Kinetics of Reduction of Iron Oxide With Carbon Monoxide and Hydrogen

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This investigation was undertaken to determine the rate controlling step in the reduction of iron oxides with hydrogen and carbon monoxide. For the reduction of porous hematite pellets, and bars it was found that the reduction rate is controlled by the counterdiffusion of reactant gas and product gas between the reaction zone and the main gas stream.

The reduction specimens were spheres ranging in size from 1.5- to 4.4-cm. diameter and 5.1- by 7.6-cm. bars either 0.69 or 1.24 cm. thick. They were prepared from electrolytic iron powder, partially oxidized in a rotary kiln. The final oxidation of the specimens to hematite was accomplished by firing them at 1,149°C. in an oxidizing atmosphere. The bulk density was 3.5 g./cc. The specific surface area was 0.08 sq.m./g. and the void faction was 0.31. The oxide specimens were reduced in streams of pure hydrogen or carbon monoxide at temperatures between 700° and 1,200°C. The reduction was followed by measuring the sample weight during the reaction. Reduction rates were studied at system pressures of 1 and 2 at.

The samples reduced step by step, to magnetite, to wüstite, and finally to iron. A shell of reduction, clearly visible in sections of partially reduced specimens, moved concentrically into the core of the samples. Ahead of the receding interface the specimens were known to be pervious to the reactant gases. This led to the conclusion that the gas composition at the interface was in equilibrium with the oxide phases present.

Except for the removal of the last portions of oxygen at the lower reduction temperatures, the course of the reduction followed Fick's first law of diffusion. Values of the diffusion coefficients, determined from the experimental data, were in close agreement with values predicted from empirical equations. Varying the total pressure of the system had no effect on the rate of reduction, which is consistent with the equations developed from Fick's law for the diffusion-controlled reaction under investigation.

It is speculated that the retarding of the reduction reaction at the lower reduction temperatures is due to the entrapment of oxide inside shells of iron, which are impervious to the reducing gas. Reduction of the trapped oxide then proceeds by solid state diffusion in a manner proposed by Edström (6).

A survey of the literature reveals that the equilibrium conditions for the reactions of iron oxides with reducing gases have been well established but that data on the mechanisms and rates of reaction are discordant.

At temperatures above 560°C. the reduction of hematite proceeds step by step. Hematite is first reduced to magnetite, which is then reduced to wüstite, which is finally reduced to iron. Below 560°C. wüstite is not stable, and the reduction of magnetite proceeds directly to iron.

The gaseous reduction of iron oxides is reported to consist of a series of steps:

1. Diffusion of reactant gas to a reaction site
2. Adsorption of reactant gas at the wüstite-iron interface
3. Chemical reaction
4. Desorption of product gas
5. Diffusion of product gas to the bulk gas stream

Because the reduction of hematite proceeds through a series of oxides of iron the following additional processes for hematite reduction also are possible:

6. Iron ion and oxygen ion and electronic diffusion across a dense wüstite layer
7. Diffusion of iron ions, of oxygen ions, and electrons across a dense magnetite layer
8. Phase boundary reactions: magnetite to wüstite and hematite to magnetite

Any of the above steps may control the rate of the over-all reduction process.

The literature indicates that there has been a question whether an ore mass is reduced entirely to one oxide of iron before reduction to other oxides takes place. Stalhane and Malmberg (*12*) have reported that three zones, iron, wüstite, and magnetite, were present in all particles during reduction. Edström (*6*) concurs with this finding. Diepschlag, Zillgen, and Poetter (*5*) claim that no ferric iron is present in samples which contain metallic iron.

