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Alkali and Alkaline Earth Catalyzed Reduction of Magnetite to Wustite

I. Graphite as Reducing Agent

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It is shown that the rate-limiting step in the reduction of magnetite (Fe_3O_4) to wustite (FeO) by graphite, incorporating the Boudouard reaction, is catalyzed by small additions of alkali and alkaline earth carbonates according to two mechanisms. One of these involves an oxidation–reduction cycle for some catalysts; the other involves the incorporation of catalyst cations into graphite, followed by charge transfer.

INTRODUCTION

An isothermal thermogravimetric study of the reduction of magnetite (Fe_3O_4) to wustite (FeO) by particulate carbon is presented in this paper. It forms part of a wider investigation directed at establishing the influence of alkali and alkaline earth carbonates (and other salts) on the reduction kinetics of iron oxides.

It is generally accepted that the reduction of iron oxides by solid carbon occurs through gaseous intermediates CO and CO_2 in a step-wise process wherein each oxidation state of iron is derived in turn from the next highest one (*1*). CO is consumed in the oxide/gas reaction whereas the Boudouard reaction between reduction product gas CO_2 and the carbon particles restores the reducing potential of the gas phase by the regeneration of CO. Thus the two reactions are:

$$Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2$$

$$CO_2 + C \rightleftharpoons 2CO$$

Although the mechanism and kinetics of reaction between carbon and hematite Fe_2O_3 (and lower oxides) have been extensively investigated (*2*), with particular emphasis on the wustite to iron step, the reduction of magnetite to wustite has received little explicit attention.

Rao (*3*) reported the results of an investigation of the reduction kinetics in mixtures of hematite and carbon in the temperature range 850–1087°C under an argon atmosphere. The results were analyzed by means of a simple first-order kinetic model based on the assumption that the Boudouard reaction is rate limiting. In two subsequent papers (*1, 4*) Rao refined the analysis to take account of mass transfer processes between the gaseous species CO and CO_2 and the porous sample without altering the conclusion on the identity of the rate-controlling step. Eck (*5*) also found that, at least at the start of reaction, the rate of reduction of magnetite was limited by the supply of CO. Following this initial stage, he iden-

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tified two other types of reduction processes for which the rate-controlling reactions were no longer determined by the Boudouard reaction. In the first of these at temperatures near 950°C, the rate of reduction decreased rapidly from an initial high value. The decrease was postulated to be the result of the growth of a wustite layer on magnetite particles which inhibited the reaction $Fe_3O_4 + Fe \rightarrow 4FeO$ due to a decrease of the magnetite/wustite interface. In the second process at temperatures near 1050°C the rate of reduction was observed to increase continuously until the reduction of wustite commenced. This mode of reduction was thought to result from the autocatalytic growth of a surface reaction on the magnetite particles.

Zhuravleva *et al.* (*6*) studied the effects of additions of 1% by weight of lithium, cesium, rubidium, and strontium carbonates on the reduction of magnetite by graphite at 990°C. Cesium and rubidium strongly accelerated the reduction step to wustite; strontium exerted a much lesser effect, and lithium none. The enhancement of reduction was postulated to be a consequence of the incorporation into the oxide lattice of alkali cations. This induced an alteration of the free electron density in the surface layer and thereby promoted the reaction between CO and oxide. The implicit assumption here was that this reaction was rate determining. Kurchatov *et al.* (*7*), on the other hand, concluded that additions of alkalis (sodium and potassium) accelerated the Boudouard reaction and thereby the rate of reduction.

It is evident from the literature that under different experimental conditions the rate-controlling step of reduction may not necessarily be the same. This has given rise to a diversity of opinion regarding the reaction mechanism and the effect of catalysts. The present investigation was undertaken to examine the effects of some 30 alkali and alkaline earth salts on the reduction of magnetite to wustite. A clear distinction was drawn between the effects exerted by the salts on the Boudouard reaction on the one hand and on the chemical reaction between CO and the oxide lattice on the other. The results reported here pertain to the catalysis of the Boudouard reaction by carbonates; catalysis of the gas/oxide reaction is reported separately.

