JOURNAL OF CATALYSIS 59, 15–25 (1979)

Alkali and Alkaline Earth Catalyzed Reduction of Magnetite to Wustite

II. Charcoal as Reductant

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Received July 4, 1977; revised October 6, 1978

The use of charcoal as reductant results in rates of reduction which are invariant with respect to carbon additions at temperatures near 800°C; the rate-limiting step of reduction is an interface reaction between reduced and unreduced phases. The catalysis of this reaction by a large number of alkali and alkaline earth salts is explained in terms of changes of point defect concentrations in magnetite induced by additive cations.

INTRODUCTION

In Part I (*1*) we have shown that the reduction of magnetite (Fe_3O_4) to wustite (FeO) by particulate graphite is controlled by the rate of the Boudouard reaction which generates the reducing gas CO. The catalysis of this reaction by alkali and alkaline earth carbonates was demonstrated and two mechanisms were invoked for its explanation. In an attempt to avoid the rate-limiting control imposed by carbon gasification on the reduction and to examine the effects of the carbonates (and other salts) on the phase boundary reaction between reducing gas and oxide lattice, additional reduction tests have been performed using charcoal as reductant. It is well known that charcoal is much more reactive to gasification than graphite.

This investigation demonstrates that by the use of charcoal reductant the rate-limiting step of reduction is altered from carbon gasification to a phase boundary reaction on the oxide particles. The acceleration of this reaction by alkali and alkaline earth salts was determined, and the activation energy of reduction established. An explanation is proposed for the catalytic effect of salt additions based on changes of point defect concentrations in magnetite induced by additive cations.

EXPERIMENTAL

Materials. Red precipitated ferric oxide (Hopkin and Williams) was used (*1*) to make up reduction mixtures with peat charcoal (Norit R, Holland). Charcoal particle size was in the range −149 + 104 μm.

Apparatus. The degree of reduction at constant temperature as a function of time was determined by means of thermogravimetry using a Mettler thermoanalyzer. The analyses were performed in a dynamic argon atmosphere. The apparatus and experimental procedures have been described in Part I (*1*).

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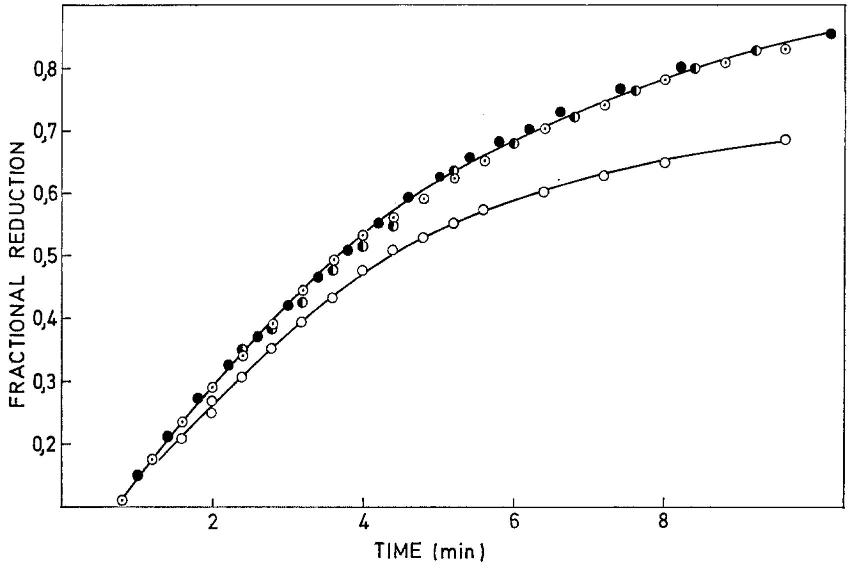

Fig. 1. Effect of increasing charcoal (Norit) additions on the reduction of magnetite to wustite at 815°C. Additions are measured in units of the stoichiometric requirement (C_s): ○, 1.0 C_s; ⊙, 3.7 C_s; ●, 5.0 C_s; ◐, 6.4 C_s. In all cases mass of Fe_2O_3 is constant (240 mg).

RESULTS

Charcoal lowered the temperature required for the reduction of magnetite from ca. 1000°C when graphite is used to values near 800°C. It did not, however, alter the general nature of the reduction. The characteristic two stage pattern of the differential thermogravimetry curve (DTG) such as was previously displayed [Fig. 1 of (*1*)] was preserved. Furthermore, X-ray diffraction analysis of reduction residues again confirmed that the elimination of the Fe_2O_3 phase preceded the onset of Fe_3O_4 reduction which yielded FeO but not metallic iron. On the basis of these observations the same procedure as for reduction by graphite was adopted for the evaluation of magnetite fractional reduction values. Three significant observations were made regarding the reduction curves.