There are further differences of opinion in the literature whether iron oxide reduction is controlled by diffusion or by a chemical reaction. Udy and Lorig (*15*) claim that the controlling step is the internal diffusion of water vapor from the reaction zone to the gas stream. Joseph (*10*) has reported that the rate of reduction is directly proportional to the porosity of the ore specimen, which strongly indicates a diffusion controlled reaction. Bitsianes and Joseph (*2*) and Edström (*6*) have offered theories that the conversion of hematite and magnetite to wüstite results from gas penetration to all the solid-phase interfaces. Countercurrent diffusion of carbon monoxide inward and of carbon dioxide outward through the porous solid phases is possible under partial pressure gradients which are imposed by equilibrium gas mixtures at the respective solid-phase interfaces. Tsylev (*14*) has found that the mechanism of reduction is dependent on the mineralogical composition of the ore. Diepschlag (*4*) and Tenenbaum and Joseph (*13*) have reported increased reduction rates with increased gas pressures and attribute this phenomenon to the increased adsorption of hydrogen at the higher pressures. Edström (*6*) claims that the reduction of single crystals proceeds and is controlled by the solid state diffusion of oxygen and iron atoms in a partially reduced phase. It is further claimed by Edström (*7*) that the gas-solid type of reaction is found only at the iron-wüstite interface. Stalhane and Malmberg (*12*) and Wetherill and Furnas (*16*) have reported that the reduction proceeds linearly toward the center of an ore mass and that the rate is constant with time. McKewan (*11*) concurs with this finding and claims that the rate is also directly proportional to the partial pressure of hydrogen. McKewan has developed equations which mathematically express the rate of reduction as a function of the area of the receding interface.

Arkharov et al. (*1*) and Edström and Bitsianes (*7*) have proposed that the conversion of hematite and magne-

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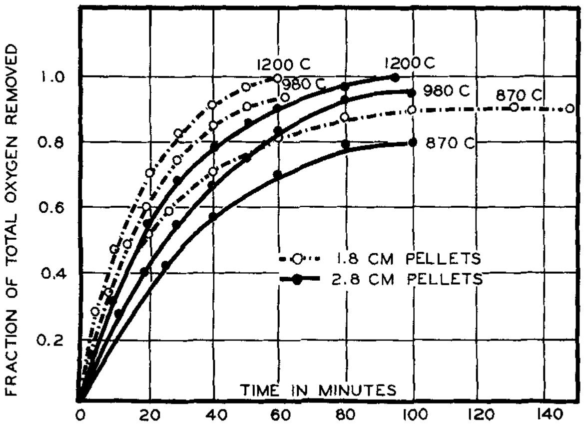

Fig. 1. Reduction of pure hematite spheres by carbon monoxide.

tite results from the inward diffusion of iron ions in the solid phases. Between 700° and 1,000°C. (7) the mobility of iron ions in wüstite varies over one hundredfold, while observed reduction velocities vary only twofold over the same temperature range (6). This wide difference in temperature effects suggests that for the most part the reduction of both hematite and magnetite depends not on iron ion mobility but on penetration and attack of the solid phases by reducing gas.

Although it might seem that there is a wide variance among authors as to how reduction of iron ores takes place, their differences in opinions can generally be traced to differences in experimental technique and ore specimens. The conclusions reached are probably valid for the experimental conditions of each reduction investigation. No single expression for the reduction mechanism seems possible that will cover all ores or all reduction conditions. The reduction of single crystals could very likely occur by solid state diffusion, but for porous polycrystalline ore masses gas diffusion must be taken into account.

This investigation was undertaken to determine the rate-controlling step of the gaseous reduction of porous hematite in the form of pellets or other geometric shapes.

SAMPLE PREPARATION

The starting material for the oxide specimens used in the present experiments was electrolytic iron powder. This material was partially oxidized in a rotary kiln, blended with starch and water, and then formed into 5.1-by 7.6- cm. bars in a hydraulic press or rolled into spheres in a pelletizing drum. The bars were either 0.69 or 1.24 cm. thick and the pellets ranged from 1.5- to 4.4-cm. diameter.

After oven drying the partially oxidized specimens were fired at 1,149°C. in a stream of air to complete the oxidation and to burn out the starch binder. Chemical analyses of random specimens showed less than 0.4% ferrous iron left in the fired specimens.

The final test specimens were well-bonded and very hard with a density of 3.5 g./cc. and a voids fraction of 0.31. Their specific surface area, which was determined by the Brunauer, Emmett, Teller nitrogen adsorption technique (3), was 0.08 sq. m./g.

