Thermochimica Acta, 59 (1982) 361–377
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

THE REDUCTION OF IRON ORES BY HYDROGEN AND CARBON MONOXIDE AND THEIR MIXTURES

R. HUGHES, E.K.T. KAM and H. MOGADAM-ZADEH *

Department of Chemical Engineering, University of Salford, Salford (Gt. Britain)

(Received 19 May 1982)

ABSTRACT

Experimental measurements of the rate of reduction of particles of Carol Lake and Kiruna ores have been made using pure hydrogen and pure carbon monoxide and mixtures of these two gases. The temperature range covered was 773–1143 K and throughout this range the reduction rate with hydrogen was greater than that with carbon monoxide. A retracting core model was found to best fit the experimental data even when granules of 9×10^{-4} m diameter were used. Reduction with gas mixtures of hydrogen and carbon monoxide give rates intermediate between those of the pure gases.

INTRODUCTION

Because of its industrial importance the reduction of the oxides of iron has produced a very extensive literature over many years. Much of this work has been reviewed by Themelis and Gauvin [1] and Von Bogdandy and Engell [2] and more recently by Szekely et al. [3]. Most of the early work was concerned with basic studies using just one reductant gas or gas mixture, i.e., single mixtures of H_2/H_2O [4–12] or CO/CO_2 [13–17] were employed. More recently there has been a growing interest in the development of 'direct reduction' processes as an alternative to the conventional blast-furnace for iron production. Such processes are favoured when there is ready availability of natural gas but a shortage of coking coal.

Many processes have been developed for direct reduction. In some, a solid reductant such as coal is employed in a rotary kiln arrangement but in the vast majority of current production processes (MIDREX, ARMCO, PUROFER) pellets of hematite are reacted with a hydrogen–carbon monoxide mixture in a countercurrent moving bed to produce sponge iron pellets. The H_2/CO gas mixture is obtained by reforming of methane or higher hydrocarbons in a catalytic reformer.

---

* Present address: Iranian Iron and Steel Corporation, Tehran, Iran.

Some previous work has been done using gas mixtures of H_2 and CO. Turkdogan and Vinters [8,9] made some limited measurements and some preliminary experiments have been reported by Szekeley and El-Tawil [18] using discs of laboratory grade hematite. In both cases the rate of reduction increased with increasing hydrogen content of the gas mixture.

The ultimate objective is to produce a model for the direct reduction of iron ore in a moving bed. To do this it is essential to have data on the rates of reduction for gas mixtures. Consequently, this paper describes experiments on the direct reduction of commercial Carol Lake and Kiruna ores. Initial experiments were made using pure gases in order to obtain intrinsic kinetics and activation energies. These were followed by measurements of the reduction rates with gas mixtures. Because of carbon deposition with pure CO and some CO/H_2 gas mixtures, measurements for these gases had to be made at temperatures above 1070 K.

THEORY

Models for reduction

In order to obtain a satisfactory explanation for the observable kinetics of the process a suitable model must be used. A number of models have been proposed for non-catalytic gas–solid reactions which include, of course, the reduction of iron ore (see for example ref. 3). Basically, all of these models are modifications of two extreme cases: the retracting core model and the homogeneous (or uniform reaction model). Which model will more closely represent the true situation depends on a number of factors, but one criterion is based on the porosity of the solid reactant. If the particles are sufficiently dense with little porosity, then a reaction interface will tend to form between unreacted and reacted solid, giving rise to the retracting core model in which the reaction interface progresses from the outside of the particle to the centre during the course of the reaction. At the opposite extreme if the particle is sufficiently porous, then the reacting gases can penetrate throughout the particle prior to reaction, so that when reaction occurs it is uniform throughout the particle, modified only by any pore diffusional gradients.

Retracting core model

In reduction of small iron ore particles where intrinsic diffusion effects are negligible it is realistic to assume that the overall reaction mechanism is controlled by the iron/Wüstite interface. Since the reaction has been shown to be of first order then the rate of reaction may be written as

$$\frac{\mathrm{d}N_{\mathrm{n}}}{\mathrm{d}t} = k'_{\mathrm{A}}\left(C_{\mathrm{Ai}} - \frac{C_{\mathrm{Bi}}}{K_{\mathrm{e}}}\right) \tag{1}$$

where C_{Ai} and C_{Bi} are the respective interface concentrations of hydrogen and water vapour, and dN_n/dt is the net rate of reaction. If small particles and high flow rates are employed then it is reasonable to assume that the concentrations of A and B are the same at the interface and in the bulk gas. Thus (1) may be written as

$$\frac{dN_n}{dt} = k'_A\left(C_{Ab} - \frac{C_{Bb}}{K_e}\right) \tag{2}$$

where the subscript b refers to bulk concentrations.