(i) The curves were invariant with respect to charcoal concentration at quite moderate values of concentration. This is illustrated in Fig. 1. The fractional reduction values, α, obtained with increasing additions of charcoal are seen to fall on the same reduction curve for $C \gtrsim 4C_s$.

(ii) The reduction curves conformed to the surface reaction equation (*2*)

$$1 - (1 - \alpha)^{\frac{1}{3}} = k_s t \qquad (1)$$

which is generally interpreted as describing the phase boundary reaction between gases and solids. This equation has been found (*1*) to be applicable to catalyzed reductions of magnetite by graphite. In this case, when the rate of reduction is no longer determined by the carbon–CO_2 reaction, the physical meaning of Eq. (1) can be understood provided it is interpreted as describing the progress of a topochemical reaction on the surface of the oxide particles. This interpretation admitted a straightforward check on its validity.

An implicit premise of the interpretation is that the source of the reducing gas CO has no influence on the kinetics of reduction provided the source generates sufficient CO for its supply to the oxide/gas reaction front not to be rate limiting. Thus different reductants are expected to yield the same

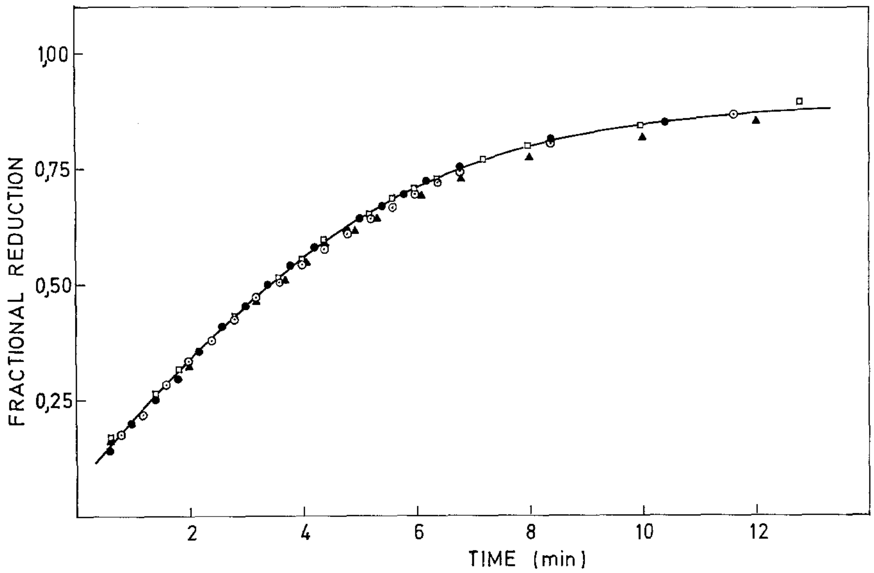

FIG. 2. Reduction of magnetite to wustite at 815°C with various charcoals (size range −144 + 105 μm): ⊙ and ●, Norit (5 C_s); □, Pittsburgh PCB (7.1 C_s); ▲, Aquaraffin BKA (4.0 C_s).

reaction constant k_s at a fixed temperature provided they are present in sufficient quantities. This observational consequence of the interpretation was confirmed directly by determining the reduction kinetics obtained with two other charcoals in addition to Norit R. These were Pittsburgh PCB (Calgon Center, Pittsburgh) and Aquaraffin BKA (Lurgi Apparate, Frankfurt).

The data are displayed in Fig. 2. The k_s values measured for each charcoal are listed in Table 1. It is evident that k_s is essentially independent of the nature of the charcoal or its proportion in the reduction mixture above a certain level of addition.

TABLE 1

Rate Constant k_s for Reduction of Magnetite by Various Charcoals at 815°C

Charcoal	Amount[a] (C_s)	k_s (min^{-1})
Norit R1	5.0	0.052
Norit R1	5.0	0.054
Pittsburgh PCB	7.1	0.051
Pittsburgh PCB	9.5	0.052
Aquaraffin BKA	4.0	0.053
Aquaraffin BKA	2.9	0.055

[a] Given in units of the stoichiometric requirement C_s.

All further work was carried out with Norit charcoal at a concentration of 4.5 C_s.