REDUCTION APPARATUS AND PROCEDURE

Reduction of the specimens was carried out in a 4-in. cylindrical muffle, 27 in. long. All parts of the muffle exposed to high temperatures were made of Inconel. The muffle was suspended from one arm of a beam balance into an electrically heated pot furnace. A counterweight was hung from the other beam balance arm and rested on the weighing pan of a direct-reading balance. The weight of the sample during reduction was measured with the balance. Heat baffles were placed in the upper part of the muffle to reduce radiant heat losses. Two chromel-alumel thermocouples, in wells, were placed adjacent to the samples inside the muffle. Reducing gas from cylinders was metered and admitted to the muffle under the sample support grid. Ten feet of ⅜-in. tubing wrapped around the outside of the muffle served as the gas preheater. A flexible ¼-in. tube served to transport the reducing gas to the preheater. The exhaust from the top of the muffle was burned as a safety measure. A valve in the exhaust line was used to adjust the pressure in the muffle when runs were made at greater than atmospheric pressure.

TABLE 1. DEGREE OF REDUCTION OF CORE AND SHELL SECONDS OF 5.1 × 7.6 × 1.24 CM. BRIQUETTES OF PURE HEMATITE PARTIALLY REDUCED AT 1,090°C. BY CARBON MONOXIDE AT ATMOSPHERIC PRESSURE

	Degree of reduction	
Total specimen	Shell sample	Core sample
0.0%	0.0%	0.0%
11.0	11.5	11.0
17.4	25.5	15.5
20.0	24.5	14.5
27.5	30.0	28.4
43.0	91.5	32.0
58.5	94.5	33.0
72.0	98.0	33.0
92.6	99.7	40.0
96.3	—	—

In a typical reduction experiment about 100 g. of hematite specimens were measured and weighed and then placed in a single layer on the coarse grid near the inside bottom of the muffle. The loaded muffle was hung in the electric furnace and was flushed out with a low flow of nitrogen while it was heated up to the predetermined reaction temperature. During this time the beam balance counterweight was adjusted to tare the muffle weight so that the balance was indicating near the bottom end of its 100 g. direct-reading scale. A 50 g. analytical weight was used to check the setup, and a precision of 0.1 g. was always attained before each run was continued. Twenty minutes after the temperature inside the muffle had reached reaction temperature, the nitrogen was turned off and the reducing gas was metered into the muffle. The progress of the reduction was followed by recording the scale reading of the laboratory balance at fixed time intervals. Total reduction experiments were considered complete when the rate of weight removal diminished below 0.1 g./min. The partial reduction experiments were terminated when the weight loss corresponded to a predetermined percentage of the total reduction. At the end of each experiment the muffle was removed from the furnace and cooled to room temperature in a low flow of reducing gas. The reduced specimens were removed, weighed, and measured for comparison with their unreduced size and weight. The actual loss in weight always compared within 0.2 g. with the weight loss measured during reduction.

RESULTS AND DISCUSSION

Critical Gas Velocity

It was realized at the start of this investigation that there is a critical velocity, below which the reduction of the samples would be controlled by the rate of gas flow. This critical velocity was determined experimentally by a series of reaction rate runs at each temperature level in which gas velocity was the independent variable. All reduction runs were made with a reducing gas flow at least 25% greater than the critical velocity. The superficial gas velocities actually used were 0.01 to 0.03 g. mole/min./sq. cm. depending on the reaction temperature.

Partial Reduction Studies

In order to observe physically what happens inside the specimens during reduction the specimens from a series of partial reduction experiments were sectioned with a hacksaw blade. It was observed that the unreduced specimens had a uniform medium-gray color. Specimens reduced 11% were also uniform but darker gray in color. At 17.4 and 20.0% reduction a dark-gray core was surrounded by a black layer, with the black layer being thicker in the latter case. Specimens reduced 28.5% appeared uniformly black, and at 43.0% a light-gray outer layer began to show. More highly reduced specimens showed that a distinct black core prevailed as the outer layer increased in thickness, until finally, at 100% reduction, specimens were uniformly light-gray in color. It was also observed that the distinction between zones was quite sharp and that the interfaces between the zones remained parallel to the exterior surface of the specimens.

Since magnetite represents 11.1% reduction and wüstite represents about 35% reduction of hematite, it is very likely that the medium-gray color indicated hematite, the dark-gray color magnetite, the black color wüstite, and light-gray color metallic iron. To verify this concept samples of the differently colored shell and core sections of the various partially reduced specimens were analyzed to determine the degree of reduction of each. These analyses did show that the differently colored zones approximate the compositions of the respective oxide compounds of iron. In Table 1 the data are presented for 1.24 cm. thick briquettes partially reduced at 1,090°C. by carbon monoxide. Similar behavior was observed at the other temperatures and also with hydrogen.