If the retracting core model is applicable and a pseudo-steady state for the material balance is assumed, then eqn. (2) may be expressed in terms of the shrinkage of the core.

$$-\frac{dN_0}{dt} = -\frac{dN_n}{dt} = -C_0\frac{dV}{dt} = -C_0\frac{d}{dt}\left(\tfrac{4}{3}\pi r_i^3\right) \tag{3}$$

where C_0 is the atomic density of oxygen in the ore, r_i is the core radius and dN_0/dt is the rate of oxygen removal.

Based on unit area of the unreacted core we have from (3)

$$-\frac{1}{4\pi r_i^2}\frac{dN_0}{dt} = -\frac{1}{4\pi r_i^2}\frac{dN_n}{dt} = -\frac{C_0}{4\pi r_i^2}4\pi r_i^2\frac{dr}{dt} \tag{4}$$

and on equating (2) and (4) and integrating between $r = r_0$ at $t = 0$ and $r = r_i$ at $t = t$

$$1 - \frac{r_i}{r_0} = \frac{k'_A}{C_0}\left(C_{Ab} - \frac{C_{Bb}}{K_e}\right)t \tag{5}$$

and in terms of the fractional reduction F

$$\left[1 - (1-F)^{1/3}\right] = \frac{k'_A}{r_0C_0}\left(C_{Ab} - \frac{C_{Bb}}{K_e}\right)t \tag{6}$$

Thus, if the reaction were interface controlled a plot of the left-hand side of (6) against time should yield a straight line.

Porous solid model

For the case of almost uniform gas penetration within the pores of the particle, internal reduction predominates and the rate is controlled primarily by gas–solid reaction on the pore walls. The model assumes that after the formation of a thin layer of iron the product gas diffuses outwards through this thin layer and its diffusion is rapid so that the reaction rate is determined by reaction of H_2 (or CO) with the oxide. If the reaction is assumed to take place uniformly throughout the whole particle then the rate of reaction can be written as

$$\frac{dW_r}{dt} = -W_rSk'_A(C_{Ab} - C_{Ae}) \tag{7}$$

TABLE 1

Apparent density, porosity and true density measurements of Carol Lake and Kiruna ores

Sample	Carol Lake			Kiruna		
	Apparent density (kg m^{-3})×10^{-3}	Porosity (%)	True density (kg m^{-3})×10^{-3}	Apparent density (kg m^{-3})×10^{-3}	Porosity (%)	True density (kg m^{-3})×10^{-3}
Broken	3.21	22.3	4.82	4.12	13.6	5.12
	3.37	21.02	4.95	4.26	12.1	5.31
	3.14	23.2	4.77	4.06	13.9	5.10
Unbroken	3.11	20.9	4.62	4.18	12.9	5.06
	3.29	23.5	4.91	4.21	13.1	5.17
	3.16	22.4	4.66	4.15	12.7	5.02
Mean	3.21	22.21	4.78	4.16	13.05	5.13

TABLE 2

Pore surface area measurements with BET technique of samples before and after reduction by hydrogen

Condition	Carol Lake ore		Kiruna ore	
	$S \times 10^{-3}$ ($m^2\ kg^{-1}$)	$\bar{r}$ (m)	$S \times 10^{-3}$ ($m^2\ kg^{-1}$)	$\bar{r}$ (m)
Pre-reduction ore	3.02	0.271	1.45	0.188
Reduced at 873 K	2.07	0.447	0.65	0.477
973 K	1.45	0.699	0.54	0.626
1173 K	0.906	1.119	0.42	0.805

where W_r is the amount of oxygen in the sample at time t, S is the usable pore surface area of Wüstite per unit mass of oxygen and the other quantities have their usual meaning.

Equation (7) can be written in terms of the fractional reaction F as

$$F = \frac{W_0 - W_r}{W_0} = 1 - \frac{W_r}{W_0} \quad or \quad \frac{W_r}{W_0} = 1 - F \tag{8}$$

where W_0 is the initial weight of oxygen in the sample. Substituting (8) in (7) and integrating we get

$$\ln(1 - F) = -Sk'_A(C_{Ab} - C_{Ae})\,t \tag{9}$$

Thus, a plot of $\ln(1 - F)$ against time should give a straight line if this mechanism is obeyed.

EXPERIMENTAL

Measurements of the reduction rate of iron ore particles were made using a gravimetric system. Use of such a system is convenient since a continuous record of the reduction is obtained and the small sample size enables a large number of experiments to be done. The particles were obtained by crushing sintered pellets of both Carol Lake and Kiruna ores; particles were screened into size ranges to give average particle sizes of $(9 \pm 0.8) \times 10^{-4}$ m, $(1.8 \pm 0.2) \times 10^{-3}$ m and $(4.8 \pm 0.45) \times 10^{-3}$ m. Larger sizes of approximately 7.1×10^{-3} m and 0.011 m diameter were used in a few experiments. All the kinetic data were obtained using the smallest particle size.

