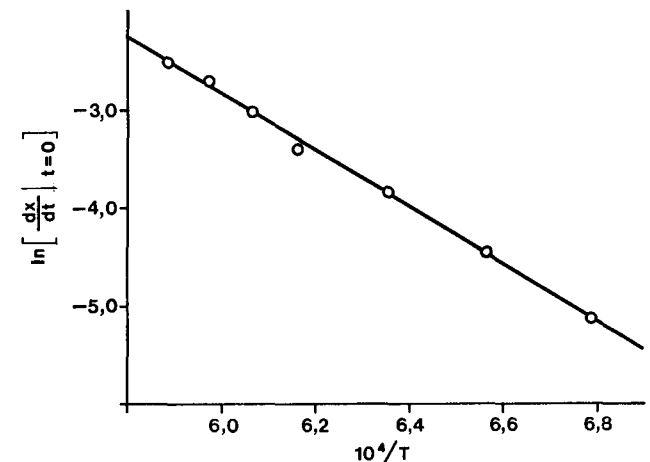4. 10% Na_2CO_3

Temp. 1350 °C

Fig. 14—Arrhenius plot for the reduction of MnO by graphite based on the data of Fig. 3

temperatures. The slopes at the origin are shown as a function of temperature in Fig. 15. The relationship is linear, as expected, up to 1100 °C, but then deviates from linearity. The reason for this is probably that, at the flowrate of CO_2 used, the rate of reaction is controlled chemically below 1100 °C but diffusion-controlled above that temperature. Nevertheless, there are sufficient points to give a fairly accurate value of the activation energy. The linear portion of the curve is described by the equation (obtained by linear regression):

$$\ln \frac{dx}{dt}\bigg|_{t=0} = 30\ 790/T + 17,134. \qquad \ldots \ldots (9)$$

Hence, the activation energy of the Boudouard reaction is 61,5 kcal per mole of graphite.

This value agrees fairly well with the value for the reduction of MnO by graphite, and this is considered to be very strong evidence that the rate-controlling step is the gasification of graphite.

Model for the Reduction of MnO by Graphite

As a further test of the above conclusion, the experimental data were treated by a modification of Rao's model[4] for the reduction of hematite by graphite. The following assumptions were made.

(i) The gasification of graphite by CO_2 is rate-controlling.
(ii) The temperature of the reaction mixture is constant.
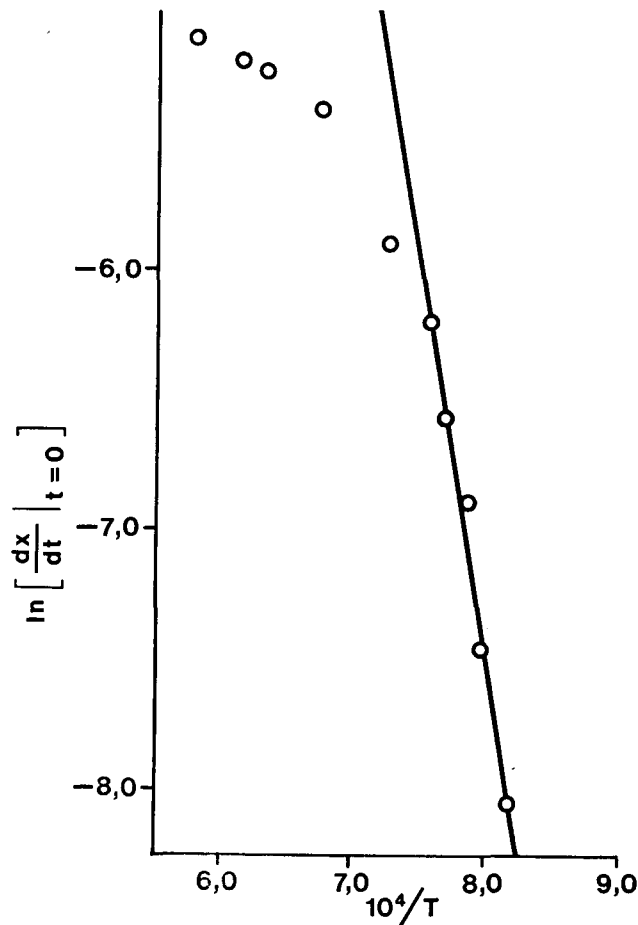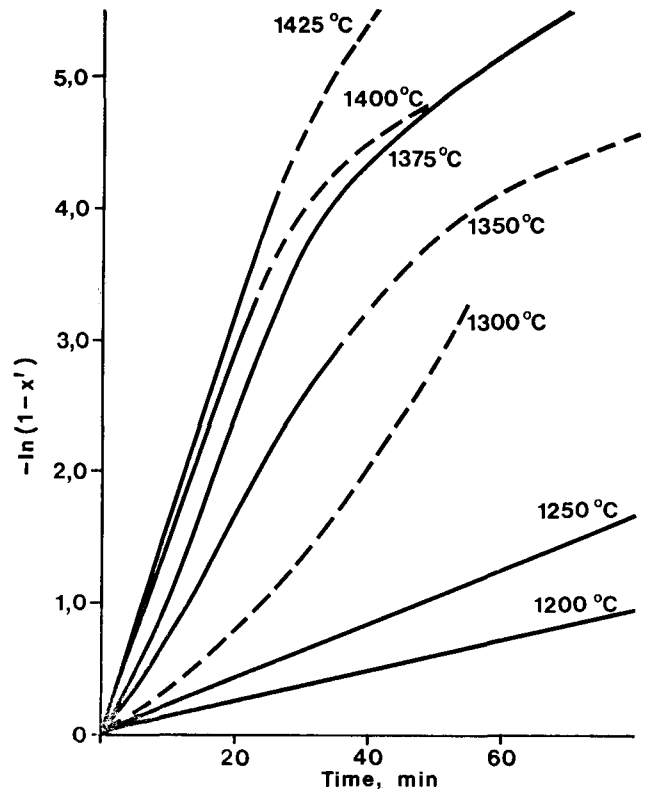(iii) The penetration of argon is limited, and for practical

Fig. 16—Data of Fig. 3 plotted according to equation (20)

purposes the gas phase in the mixture is composed principally of CO and CO_2.