These results indicate that the reduction process had taken place in three distinct steps commensurate with the degree of oxidation of the solid phases and their corresponding equilibrium gas compositions. Apparently the hematite specimens were first converted almost entirely to magnetite, then to wüstite, and finally to iron. The reduction reactions took place mostly at the solid phase interfaces which remained parallel to the external surface of the specimen.

Specimens partially reduced at 870°C. by carbon monoxide and at 704°C. by hydrogen showed that the black wüstite core had disappeared when the specimen was only about 80% reduced. This observation suggests that at the lower reduction temperatures only part of the third reduction step took place at the macroscopic wüstite-iron interface. Some 25% of the wüstite remained behind in the iron layer, and the reduction of this residual wüstite was evidently not accomplished by the same process that accounted for the reduction of the main body of the wüstite core. This same phenomenon was mentioned by some previous investigators (2), and they proposed that the residual wüstite was encased in an impervious layer of iron which had been consolidated by sintering.

Reaction Rate Studies

Some typical data from the reduction of spherical pellets by carbon monoxide are shown in Figure 1. It is apparent that the reaction rate is faster for the smaller pellets and the higher temperatures. It also appears that the reduction reaction does not approach 100% completion at the lower temperature.

To prove that the incomplete reduction phenomenon at the lower temperature is a real effect and not an experimental difficulty, some experiments were made in which the temperature was raised after the reaction had essentially stopped. Figure 2 shows that the oxygen remaining at the lower temperature may be readily removed by going to a higher temperature.

Hydrogen proved to be a much more effective reducing gas than carbon monoxide. In Figure 3 it can be seen that the removal of oxygen by hydrogen is about five times as fast as by carbon monoxide. Complete reduction is also reached at a lower temperature with hydrogen.

INTERPRETATION OF RESULTS

Mechanism

The large effective pore radii and the sequence of solid phases observed in the partial reduction studies suggest that the step-by-step reduction of the pure hematite specimens to iron via magnetite and wüstite was due primarily to penetration and attack of the solid phases by the reducing gas. The sharp distinction between the solid phases indicated that the gas-solid reactions occurred at the macroscopic solid-phase interfaces which remained parallel to external surfaces of the specimen. However the retarded final reduction phenomenon observed at the lower reduction temperatures indicated that whereas the greater part of the reduction may have been due to direct gas-solid reaction, the reduction of the residual oxide was accomplished by a different process which is more sensitive to temperature than the direct gas-solid reactions.

When crystalline wüstite is reduced, the entire oxygen lattice of the crystal is destroyed and the iron ions must rearrange and coalesce to form iron crystals. During this rearrangement and coalescing of iron atoms small segments of dense wüstite could be separated from the main structure and become encased in dense layers of crystalline iron. Reduction of such entrapped wüstite would have to be accomplished by a very retarded diffusion of gases through the dense iron layer or else by ion mobility in the solid state.

The extreme sensitivity of the rate of the final wüstite reduction to temperature indicates that it is probably not controlled by a gaseous diffusion mechanism through a dense iron layer. Edström (6) has demonstrated that the rate of iron ion mobility in wüstite varied over one hundredfold between 700° and 1,000°C. Above 1,000°C. it was commensurate with observed re-

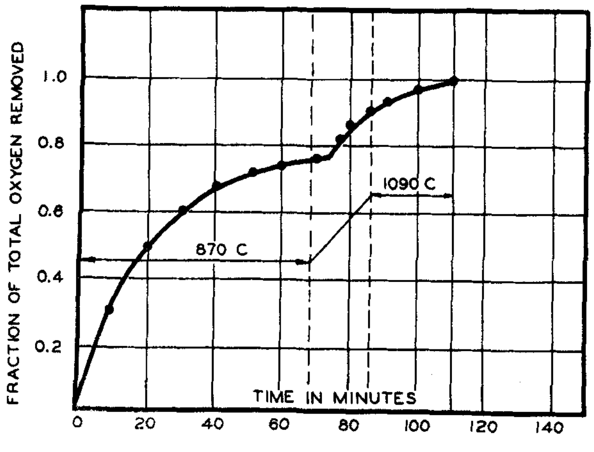

Fig. 2. Reduction of pure hematite spheres by carbon monoxide.