Analysis of the Carol Lake and Kiruna ores (kindly provided by the Sheffield Laboratories of BSC) gave a total iron content of 64.5% and an Fe_2O_3 content better than 89.5% for both ores. The porosity of the pellets was measured by means of kerosene penetration into previously evacuated particles or pellets. This, together with the bulk density, enabled the true pellet density to be determined. Surface areas of the ore and reduced particles were measured using conventional adsorption techniques. Results for all these physical measurements are presented in Tables 1 and 2. It will be noted from Table 1 that the densities and porosities from whole and broken pellets are essentially the same. Combination of the surface areas and porosities enables a mean pore radius to be calculated from the formula

$$\bar{r} = 2\, V_g/S_g$$

and the values obtained are also listed in Table 2.

The tubular reactor was constructed from type 316 stainless steel and was 0.025 m inner diameter and 0.86 m in length. The ore sample was suspended in this tube by means of a thin platinum wire attached to the arm of a thermobalance (C.I. Electronics Ltd.). Connections between the thermobalance case and the reactor tube were by means of stainless steel flanges. The reactor was heated by Nichrome resistance wire and was controlled using a thermocouple sensor placed beneath the sample basket. Another thermocouple positioned adjacent to the sample served to measure the reaction temperature which was taken to be that of the gas at the same horizontal plane as the sample. The ore was contained in a platinum mesh basket.

The gases used were dried with silica gel and a pre-heater was employed to facilitate the attainment of the correct gas temperature. To prevent cracking of the ore samples and following previous recommendations [19] a linear heating rate of 513 K h^{-1} was adopted. The initial temperature rise to about 673 K was achieved manually using an autotransformer; above this temperature a motor-driven potentiometer connected to the set point of the temperature controller gave the required heating or cooling rate.

The procedure followed was to heat the weighed sample in a stream of nitrogen until the required temperature was attained. During this process water vapour was evolved. When a constant weight was recorded the gas was changed to the appropriate reducing mixture and the weight loss recorded continuously as a function of time. After the run the sample was cooled, removed and weighed again.

Preliminary experiments were carried out on the whole range of particle sizes employed to determine the flow rate at which external mass transfer resistances could be neglected. This was found to be achieved at Reynolds numbers (based on the open tube diameter and the appropriate values of density and viscosity) of 62 and 429 for hydrogen and carbon monoxide, respectively. All subsequent experiments were performed at Reynolds numbers at or above these values.

RESULTS AND DISCUSSION

General observations

Reduction rates in the form of weight loss vs. time curves were determined for pure hydrogen, pure carbon monoxide and mixtures of the two gases. Due to the carbon deposition with pure carbon monoxide and carbon monoxide rich mixtures, measurements for this gas and its mixtures had to be made at temperatures of 1070 K and above. A typical plot of weight loss vs. time curve is shown in Fig. 1 for carbon monoxide reduction of both Carol Lake and Kiruna ores of particle diameter 9×10^{-4} m at 1143 K. Under these conditions, the time required for Carol Lake reduction was less than that of Kiruna because the former ore is more porous. Similar results were also observed for hydrogen reduction but with less difference in reduction time as the mass transfer and reaction rates were higher.

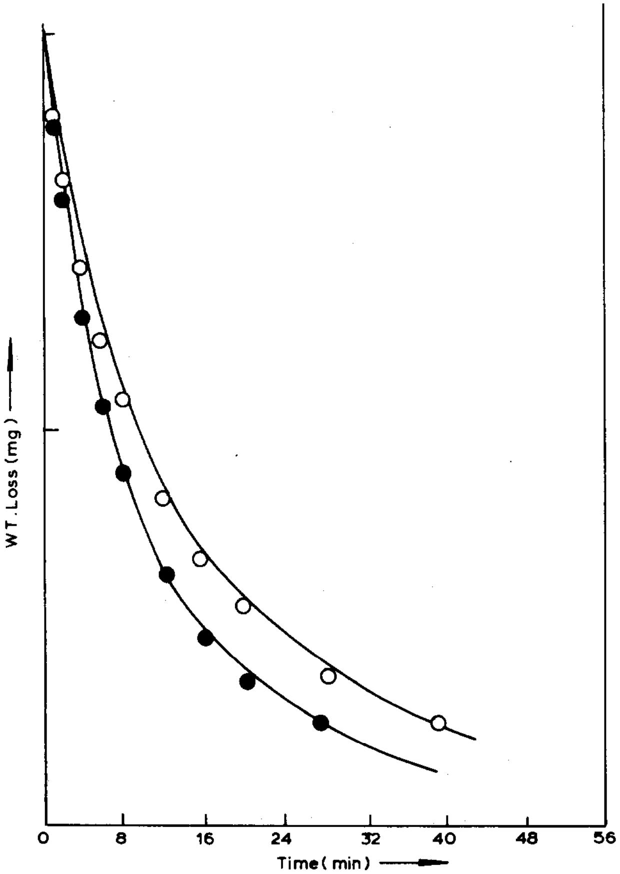

Fig. 1. Typical weight loss vs. time plots for CO reduction at 1143 K. ●, Carol Lake; ○, Kiruna.