EXPERIMENTAL

Materials. Precipitated red ferric oxide from Hopkin & Williams (England) of 97.4% purity was used in all reduction testwork. Impurities comprised predominantly Ca, Na, Si (spectrographic analysis). Prior to reduction, the powder was calcined in air at 700°C for periods of 20 hr or more. Following this treatment, no phase other than α-Fe_2O_3 was identified by X-ray diffraction analysis, and the ferrous ion content was less than 0.1%.

Spectrographic graphite, SP2X, from Union Carbide Corporation was used as reductant. Only the size fraction -144 $+ 105$ μm was used in the preparation of reduction mixtures.

Hematite and graphite were stored under glass cover in a drying oven at 130°C.

Thermal analysis. Thermogravimetric (TG) and differential thermogravimetric (DTG) studies of the course of reduction were made at ambient pressure using a Mettler thermoanalyzer (*8*). Sample specimens consisted of 240 mg Fe_2O_3 premixed with 10 mg or more of carbon and were heated in cylindrical alumina crucibles at a rate of 25°C/min to preset temperatures which were kept constant with an accuracy of ±1°C until reduction to wustite was complete. Temperature measurement was by means of a Pt–Pt_{10}/Rh_{90} thermocouple placed in contact with the bottom of the crucible. Thermal analysis was performed in a flow of argon (50 ml min^{-1} STP) but it is estimated that the porous sample was immersed in a self-generated

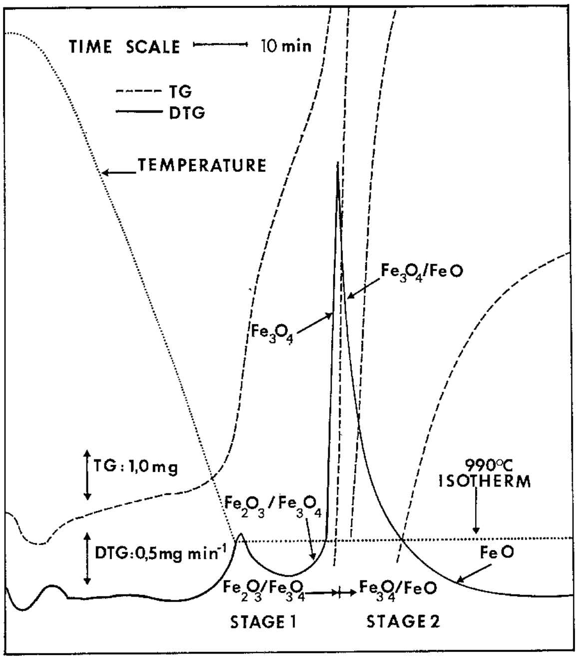

Fig. 1. The two stage reduction of hematite to wustite as depicted by TG and DTG curves at 990°C. Linear time scale along horizontal axis.

CO–CO_2 atmosphere during reduction. This estimate is based on considerations of the size of the crucible (8 mm diam. × 20 mm depth) and typical values of rates of reduction (1–5 mg min^{-1}): From 2 to 10 crucible volumes of CO_2 were generated per minute during reduction of magnetite.

A 12-point recorder plotted the concurrent values of three experimental variables, namely, temperature, weight loss on two sensitivity scales, and rate of weight loss. A fourth variable, the time elapsed from the start of the constant temperature condition, could be read off the chart.

RESULTS

Data Analysis

Reduction results are presented as fractional reduction versus time curves at constant temperature. The calculation of fractional reduction values from the measured weight losses was facilitated by the observation that reduction was a sequential process wherein hematite was first converted to magnetite, then to wustite. This is illustrated in Fig. 1.

The figure displays the cumulative weight loss suffered by the reduction mixture together with the corresponding rates of weight loss as a function of time at 990°C. X-Ray diffraction analyses of solid products of reaction are indicated on the figure at the points where the reduction of partially reduced samples was terminated. The figure highlights two notable features of reduction. First, the occurrence of reduction in two distinct stages which are distinguished by large rate differences is clearly evident. Second, in each stage only two oxide phases coexist.