(iii) Alkali and alkaline earth salts catalyzed the reduction in the carbon independent mode but left the characteristic shape of the reduction curves unaltered. This is demonstrated in Fig. 3 which compares the variation of the rate of reduction, as reflected by the DTG curve, with the expected variation obtained by taking the time derivative of the surface reaction Eq. (1):

$$\frac{d\alpha}{dt} = 3k_s(1 - \alpha)^{\frac{2}{3}}. \tag{2}$$

The use of derivatives afforded a sensitive way of comparing experimental data with theory. The rate values plotted in Fig. 3 were normalized relative to the value at 50% reduction. It may be seen that over a large portion of reduction, its rate may be fitted to the surface reaction equation. The fit is improved in the presence of catalysts.

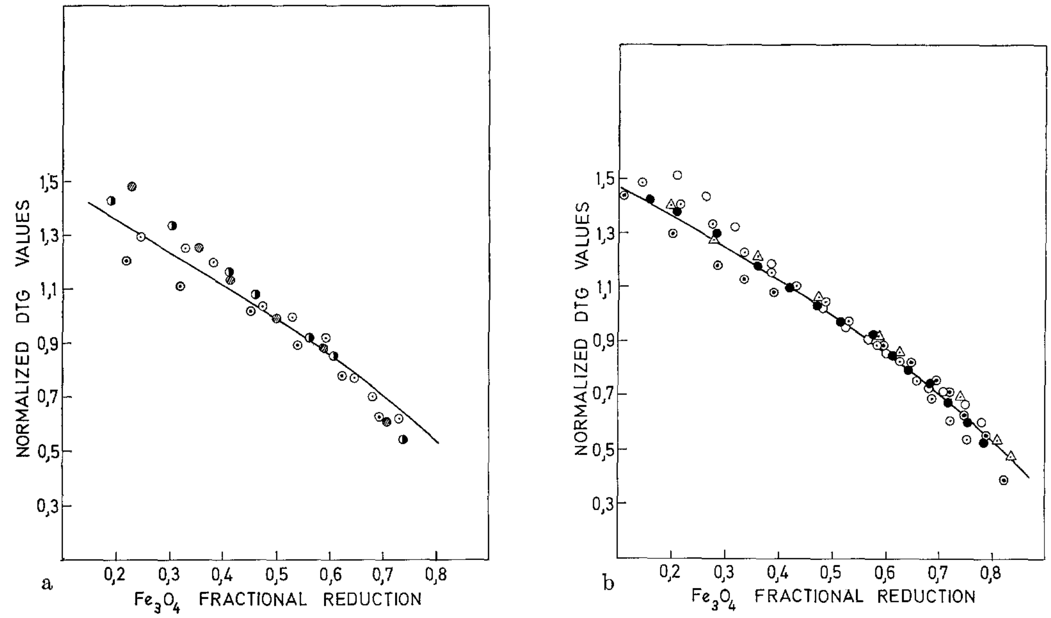

FIG. 3. (a) Variation of rate of reduction with degree of reduction in the absence of catalysts. Solid line represents the function $(1 - \alpha)^{\frac{2}{3}}$. ◑, 820°C; ⊙, 830°C; ▨, 840°C; ◉, 850°C. (b) Variation of the rate of reduction with degree of reduction in the presence of catalysts. ⊙, $Ca(NO_3)_2 \cdot 4H_2O$; ●, NaOH; ○, $Ba(OH)_2 \cdot 8H_2O$; ◉, KOH; △, CsCl. Solid line is the function $(1 - \alpha)^{\frac{2}{3}}$.

Figure 4 shows typical reduction curves obtained with and without catalyst additions; the curves are plotted according to the surface reaction equation in Fig. 5. As expected, the equation is valid to higher values of α in the presence of catalysts.