The general effect of particle size was as expected for all gas mixtures within the temperature range investigated, i.e., the smaller the particle size, the greater was the rate of reduction. This applied to both ore samples. This is due to the fact that for the smaller particles, the reaction system is under chemical control until the later stages of reduction when diffusional control through the layer of reduced iron may become significant. For the larger particles, diffusional control becomes established quite early in the reaction process and hence a greater time is required to achieve the same degree of reduction. The results obtained are in good agreement with those of other workers [6–11] using other analysis systems.

Similar results were obtained during this investigation for operating temperatures in the range 673–1143 K. With increase in temperature the reduction time required for a given conversion at a given particle size is decreased. This is because both the reaction rate and diffusional rate increase with increase in temperature; hence, a reduction in the time required will result.

Effect of hydrogen partial pressure on the rate of reduction

The reaction order in hydrogen may be determined from a plot of initial rates against the hydrogen concentration (or more conveniently in this case,

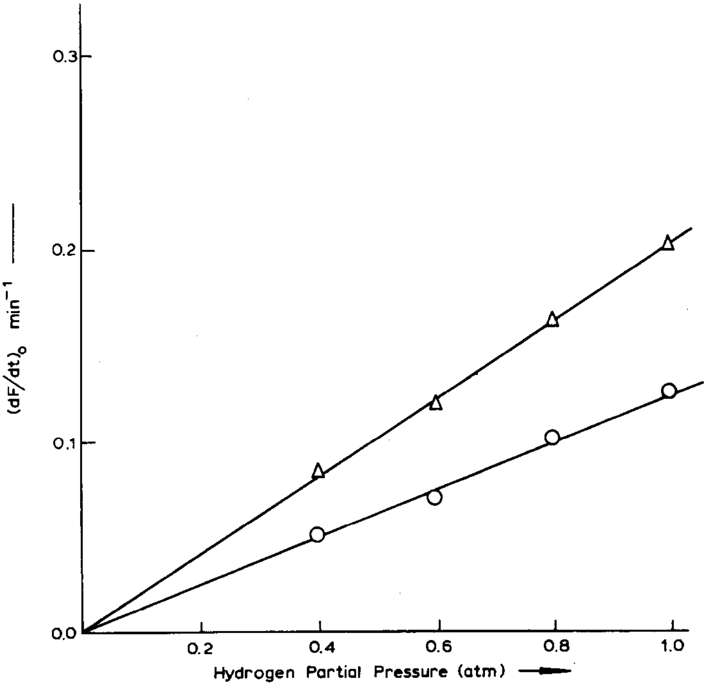

Fig. 2. Effect of hydrogen partial pressures on time to reach a specified conversion for 9×10^{-4} m Carol Lake ore particles at 1143 K.

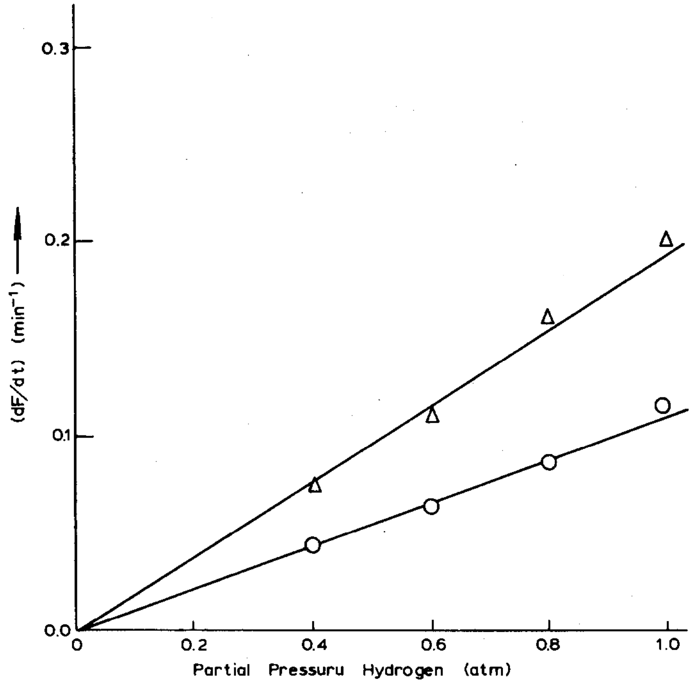

Fig. 3. Effect of hydrogen partial pressures on time to reach a specified conversion for 9×10^{-4} Kiruna ore particles at 1143 K.