(iv) The mixture behaves as if it were an assemblage of numerous individual particles each entirely submerged in an atmosphere of CO and CO_2.

(v) For the greater part of the reduction, the composition of the gas phase changes only slowly.

(vi) Mass-transfer resistances are negligible compared with the chemical resistance of the Boudouard reaction.

(vii) The gasification of graphite in an atmosphere of CO and CO_2 obeys first-order kinetics.

Therefore, the rate of reaction of graphite is given by

$$-\frac{dW_C}{dt} + RW_C, \qquad \ldots \ldots \ldots \ldots \ldots (10)$$

where R is a rate constant and W_C is the mass of carbon in the mixture. Integration gives

$$\triangle W_C = W_C^*[1 - e^{-Rt}]. \qquad \ldots \ldots \ldots \ldots (11)$$

where $\triangle W_C$ is the mass of carbon gasified in time t and W_C^* is the mass of carbon initially in the mixture. If β is the fraction of CO utilized in the reduction,

$$\triangle W_{oxide} = \frac{8}{3}\beta\triangle W_C, \qquad \ldots \ldots \ldots \ldots (12)$$

where $\triangle W_{oxide}$ is the mass loss of the oxide in time t.

$$\triangle W_{total} = \triangle W_C + \triangle W_{oxide}$$

$$= \triangle W_C + \frac{8}{3}\beta\triangle W_C$$

$$= \triangle W_C[1 + \frac{8}{3}\beta] \qquad \ldots \ldots \ldots \ldots (13)$$

Fig. 15—Arrhenius plot for the gasification of graphite by carbon dioxide

For the simplest case where no CO_2 is evolved from the reaction mixture, $\beta=0,5$, as can be seen by reference to equations (1) and (2), and

$$\triangle W_{total}=\frac{7}{3}W^*_C[1-e^{-Rt}]. \qquad (14)$$

The fractional reaction, x, is given by

$$x=\triangle W_{total}/QW_o, \qquad (15)$$

where Q is the maximum fractional reaction and W_0 is the initial mass of the oxide-graphite mixture. For a mixture of 2 g of MnO and 0,34 g of graphite,

$$W_o=6,88\ W^*_C \qquad (16)$$

and

$$x=\frac{0,339[1-e^{-Rt}]}{Q}. \qquad (17)$$

Theoretically, Q is equal to 0,72, but in all cases the actual values were somewhat higher because of the evolution of some CO_2. Since the case $\beta=0,5$ was taken, equation (17) applies only to cases in which the evolution of CO_2 was small. This is best approached by the data in Fig. 3 for the effect of temperature on the rate of reduction

Equation (17) can be simplified further if

$$x^1=Qx/0,339, \qquad (18)$$

i.e.,

$$x^1=1-e^{-Rt} \qquad (19)$$

and therefore

$$-\ln(1-x^1) = Rt. \qquad (20)$$

If the assumptions made above apply to the reduction of MnO by graphite, then the relation between ln $(1-x^1)$ and t is linear.

The data of Fig. 3 were expressed in the form ln $(1-x^1)$, and these values are presented as a function of time in Fig. 16. The relationships are approximately linear over a considerable period for each run, and the deviation generally occurs late in the run at a time when the graphite is nearing depletion. At that time, the reaction becomes diffusion-controlled and the model no longer applies.

Conclusions

The following conclusions were drawn from the study.
(i) At temperatures between 1200 and 1425°C, the reduction product of mixtures of MnO and graphite is Mn_5C_2.
(ii) The rate of reduction of MnO by graphite is increased by an increase in the temperature and a decrease in the ratio of MnO to C. The effect of the particle size of MnO and of graphite on the rate of reduction at 1350°C is very slight in the range 63 to 250 μm for MnO and 45 to 355 μm for graphite.
(iii) The rate of reduction of MnO by graphite at 1350°C is increased markedly by the addition of Na_2CO_3 and K_2CO_3, slightly increased by the addition of Fe_2O_3, unaffected by the addition of CaO, MgO, and Al_2O_3, and decreased by the addition of SiO_2.

(iv) The gas evolved from the mixture is predominantly CO, but in all cases some CO_2 was evolved, this being greatest when one of the additives (CaO, MgO, Al_2O_3, Na_2CO_3, or K_2CO_3) was present.
(v) The presence of CO_2 in the effluent gas is evidence that reduction occurred by way of CO_2 as an intermediate product. The alternative mechanism, the reduction of MnO by graphite at points of contact, produces only CO at the temperatures used in the work.
(vi) The activation energy of the rate-controlling reaction in the reduction of MnO by graphite is 57,5 kcal. This is similar to 61,5 kcal, the experimentally determined activation energy of the Boudouard reaction, and suggests that the rate of gasification of graphite is the rate-determining step in the reduction of MnO.
(vii) The relation between ln $(1-x^1)$, where x^1 is defined by equation (18), and time is linear for the reduction of MnO by the graphite over the range 1200 to 1425°C. This is to be expected if the Boudouard reaction is rate-controlling.

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