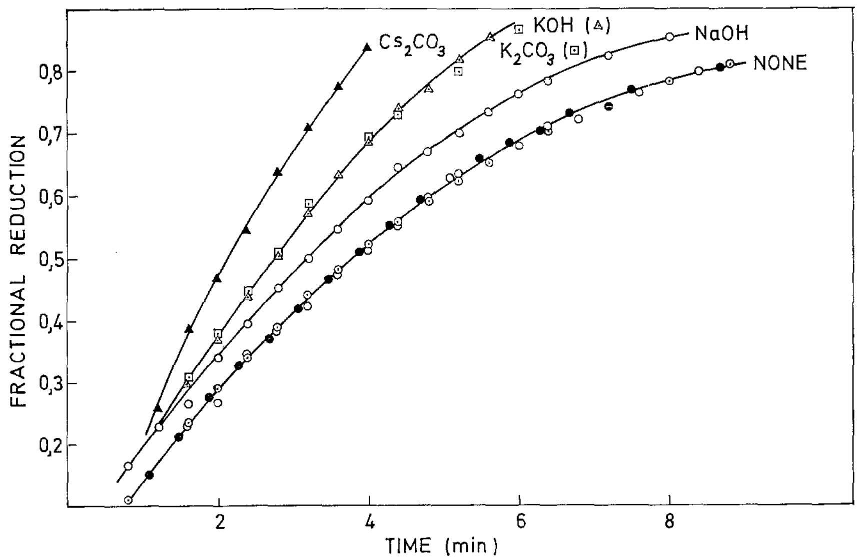

FIG. 4. Reduction of magnetite to wustite at 815°C catalyzed by 1% cation/Fe additions of alkali salts. Additions made in solid form to reduction mixtures. Uncatalyzed reduction curve is a composite of three tests.

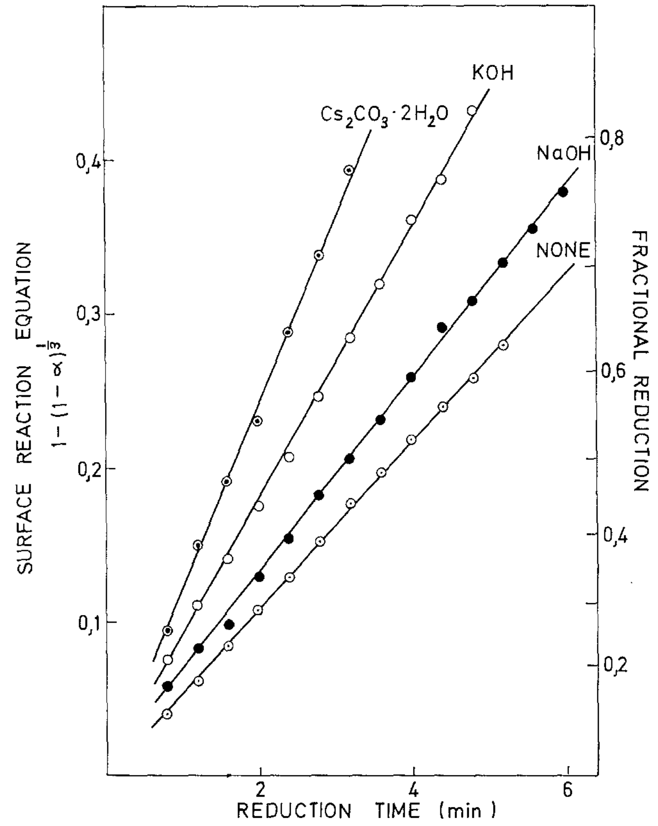

Fig. 5. Reduction results of Figs. 4 replotted according to Eq. (1). Right-hand ordinate indicates the range of validity of this equation.

k_s values obtained in reduction tests catalyzed by carbonates are listed in Table 2. They are seen to differ in one important respect from the values obtained with graphite as reductant: $BaCO_3$ is catalytically inactive.

This difference is readily understood in terms of the new rate-limiting reaction. At reduction temperature, which is well below the Tammann temperatures of both $SrCO_3$ and $BaCO_3$, there seems to be no mechanism available whereby these stable salts can influence the reaction taking place on the surface of the magnetite particles. This suggested that salts which are thermally less stable would exhibit a higher catalytic activity. This was borne out by the results obtained with hydroxides and nitrates (Table 2). It is seen that in general both for alkali and alkaline earths the use of salts with lower melting points or thermal stability than the carbonates resulted in higher k_s values.

The chlorides were found to be extremely catalytic. The effects of 0.25 molar% (metal/iron ratio) additions are compared in Table 3. The rate in the absence of catalysts was again 0.053 ± 0.002 min^{-1}. The methods by which the k_s values were derived are indicated.

It is seen that many of the k_s values lie in the vicinity of 0.080 min^{-1}, suggesting that this may be some sort of saturation limit. This was, however, discounted by the determination of k_s at increasing Na additions (Fig. 6). The dependence of k_s on catalyst concentration was linear up to the highest concentration tested, at which k_s

TABLE 2

Catalyzed Reaction Rates for the Reduction of Magnetite by Charcoal at 815°C[a]

Metal	Surface reaction rate constant k_s (min^{-1})		
	Carbonate	Hydroxide	Nitrate
Li	0.054	0.060 (1.6%)	—
Na	0.055	0.065	0.075
K	0.083	0.083	0.107 (0.7%)
Rb	—	—	0.071 (0.2%)
Cs	0.120	—	—
Mg	0.050	0.057	0.065
Ca	0.052	0.055	0.063
Sr	0.053	—	0.065
Ba	0.054	0.061	0.058

[a] Uncatalyzed k_s = 0.053 min^{-1}; unless otherwise indicated, additive cation concentration is 1% with respect to Fe.