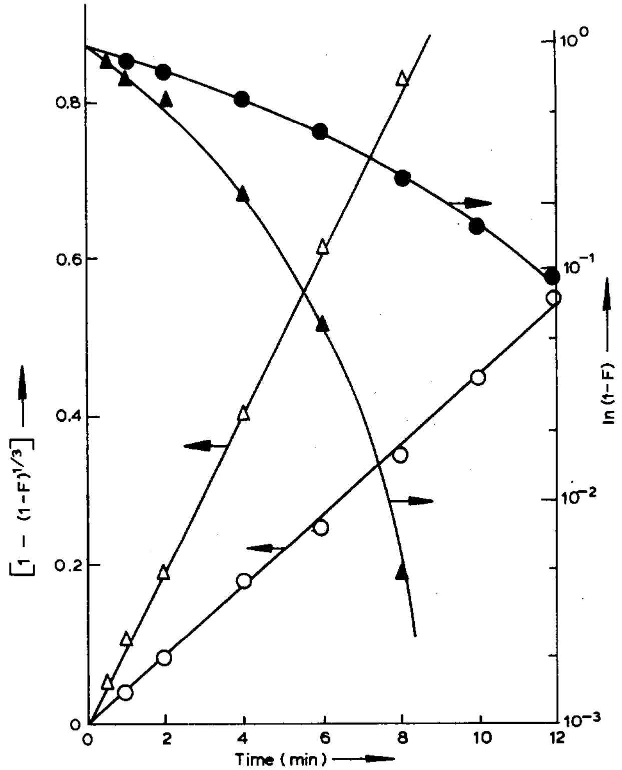

Fig. 4. Plots of data according to eqns. (6) and (9) for 9×10^{-4} m Carol Lake ore particles. ○, ●, 873 K; △, ▲, 1073 K.

the hydrogen partial pressure). The total pressure was kept constant at 1 atm and the partial pressure of hydrogen was adjusted by changing the percentage of nitrogen in the feed gas. It is preferable to use initial rates since this avoids any complications due to diffusional effects which may arise even for the small particles used in this investigation. Initial rates were computed from curves using a non-linear regression analysis to determine the slope at zero time. Results for the plot of initial rate vs. hydrogen partial pressure for Carol Lake and Kiruna ores are shown in Figs. 2 and 3, respectively. Two reduction temperatures are given in each case and the satisfactory straight lines obtained confirm that the reduction is first order in hydrogen over the temperature range 873–1143 K for both ore samples.

Kinetic model for the reduction process

As indicated previously two models representing extreme situations may be applied to the rate data: the retracting core model and the porous solid (or homogeneous) model. Which model will be applicable will depend on a number of factors including the relative rates of diffusion and reaction under the given conditions but an important factor is the porosity of the particle. In the present work the particles are of fairly low porosity (~ 13%) as shown in Table 1. Therefore, either model may be applicable and only a detailed examination will reveal which is most suitable.

The data for the Carol Lake ore sample were first plotted using the porous solid model by plotting $\ln(1-F)$ vs. time in accordance with eqn. (9), as shown in Fig. 4. For particles of 9×10^{-4} m diameter it was found that good straight lines were obtained at reduction temperatures of 673 and 773 K (not shown), but at 873 and 1073 K there was marked curvature in the plots and reaction rates were much faster than would be predicted by theory in this upper temperature range. A possible explanation for the increased rate above that predicted by the model may reside in the increase in average pore diameter observed when the pellet is reduced (Table 2). This would modify the basis of the model.

Plots were then made of $[1-(1-F)^{1/3}]$ vs. time on the assumption that the retracting core model was followed. Good straight lines were obtained, as shown in Fig. 4 where for clarity only the 873 and 1073 K lines are shown.

Similar results were also obtained for Kiruna ore samples, as shown in Fig. 5. Again, for clarity, only the 873 and 1073 K lines are indicated for both models. It may be concluded that for reduction of 9×10^{-4} m Carol Lake and Kiruna ore particles with pure hydrogen, the retracting core model gives the best representation of the experimental results.

Activation energy

This was obtained by plotting the logarithm of the initial reaction rates vs. the reciprocal temperature. The resultant plots for both ores are shown in

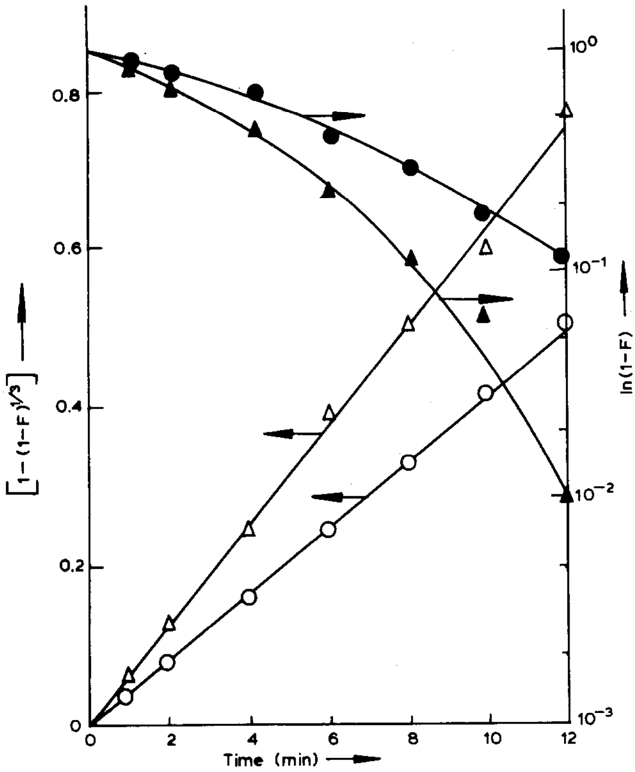

Fig. 5. Plots of data according to eqns. (6) and (9) for 9×10^{-4} m Kiruna ore particles. ○, ●, 873 K; △, ▲, 1073 K.