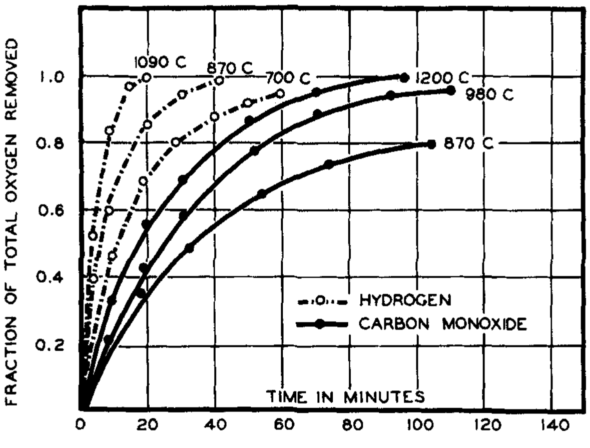

Fig. 3. Reduction of pure hematite spheres 2.8-cm. diameter.

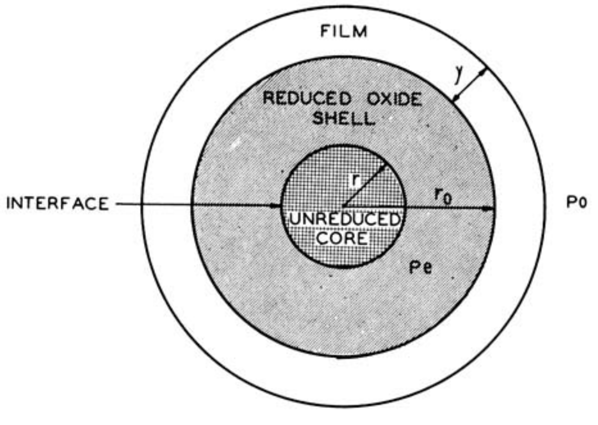

Fig. 4. Sketch of reduction model.

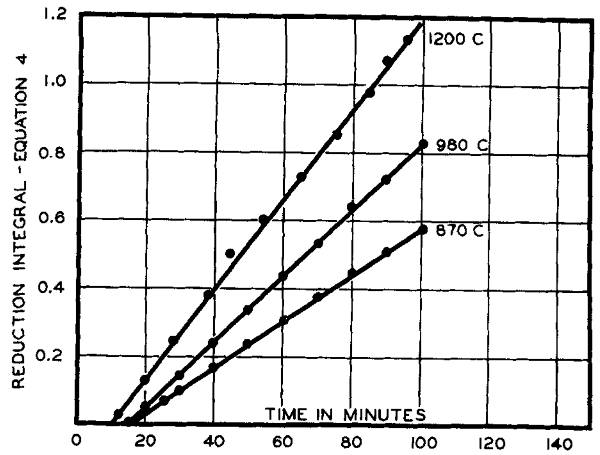

Fig. 5. Diffusion mechanism for the reduction of 2.8-cm. hematite spheres from wustite to iron by carbon monoxide.

duction velocities. This evidence tends to support a theory that part of the reduction of wüstite is due to iron ion mobility in the solid wüstite phase. The retarded final reduction phenomenon below 1,000°C. exists because the rate of iron ion mobility is far less than the rate of gas-solid reaction. Above 1,000°C. the rate of iron ion mobility far exceeds the gas-solid reaction rate, and the entire reduction process is controlled by the gas-solid reaction.

Reduction Model

The sharp solid phase interface moving concentrically into the porous specimens during their reduction implies that the gas composition at this interface is an equilibrium mixture of reactant gas and product gas. If this were not so, the reducing gas would diffuse father into the sample and the specimens would reduce more uniformly.