TABLE 3

Surface Reaction Rates for the Reduction of Magnetite by Charcoal at 815°C Catalyzed by 0.25 Molar% Chlorides

Metal	k_s (min^{-1})
Li[a]	0.058
Na[b]	0.077
K[c]	0.085
Rb[a]	0.073
Cs[c]	0.069
Mg[d]	0.075
Ca[a]	0.071
Sr[a]	0.080
Ba[c]	0.078

[a] Average of two determinations.
[b] Interpolation of k_s vs concentration plot (Fig. 6).
[c] Arrhenius plot values (Fig. 7).
[d] Interpolation of k_s at 0, 0.15, and 0.50% concentrations.

attained the value of 0.13 min^{-1}. Considering the accuracy of the determination of k_s, little significance can be placed on such small differences as are observed for the alkaline earths. The range of variation of k_s for alkalis is, however, sufficiently large

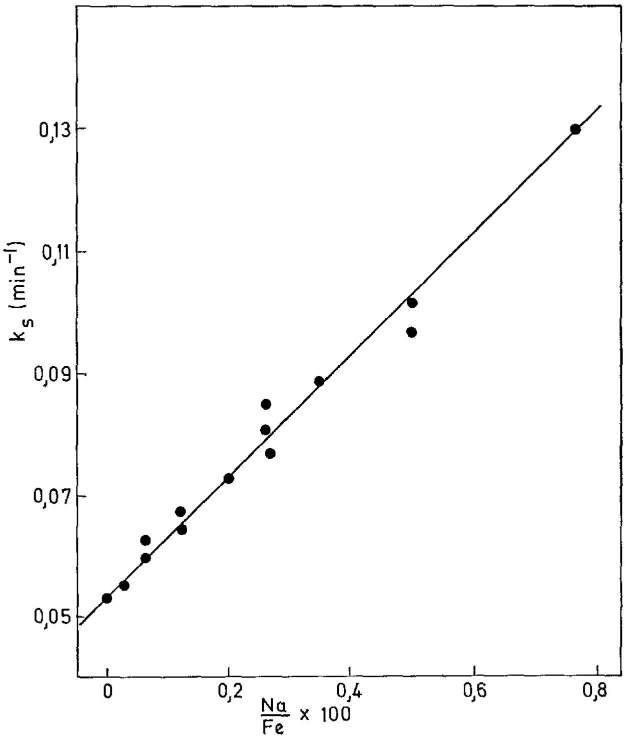

FIG. 6. Effect of increasing additions of sodium (as chloride) on the rate of reduction of magnetite at 815°C.

TABLE 4

Temperature Variation of Surface Reaction Rates (min^{-1}) for Catalyzed[a] Reduction of Magnetite by Charcoal

Temperature (°C)	No catalyst	k_s (KCl)	k_s (CsCl)	k_s ($BaCl_2$)
785	—	0.037	—	0.031
790	—	0.042	—	0.037
795	0.032	0.047	0.038	0.049
800	0.036	0.057	0.047	0.051
805	0.041	0.071	0.053	0.068
810	—	0.081	—	—
815	0.050	—	0.068	0.079
820	—	0.105	—	0.086
825	0.073	0.114	0.092	0.104
830	0.089	—	0.107	—
835	0.093	—	0.116	—
840	0.102	—	—	—
845	0.107	—	—	—

[a] Concentration of additive cation is 0.25% with respect to Fe.

that it must represent a genuine physical effect.

Catalyzed and uncatalyzed k_s values are compared in Table 4 for KCl, CsCl, and $BaCl_2$ at a number of temperatures. The Arrhenius plots of these values are displayed in Fig. 7. It is seen that the least squares values of the activation energy lie within one standard deviation of one another (± 5 kcal/mole).

DISCUSSION

On the available evidence it is concluded that alkali and alkaline earth salts catalyze the phase boundary reaction between reducing gas and oxide lattice.

Furthermore, the data of Table 2 can be interpreted to give support to the view that, irrespective of any details of the mechanism, the interaction of additives and oxide particles has an important role to play.