Fig. 6 and give an activation energy of 41.28 ± 0.7 kJ mole^{-1} for Carol Lake and 48.9 ± 0.6 kJ mole^{-1} for Kiruna. These values apply over the temperature range 673–1143 K.

The magnitude of the activation energy may be considered small for an intrinsic chemical process; the usual explanation for low values of the activation energy is to suggest that mass transfer limitations are controlling the overall reaction and since such mass transfer rates have small temperature coefficients a low apparent activation energy will result. However, it is believed that the value obtained is the true activation energy because of the precautions taken to avoid mass transfer resistances. Thus, care was taken to have a sufficiently high flow rate to eliminate the external film resistance and the use of initial rates for the small particles ensures the absence of intraparticle diffusional effects.

The literature gives a wide variation in reported values of the activation energy. Values quoted range from about 10.32 to 123.83 kJ mole^{-1} and this variation may be due to different samples and conditions employed. Themelis and Gauvin [1] have reported a value of 17.34 kJ mole^{-1} for reduction

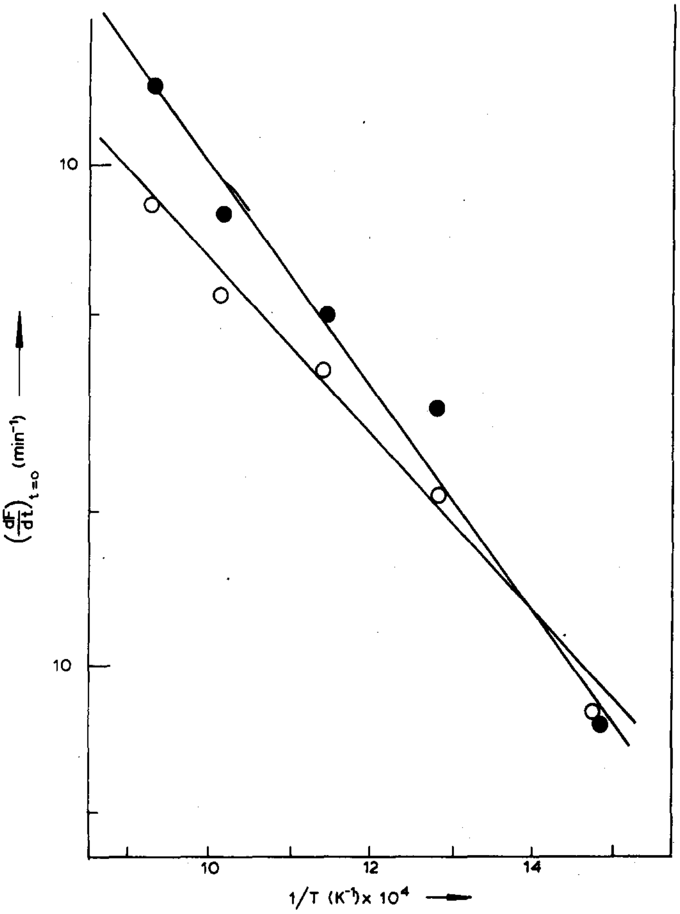

Fig. 6. Arrhenius plots for 2×10^{-4} m Carol Lake (●) and Kiruna (○) ores reduced in pure hydrogen.

temperatures from 773 to 1373 K for particles of 5–100 μm diameter, and recent work on the reduction of fine ore particles gives values of the activation energy between 16.51 and 41.28 kJ mole^{-1} at temperatures above 773 K [20].

Reduction with carbon monoxide

Attempts to reduce both ores by carbon monoxide at lower temperatures produced considerable amounts of deposited carbon on the sample, container and suspension wire. This deposition was greatest in the temperature range 873–1073 K and invalidated gravimetric observations made in this range. The cause of the deposition is the decomposition of CO according to the Boudouard reaction

$$2\,CO \rightleftharpoons CO_2 + C$$

which occurs at temperatures between 523 and 1023 K and the maximum rate of deposition is stated to occur at either 723 K [21] or 873 K [15]. In this work, however, it was observed that in the temperature range 873–1073 K the extent of carbon deposition was greatest at the end of the reduction, a conclusion confirmed by Szekely and Karatus [13]. Carbon deposition was found to be insignificant at temperatures above 1073 K and most data were collected in this range.