The reduction stage investigated in the present paper is stage 2, where from an initial high value the rate of reduction of Fe_3O_4 declines continuously as FeO is

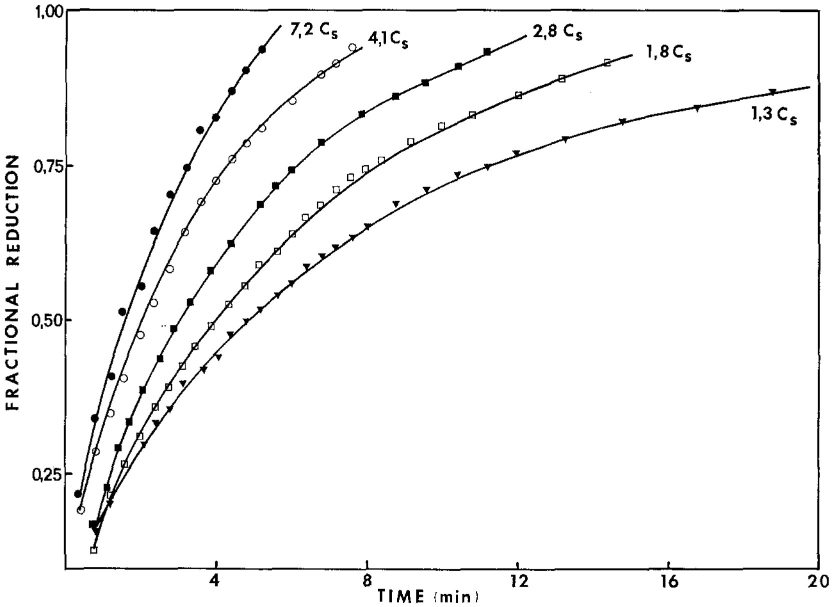

FIG. 2. The effect of increasing graphite additions on the reduction of magnetite at 990°C. Graphite additions are given in units of the stoichiometric requirement C_s.

formed. In this region fractional reduction values α were calculated from the corresponding weight losses according to the relation

$$\alpha = \frac{\Delta W(\alpha)}{\Delta W(\alpha = 1)} \tag{1}$$

where $\Delta W(\alpha)$ is the weight loss at some chosen stage of the reduction, and ΔW $(\alpha = 1)$ is the weight loss corresponding to complete reduction.

The start of magnetite reduction, $\Delta W(\alpha) = 0$, was fixed at that value of mass loss which corresponded to the complete conversion of hematite to magnetite. This conversion always occurred after reaction temperature was reached. Hence at all temperatures tested the starting material for stage 2 of Fig. 1 was 100% Fe_3O_4.

The calculation of $\Delta W(\alpha = 1)$ assumed that the reduction of magnetite proceeded under equilibrium concentrations of CO–CO_2. This assumption was justifiable on two grounds. First, the gas composition was certainly within the thermodynamic stability range of the coexisting phases Fe_3O_4/FeO [16 to 72% CO (*9*) at 1000°C] as the reduction of FeO concomitant to the reduction of Fe_3O_4 was not observed. Second, the calculated value of $\Delta W(\alpha = 1)$ was found to be insensitive to deviations of CO (and CO_2) from the equilibrium value over Fe_3O_4 by as much as 30 volume percent.

The analysis of reduction results was completed by modelling the fractional reduction curves according to a specific kinetic equation which reflected the rate-controlling step of the reaction. This permitted the derivation of rate constants and the examination of their dependence on temperature and additions of catalytic salts.

Reduction kinetics. The rate-controlling influence of the carbon gasification reaction on reduction is demonstrated in Fig. 2 where fractional reduction curves obtained with increasing additions of graphite are reproduced. The strong dependence of the rate of reduction on the amount of graphite present up to the highest addition tested (ca. sevenfold excess over the stoichio-