The interpretation of the relative values of k_s given in Table 2 is complicated by the differing thermal behavior of the additives, but some general points can be noted. Whereas the alkali hydroxides are molten at reduction temperature (bp > 1300°C), the nitrates with their low melting points decompose at ca. 500°C. If the end products of the decomposition are the oxides, then Li and Na are present as solids during reduction, whereas the chemical forms of the heavier alkalis are uncertain as their oxides are unstable at reduction temperature. Alkaline earth nitrates are thermally decomposed to oxides at or below reduction temperature; the decomposition is preceded or accompanied by melting. It is concluded that melting is beneficial to catalysis and, further, that melting followed by decomposition and vaporization, as for the heavy alkali nitrates, is also beneficial. The latter conclusion indicates that the presence of a flux of ionic melt is not a prime requisite for catalysis. This suggests that the catalytic effect of additives is determined in the main by the extent to which they are deposited on the magnetite particles in their molten state or following decomposition. It may further be surmised that the anionic part of additives influences catalysis only in so far as they permit the deposition of cations on the oxide surface.

Consequent to deposition, how do cations catalyze the oxide/gas reaction? Two conclusions can be made here.

First, catalysts do not alter the nature of the rate-limiting step of reduction. This conclusion is based on two observations. (i) Both catalyzed and uncatalyzed reductions conform to the surface reaction equation which is interpreted to reflect the nature of the rate-limiting step. (ii) The activation energy of reduction remains the same in the presence of catalysts.

Second, the increase of the rate of reduction results from an enhancement of the Arrhenius frequency factor. On the basis of the theory of activated complexes, this increase is equivalent to the enhancement of the probability of occurrence of the activated process.

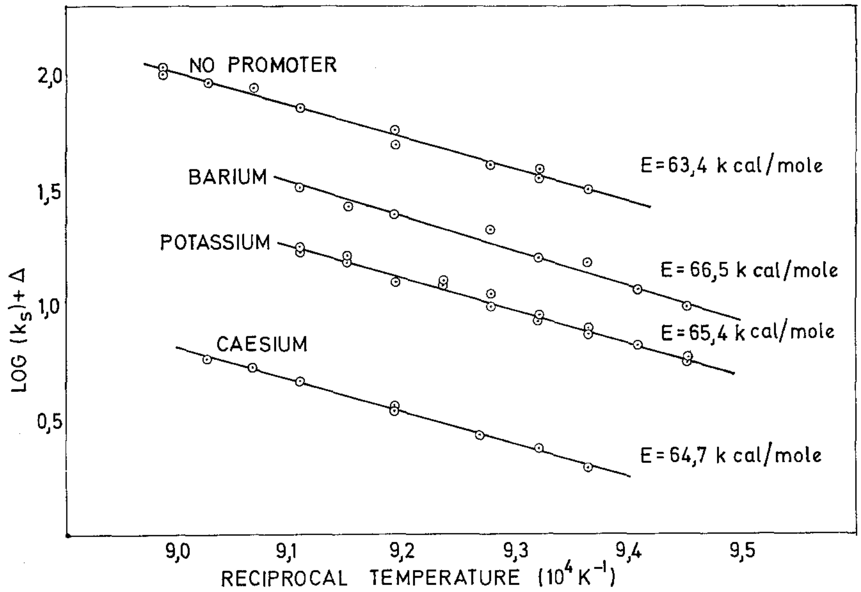

FIG. 7. Arrhenius-type plots for the determination of enthalpy of activation for catalyzed and uncatalyzed reduction of magnetite. Data points separated along the ordinate by an arbitrary amount Δ (different for each set) for clarity of presentation. The preexponential terms (min^{-1}) in the Arrhenius expression are: no catalyst addition, 3.1×10^{11}; K. 1.2×10^{12}; Cs, 7.2×10^{11}; Ba, 1.9×10^{12}.

For reasons discussed below, we identify the activated process with the diffusion of iron in magnetite. It is then possible to interpret the catalytic effect of foreign cations on reduction qualitatively on the assumption that the cations induce changes of point defect concentrations in magnetite.

The rate-controlling influence that lattice defects may exert on the reduction of magnetite is well established. Ulrich *et al.* (*3*) found that the velocity of the phase boundary reaction between magnetite and H_2 (or CO) exhibited a third-order dependence on defect concentration; Pluschkell and Sarma (*4*) found a similar dependence for the growth of wustite on magnetite during the reduction of magnetite by CO. In addition, the catalysis by alkalis of the reduction of magnetite, by H_2 (*5*) and by charcoal in vacuum (*6*), was attributed to the enhancement of defect concentration, although the mechanism whereby this accelerates or bypasses the rate-limiting step of reduction was not clarified.