Reduction with carbon monoxide/hydrogen mixtures

Reduction of Carol Lake and Kiruna ores in both pelleted and granular form by CO/H_2 mixtures was investigated at 1143 K with particle size and gas composition as the parameters varied. Gas compositions ranged from 100% hydrogen to 100% carbon monoxide, with a number of intermediate compositions.

The effects of particle size on the reduction of Kiruna ore for gas mixtures are similar to those for reduction by pure gases, but with a closer resemblance to those for CO reduction than for H_2 reduction. The time required is longer than for reduction in pure H_2 but is shorter than for CO alone.

In between the two pure gases intermediate reduction rates are obtained.

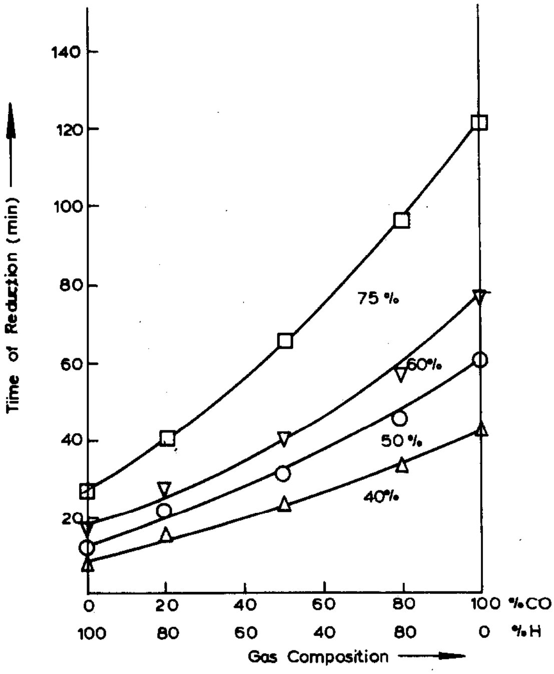

Fig. 7. Effect of gas composition on reduction time at 1143 K for 1.1×10^{-3} m Carol Lake pellets.

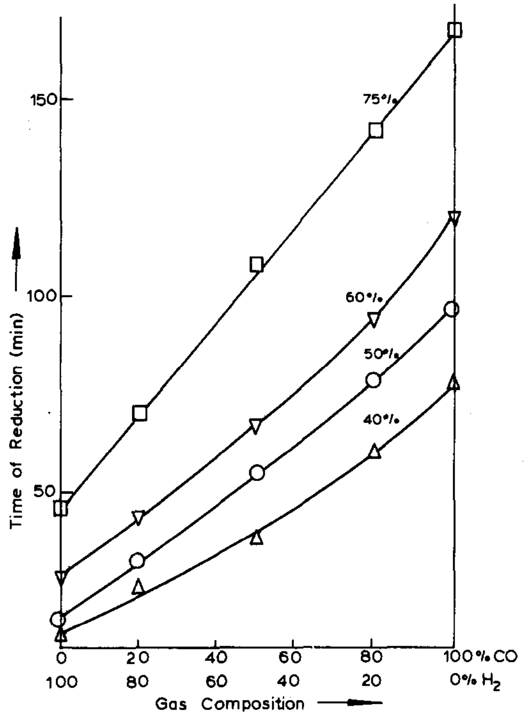

Fig. 8. Effect of gas composition on reduction time at 1143 K for 1.1×10^{-3} m Kiruna pellets.

As the amount of hydrogen in the mixture is increased the rate of reduction is markedly increased. Specific reaction rate constants for the reduction of Kiruna ore at 1173 K are $k'_{H_2} = 1.63 \times 10^{-3}$ m s^{-1} and $k'_{CO} = 2.4 \times 10^{-4}$ m s^{-1}, whereas the diffusion coefficients obtained from the data on the reduction are $D_{H_2} = 1.825 \times 10^{-5}$ m^2 s^{-1} and $D_{CO} = 6.25 \times 10^{-6}$ m^2 s^{-1}, respectively. Thus, whatever the controlling mechanism, reduction in hydrogen will always be the faster.

An alternative representation of the data is to plot the time required to achieve a given conversion against the gas composition. Results for both Carol Lake and Kiruna ore samples are shown in Figs. 7 and 8, respectively.

It can be observed that the time required to achieve a given extent of reduction is markedly dependent on the composition of the gas mixture for both ores. Use of excess hydrogen results in a much shorter reaction time compared with other mixtures. Also, the composition relations are not linear and this has also been reported by Szekely and El-Tawil [18] in similar work using CO/H_2 mixtures to reduce pressed discs of Fischer Fe_2O_3.