In order to explain this concept more fully a reduction model is shown in Figure 4. Equimolar countercurrent diffusion of reactant gas and the product gas will take place through a gas resistance film and through the reduced oxide layer according to Fick's first law:

$$N = \frac{DA_m\,(P_o - P_e)}{RT\,[(r_o - r) + y]} \qquad (1)$$

Assuming that the reduction proceeds by a series of short steady state periods one can then replace N by $\frac{1}{16}W_o$ (df/dt). For a sphere of uniform composition

$$f = \frac{r_o^3 - r^3}{r_o^3} = 1 - \left(\frac{r}{r_o}\right)^3 \qquad (2)$$

and

$$A_m = 4\pi r\,(r_o + y) \qquad (3)$$

When one substitutes Equations (2) and (3) into (1) and integrates between the limits of $f = 0$ when $t = 0$ and $f = f$ when $t = t$, the reduction relationship becomes

$$\frac{W_o\,r_o}{A_o\,(P_o - P_e)}\left[3/2\,[1 - (1-f)^{2/3}] - \frac{r_o f}{(r_o + y)}\right] = k_d t \qquad (4)$$

$$k_d = \frac{960\ DZ}{RT}\ \text{g./cm.-min.} \qquad (5)$$

The factor 960 is required to make the equation dimensionally consistent and is not an arbitrary constant.

In this investigation the reducing gas flow was always more than thirty times the reduction rate of the oxide specimens on a stoichiometric basis. This meant that the fractional conversion of the reducing gas was maintained below 3%. Combined with the fact that a single layer of oxide specimens was always used, it could be assumed that there was a negligible P_o gradient and that P_o was equal to the total pressure in the reactor.

Since each reduction rate experiment was conducted at constant temperature and pressure, both P_o and P_e could be constant. Therefore if the reduction reaction is controlled by countercurrent gas diffusion, a plot of the left side of Equation (4) vs. time should give a straight line with a slope of k_d.

A similar relationship can be derived for the 5.1- by 7.6-cm. bars if they are treated as infinite planes and if reduction of the edges is neglected:

$$\frac{W_o\,x_o}{2A_o\,(P_o - P_e)}\left[\frac{2yf}{x_o} + f^2\right] = k_d t \qquad (6)$$

The results of all of the total reduction experiments for both hydrogen and carbon monoxide were plotted according to Equations (4) or (6). In general the experimental data fell on straight lines indicating a good fit to the equations. As an example the application of Equation (4) is illustrated in Figure 5 for the wüstite-iron step of the reduction of spherical pellets by carbon monoxide.

Since the effective gas film thickness surrounding the oxide sample was not subject to direct measurement, it was calculated from the data by a trial-and-error process. Best correlations were obtained when it was assumed that the film thickness was 0.4 cm., which is reasonable for the laminar flow conditions used in this study.

A comparison of rate constants derived from the slopes of the plots for spherical pellets is made in Table 2. The consistency in k_d for a variation in pellet size at a given temperature and a given reduction step is very good. There is also a fair degree of consistency between the values for the two different reduction steps at the same temperature.

The facts that the reduction data fit Equations (4) and (6) and that the rate constants thereby obtained were fairly consistent are strong evidence that the rates of reduction of the pure hematite specimens in the present studies were controlled by countercurrent molecular gaseous diffusion.

Also included in Table 2 are calculated values for k_d with Equation (5) and the Gilliland (9) equation:

$$D = \frac{0.0043\,T^{3/2}}{P_T\,(V_A^{1/3} + V_B^{1/3})^2}\left[\frac{1}{M_A} + \frac{1}{M_B}\right]$$

The porosity-labyrinth Z factors assumed for Equation (5) were 1.0 for carbon monoxide and 0.7 for hydrogen. The Z value of 0.7 for hydrogen was based on the porosity of the specimens reduced in hydrogen relative to those reduced in carbon monoxide. The oxide specimens reduced by hydrogen contracted somewhat, and those reduced by carbon monoxide actually expanded beyond their original dimensions.

It is not claimed that the rate constants calculated by Equation (5) and the Gilliland equation represent extremely accurate values. There is no assurance that the empirical Gilliland equation applies very well at the temperatures and conditions of the present reduction experiments, and the Z factors are assumed values. What is significant however is the fact that the calculated rate constants are of the same order of magnitude as those determined experimentally, and as such may be taken as further evidence that the gaseous reduction of porous oxide specimens is controlled by countercurrent gaseous diffusion.