Lattice defects in magnetite are essentially a consequence of its nonstoichiometry. Magnetite possesses the inverse spinel structure in which oxygen ions have a cubic close-packed arrangement, with the smaller Fe^{2+} and Fe^{3+} ions arranged in the interstices. At stoichiometric composition, eight tetrahedral interstices of the ideal unit cell are occupied by Fe^{3+}, while the distribution of the remaining eight Fe^{3+} and eight Fe^{2+} in 16 octahedral interstices is random and fluctuating. Magnetite deviates from stoichiometry in the direction of increasing oxygen content. Verwey and Haayman (*7*) have shown by X-ray lattice parameter measurements that the deviations are actually associated with the presence of vacancies in the cation sites. Defects are assumed to occur only in octahedral sites, Fe^{2+} being replaced by vacancies and, in order to preserve electrical neutrality, by additional Fe^{3+} ions. The point defects are mobile. Positive holes (Fe^{3+}) migrate by interchange of electrons between Fe^{2+} and Fe^{3+} in adjacent sites (*8*). Vacancies provide the means for the self-diffusion of iron in magnetite (*9*). Recently evidence was presented (*15*) that this may be true only at high oxygen potentials; at low values, interstitial diffusion may become important.

The important role of lattice defects in the reduction of magnetite becomes apparent when the phase boundary reaction, the rate-limiting reaction, is formulated in terms of elementary atomic reactions. The formulation is based on the premise that the removal of oxygen occurs only at the wustite/gas boundary.

That this is indeed so has been amply demonstrated (*3, 10, 11*). It is the consequence of the formation of a dense pore-free layer of wustite on magnetite that confines transport of matter across the wustite to a diffusion in solid solution. The formation of such a layer is due to the similarity of the magnetite and wustite oxygen lattices, both being close-packed cubic. Buinov *et al.* (*12*) found that the reduction of Fe_3O_4 to FeO is crystallographically reversible; the oxygen lattice is not disrupted by repeated oxidations and reductions. It follows that the reduction of Fe_3O_4 to FeO may be viewed as a rearrangement of Fe cations in the interstices of the oxygen lattice.

The reduction of magnetite is represented[1] as:

(i) Oxygen abstraction

$$\mathrm{FeO} + |\mathrm{Fe}^{2+}|'' + 2\mathrm{Fe}^{3+}|\mathrm{Fe}^{2+}|^{\cdot} + \mathrm{CO} = \mathrm{Fe}^{2+}|\mathrm{Fe}^{2+}|_{\mathrm{FeO}} + \mathrm{CO}_2$$

(ii) Defect migration

$$\mathrm{Fe}^{2+}|\mathrm{Fe}^{2+}|_{\mathrm{FeO/gas}} \rightarrow \mathrm{Fe}^{2+}|\mathrm{Fe}^{2+}|_{\mathrm{FeO/Fe_3O_4}}$$

(iii) Lattice rearrangement

$$\mathrm{Fe_3O_4} + \mathrm{Fe}^{2+}|\mathrm{Fe}^{2+}| \rightarrow 4\mathrm{FeO} + |\mathrm{Fe}^{2+}|'' + 2\mathrm{Fe}^{3+}|\mathrm{Fe}^{2+}|^{\cdot}$$

Reaction (i) indicates that the abstraction of oxygen at the FeO/gas boundary is accompanied by the annihilation of an iron vacancy and two holes. Excess iron created by the removal of oxygen is accommodated in vacancies since the reducing potential of the CO/CO_2 atmosphere for the reduction of Fe_3O_4 to FeO is not sufficient to yield nucleated metallic iron.

Reaction (ii) describes the migration of Fe ions across the wustite layer; this is a consequence of the higher vacancy concentration at the Fe_3O_4/FeO boundary. It is accompanied by an equivalent migration of vacancies and holes in the opposite direction. Were it not for this transport of point defects, reaction (i) would cease as soon as the vacancy/hole concentration at the FeO/gas boundary had decreased to a value in equilibrium with the reduction atmosphere.

Reaction (iii) shows that Fe ions are "consumed" at the Fe_3O_4/FeO boundary by accommodation in the Fe_3O_4 lattice so as to yield the FeO anion–cation structure. We postulate that this reaction is slow relative to reactions (i) and (ii), and therefore constitutes the rate-limiting step of reduction. The rate of this reaction will evidently depend, first, on the area of the Fe_3O_4/FeO interface, and, second, on the rate with which Fe ions crossing this area will distribute themselves in Fe_3O_4, i.e., on the diffusion coefficient D for iron in magnetite.