An interesting possibility with reduction by gas mixtures is that the water gas shift reaction

$$CO + H_2O \rightleftharpoons H_2 + CO$$

may influence the rate under practical conditions. Estimates were made of this effect using modelling techniques. Since this is beyond the scope of the present investigation, details of the effect associated with the water gas-shift on iron ore reduction will be published in due course. However, it was concluded that for mixtures of CO and H_2 alone, with no product gases (H_2O or CO_2) present, there was only a marginal effect. However, when CO_2 or H_2O were included the effect of the water gas-shift reaction was significant. This could be important in an actual shaft reactor since the pellets will now be in an atmosphere containing these product gases and this has important consequences for the reduction time required.

CONCLUSIONS

The reduction of Carol Lake and Kiruna ores using pure hydrogen gas, pure carbon monoxide and mixtures of these two gases has been studied at reduction temperatures from 673 to 1143 K. It has been shown that the rate of the reduction reaction increases as the temperature of reduction and partial pressure of active reducing gas is increased. The rate of reduction using pure hydrogen is greater than that with pure carbon monoxide and carbon monoxide is less efficient as a reducing gas at temperatures below 1173 K because of the problem of carbon deposition. This problem of carbon deposition is also present with reducing gas mixtures containing large amounts of carbon monoxide, so that even in this case temperatures must be in excess of 1173 K to obtain consistent data. Rates of reduction are greatest for gas mixtures containing a higher proportion of hydrogen but the relation between time for a given reduction and gas composition is not linear. The kinetics of the reduction were found to best fit a retracting core model rather than a homogeneous or porous solid model even for the smallest particle size employed.

The activation energy has been determined for reduction of Carol Lake and Kiruna ores by hydrogen and values of (41.28 ± 0.7) and (48.29 ± 0.6) kJ mole^{-1} were obtained, respectively. Since care has been taken to avoid mass transfer restrictions, these are thought to be the true chemical activation energy values.

NOTATION

C_A	concentration of gaseous reactant
C_B	concentration of gaseous product
C_0	atomic density of oxygen in the ore
F	fractional reduction
K_e	equilibrium constant for Wüstite reduction
k'_A	specific rate constant for reduction

N_n	moles of reacting gas
N_0	moles of oxygen in ore
r_i	radius of core, retracting core model
r_0	original radius of particle
$\bar{r}$	pore radius
S	usable pore surface area of Wüstite/unit mass of oxygen
S_g	surface area per unit mass of ore
t	time of reduction
V	volume
V_g	pore volume per unit mass of ore
W_r	weight of oxygen in sample at time t
W_0	weight of initial oxygen in sample

Subscripts

b	refers to bulk conditions
i	refers to interface

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support from the Science Research Council which made this work possible, and the provision of ore samples by Mr. P. Roddis of British Steel Corporation, Sheffield Laboratories.

REFERENCES

1 N.J. Themelis and W.H. Gauvin, Can. Min. Metall. Bull., 55 (1962) 444.
2 L. Von Bogdandy and H.J. Engell, The Reduction of Iron Ores, Springer-Verlag, Berlin, 1970.
3 J. Szekely, J.W. Evans and H.Y. Sohn, Gas–Solid Reactions, Academic Press, New York, 1978.
4 W.M. McKewan, Trans. Metall. Soc. AIME, 218 (1960) 2.
5 N.A. Warner, Trans. Metall. Soc. AIME, 230 (1964) 163.
6 J.M. Quests, M.E. Wadsworth and J.R. Lewis, Trans. Metall. Soc. AIME, 218 (1960) 545.
7 R.H. Tien and E.T. Turkdogan, Metall. Trans., 3B (1972) 2039.
8 E.T. Turkdogan and J.V. Vinters, Metall. Trans., 2B (1971) 3175.
9 E.T. Turkdogan and J.V. Vinters, Metall. Trans., 3B (1972) 1561.
10 E.T. Turkdogan, R.A. Olsson and J.V. Vinters, Metall. Trans., 2B (1971) 3189.
11 R.H. Spitzer, F.S. Manning and W.P. Philbrook, Trans. Metall. Soc. AIME, 236 (1966) 726.
12 J. Szekely and C.I. Lin, Metall. Trans., 7B (1976) 493.
13 J. Szekely and C. Karatus, Metall. Trans., 9B (1978) 147.
14 I. Gaballah, F. Gavlier, L. Offrog and A. Rist, Cent. Doc. Sider., Circ. Inf. Tech., 30 (1973) 1871.
15 S.P. Trusenski, K. Li and W.O. Philbrook, Metall. Trans., 5B (1974) 1149.
16 T.G. Cox and F.R. Sale, Ironmaking Steelmaking, 1 (1974) 234.

17 A.G. Matyas and A.V. Bradshaw, Ironmaking Steelmaking, 1 (1974) 180.
18 J. Szekely and Y. El-Tawil, Metall. Trans., 7B (1976) 490.
19 R. Wild and H.L. Saunders, J. Iron Steel Inst., London, (1950) 198.
20 T. Gare, British Steel Corporation Laboratories, Private Communication, 1980.
21 W.H. Wetherill and C.C. Furnas, Ind. Eng. Chem., 26 (1934) 983.