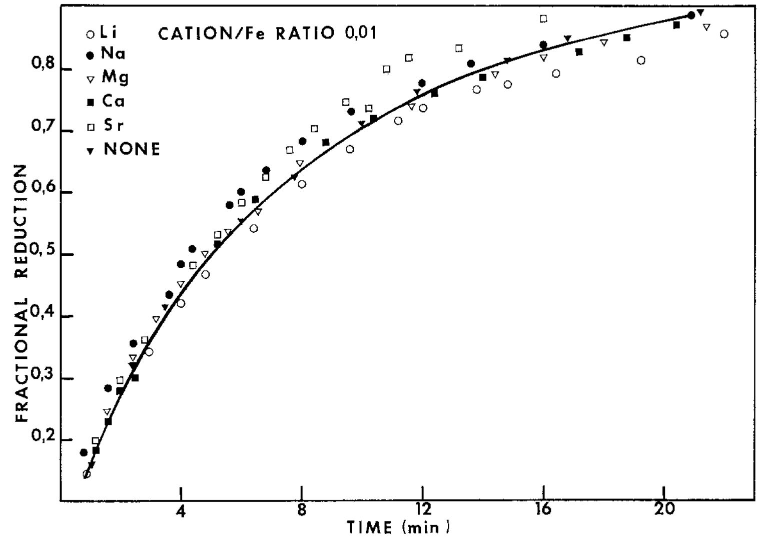

Fig. 3. The effect of poorly catalytic alkali and alkaline earth carbonates on the reduction of magnetite at 990°C. The continuous curve represents the reduction curve in the absence of additives.

metric requirement) is clearly evident. Further work on the influence of alkali and alkaline earth carbonates on the kinetics of reduction in this Boudouard reaction-controlled mode was performed using slightly more than stoichiometric graphite additions. Carbonates were added in the first instance as powders to premixed lots of Fe_2O_3/C. The weights added varied so as to yield a 1% molar concentration of additive cation relative to iron in some cases, and 0.25% in others.

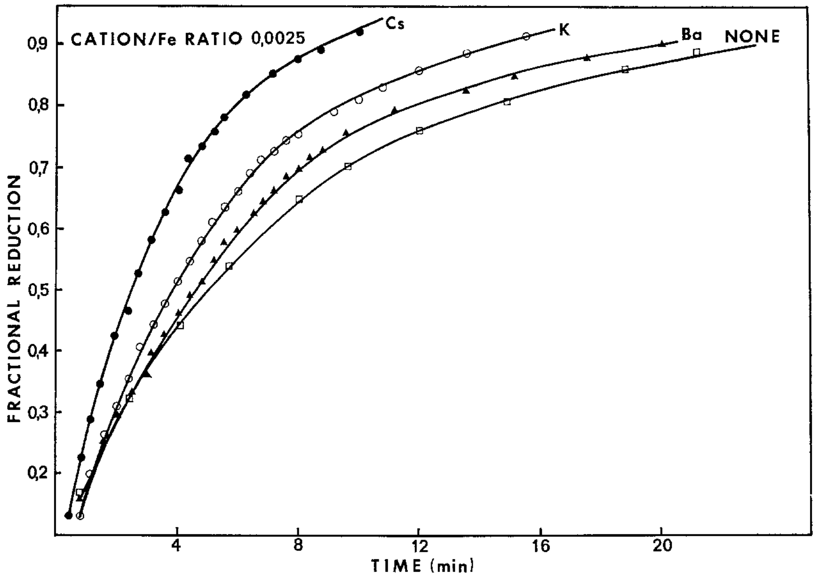

Fig. 4. The effect of highly catalytic alkali and alkaline earth carbonates on the reduction of magnetite at 990°C.

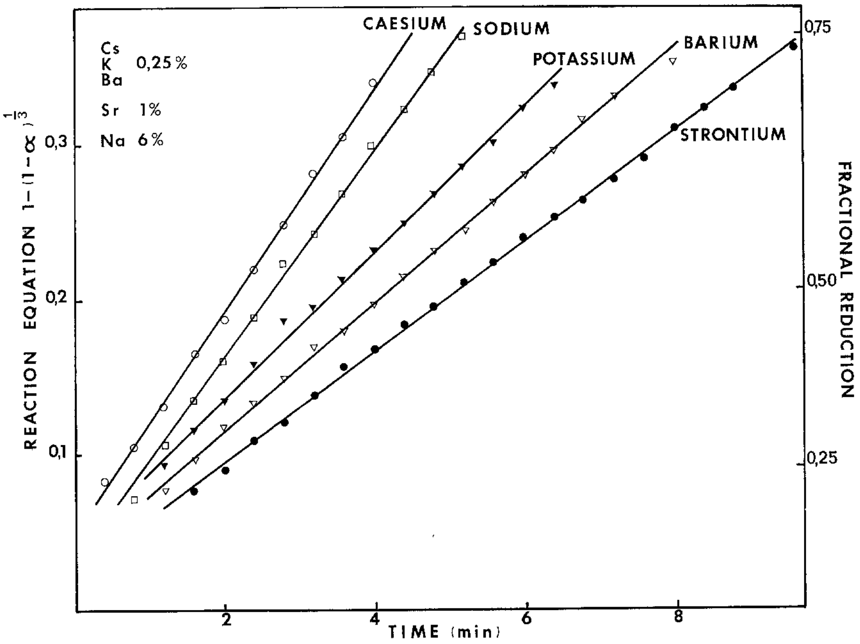

FIG. 5. Reduction curves obtained at 990°C in the presence of catalysts plotted according to the surface reaction equation.