It follows that, provided the reaction sequence (i)–(iii) has attained a steady state and the temperature is kept constant, the rate of conversion of Fe_3O_4 to FeO will vary with the degree of conversion, α, as

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[1] A notation suggested by Schottky [see Ref. (*13*)] is used to designate point defects. (i) The symbol between vertical lines denotes the lattice position which the ion written before the symbol occupies; (ii) absence of such an ion indicates a vacancy; (iii) superscripts prime (′) and dot (˙) denote, respectively, negative and positive charges of the defect relative to the undisturbed lattice; (iv) Fe^{3+} in the lattice position of Fe^{2+} is equivalent to a positive hole.

$(1 - \alpha)^{\frac{2}{3}}$ since this equation describes the change of the Fe_3O_4/FeO interface with α. This is in agreement with the experimentally determined dependence of the rate of reduction on α (Fig. 3a). It also follows that the temperature variation of the rate of reduction is determined by the temperature variation of D, that is, by the enthalpy of self-diffusion of iron in Fe_3O_4.

The generally accepted value of this enthalpy is 55 kcal/mole, as compared to 63.4 ± 4 kcal/mole determined in this investigation for the activation energy of reduction. This value has been adopted in the literature from the work of Himmel *et al.* (*9*) who did not place limits on its accuracy. We have reanalyzed the original rate data of these authors and found that the least squares value of the activation energy for self-diffusion is 57 ± 11 kcal/mole (1σ). This is not incompatible with the experimental value presented here.

It is concluded that the main features of uncatalyzed reduction of magnetite are explicable on the assumption of rate control by reaction (iii). This assumption is also capable of providing a simple explanation for the preservation in catalyzed reduction of the form of the reaction equation (Fig. 3b) and the activation energy (Fig. 7).

The rate of reaction (iii) is increased by increasing the value of the self-diffusion coefficient D. At constant temperature, this will not alter the dependence of the rate on the area of the Fe_3O_4/FeO interface as described by Eq. (2).

The value of D for iron in magnetite is determined by the point defects according to the relation (*14*)

$$D(\mathrm{Fe}) = N_\mathrm{d} D_\mathrm{d} \qquad (3)$$

where N_d is the mole fraction and D_d the diffusion coefficient of point defects. D_d is not a function of defect concentration provided the defects are discrete, noninteracting entities. This has been shown to be true for magnetite (*15*). If follows that $D(\mathrm{Fe})$ is directly proportional to N_d.

It further follows from Eq. (3) that the temperature dependence of $D(\mathrm{Fe})$ is determined by that of N_d and D_d, i.e., by the enthalpies of defect formation and motion. These too are independent of defect concentration to a first approximation. Thus, increases of N_d will enhance $D(\mathrm{Fe})$, but will not change the activation energy of reduction. Increased rates of reaction would then be reflected by increased values of the preexponential term in the Arrhenius expression.

The possible importance of the incorporation of alkali and alkaline earth cations in oxide crystals to the promotion of reduction reactions has been pointed out by a number of investigators. Zhuravleva *et al.* (*6*) and Bel'chenko *et al.* (*5*) derived supporting evidence for the accommodation of alkali in hematite and magnetite crystal lattices from measurements of the lattice constant of FeO derived from Fe_2O_3; this constant changed when reduction was performed in the presence of K. Four types of accommodation were envisaged: (i) cation substitution; (ii) interstitial; (iii) cation and anion vacancy occupation; (iv) formation of ferrites of the form $M_2O \cdot FeO \cdot Fe_2O_3$. The accommodation of foreign cations in wustite has also received attention with respect to their effects on reduction; the conclusions reached are of relevance to magnetite since the oxide lattices are closely similar. Khalafalla and Weston (*16*) concluded that alkalis and alkaline earths (added as hydroxides and nitrates) were taken up in the lattice interstitially. Piepenbrock *et al.* (*17*) pointed out that Na_2O, K_2O, BaO, CaO, and MgO form either a homogeneous series of solid solutions or a limited series of solid solutions in wustite.

These observations suggest that penetration of the magnetite lattice by alkali and alkaline earth ions may occur. We postulate that an important result of this penetration is the formation of cation point defects. This leads directly to enhanced values of the self-diffusion coefficient of iron in accordance with Eq. (3) and thereby to increased rates of reduction in situations where the phase boundary reaction between wustite and magnetite is rate limiting.

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