As a final bit of evidence that gaseous diffusion was controlling, some total reduction experiments were made with both hydrogen and carbon monoxide at 2-atm. pressure. These experiments showed identical performance to their counterparts at 1-atm. pressure. There was absolutely no measurable effect of the higher pressure on the rate or degree of reduction attained.

From Equation (5) and the Gilliland equation it can be seen that the rate constant k_d varies inversely with the total system pressure, whereas the partial pressure difference $(P_o - P_e)$ in Equation (4) will naturally be directly proportional to the total pressure. The net effect therefore is that Equation (4) is independent of total pressure, a fact which coincides with the present experimental results.

CONCLUSION

Except for the residual wüstite at the lower reduction temperatures, the entire reduction process of porous specimens of pure hematite was due to penetration and attack of the solid oxide phases by gaseous carbon monoxide or hydrogen. The rate-controlling step was the equimolar countercurrent molecular diffusion of reactant gas and product gas. The diffusion path extended from the bulk gas stream outside the oxide specimen across an effective gas film and then through the reduced shell layer to the macroscopic shell-core interface in the specimen. The driving potential for this diffusion process was the difference between the partial pressure of the reactant gas in the bulk gas stream outside the specimen and the partial pressure of the reactant gas in equilibrium with the unreduced core of the specimen.

At the lower reduction temperatures the final part of the reduction of wüstite is controlled by a process much slower than gaseous diffusion. The residual wüstite theory of previous investigators (2, 6) and the rates of iron ion mobility in dense wüstite reported by others (7, 8) are commensurate with the observations in the present study. It is probable that small dense particles of wüstite are caught up by coalescing iron atoms at the iron-wüstite interface. Being encased by a dense iron shell this entrapped wüstite is isolated from gas attack, and reduction would have to be via ion mobility in the solid phase. The above mentioned iron ion mobility is very temperature sensitive, and at the lower reduction temperatures it diminishes to a negligible rate (7).

NOTATION

A_m = mean area for diffusion, sq. cm.
A_o = outside area of specimen, sq. cm.
D = diffusivity, sq. cm./sec.
f = fractional reduction of particular oxide
k_d = diffusion constant, g./cm.-min.
N = diffusion rate, mole/sec.
M_A = molecular weight of gas specie A, g./mole
M_B = molecular weight of gas specie B, g./mole
P_T = total pressure of system, atm.
P_e = equilibrium pressure of reducing gas, atm.
P_o = reducing gas pressure in muffle, atm.
r = radius of unreduced oxide core, cm.
r_o = radius of spherical sample, cm.
R = gas constant, cc.-atm./g. mole-°K.
t = time, sec. or min.
T = absolute temperature, °K.
V_A = molecular volume of gas specie A, cc./g.-mole
V_B = molecular volume of gas specie B, cc./g.-mole
W_o = weight loss of particular oxide when fully reduced, g.
x_o = one half of oxide bar thickness, cm.
y = film thickness surrounding specimen, cm.
Z = porosity and labyrinth factor

TABLE 2. REDUCTION OF PURE HEMATITE SPECIMENS AT ATMOSPHERIC PRESSURE

	Gaseous diffusion rate constant (k_D), g./cm.-min.			
By carbon monoxide	870°C.	980°C.	1,090°C.	1,200°C.
From magnetite to wüstite				
2.8-cm. pellets	0.0070	0.0082	0.0082	0.0108
1.8-cm. pellets	0.0068	0.0084	0.0084	0.0100
From wüstite to iron				
2.8-cm. pellets	0.0070	0.0100	0.0106	0.0130
1.8-cm. pellets	0.0064	0.0095	0.0106	0.0130
Calculated* ($Z = 1.0$)	0.0085	0.0098	0.0111	0.0129
By hydrogen	700°C.	870°C.	1,090°C.	
From magnetite to wüstite				
3.7-cm. pellets	0.0230	0.0380	0.0440	
2.5-cm. pellets	0.0240	0.0270	0.0420	
1.7-cm. pellets	0.0170	0.0250	—	
From wüstite to iron				
3.7-cm. pellets	0.0170	0.0360	0.0440	
2.5-cm. pellets	0.0170	0.0260	0.0450	
1.7-cm. pellets	0.0130	0.0200	0.0320	
Calculated* ($Z = 0.7$)	0.0320	0.0340	0.0380	

* From Equation (5) and the Gilliland equation.

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