The resulting reduction curves are shown in Figs. 3 and 4.

On the basis of these curves, the carbonates may be divided into two classes, namely, poor and good catalysts, distinguished by large differences of efficacy between the groups. The former group comprises Li, Na, Ca, Mg, Sr (Fig. 3) of which only Sr, and to a lesser extent Na, enhanced the rate of reduction; the latter group comprises K, Cs, Ba (Fig. 4), and Rb, as will be demonstrated later. The reduction curves for good promoters were fitted to a kinetic equation developed for a surface reaction-control model (*10*):

$$1 - (1 - \alpha)^{\frac{1}{3}} = k_s t. \qquad (2)$$

The equation describes a heterogeneous reaction, with rate constant k_s, at an interface of spherical symmetry when the reaction is not diffusion controlled. Habashi (*11*) has shown that the same form of the equation is applicable to reactions on cubes. By extension of his line of reasoning, it is also applicable to a good approximation to particles whose dimensions are similar in all directions.

The application of Eq. (2) to the description of the reaction of a porous body such as graphite, for which the gas–solid reaction interface is not a well-defined geometrical surface, may be understood if gasification is confined essentially to a thin shell surrounding the core. This would be a consequence of the suppression of gasification in the pores of the core by a rapid accumulation of the product gas, CO (*26*). The experimental evidence suggests this suppression occurs rapidly ($\alpha < 0.25$) when catalysts are added. In the absence of catalysts, the accumulation is much more gradual. The self-inhibition of gasification then increases throughout the duration of the reaction and this is reflected by the rapidly decreasing rate of reduction (Fig. 1) at all values of α.

Figure 5 shows the reduction curves of Fig. 4 replotted according to Eq. (2). The figure also includes additional data obtained with Na and Sr at 6 and 1 molar

TABLE 1

Surface Reaction Rates for Carbonate Catalyzed Reduction of Magnetite by Graphite at 990°C

Metal	Molar%	k_s (min^{-1})	k_s (1%) (min^{-1})
K	0.25	0.046	0.100
		0.050	0.116
K[a]	0.25	0.054	0.132
Cs	0.25	0.071	0.200
		0.070	0.196
Ba	0.25	0.040	0.076
		0.038	0.068
		0.037	0.064
Rb[b]	0.25	0.058	0.148
		0.062	0.164
Sr	1.2	0.035	0.034
		0.036	0.035
Na	3.2	0.056	0.037
	6	0.070	0.035
Li	20	0.036	0.028
None[c]	—	0.028	—

[a] KNO_3.

[b] $RbNO_3$.

[c] Estimated from extrapolation of k_s values at increasing K additions.

percent concentrations, respectively. Increased additions of Li_2CO_3 (ca. 20%) also accelerated the reduction. In contrast to Na and Li, increased addition of Mg and Ca did not catalyze the reduction at all. The rate constants k_s (with dimension of min^{-1}) derived from the linear plots of Fig. 5 and from additional reduction tests, including tests with $RbNO_3$, are listed in Table 1. To facilitate comparison, these values have been recalculated by linear interpolation and extrapolation at cation:Fe ratio of 1%. The derived values are listed in the k_s (1%) (min^{-1}) column of Table 1.

That these k_s values pertain to the gasification of carbon was established as follows. If Eq. (2) describes the course of this reaction, then it follows that α is a measure of the carbon burn-off due to reaction with CO_2. At stoichiometric addition of graphite this is numerically equal to the fractional reduction value of magnetite. At higher graphite additions it is, however, less than the corresponding fractional reduction value, being related to it by a multiplicative constant f, always less than 1, that is easily calculable from the excess amount of carbon present in the reduction mixture. In this event Eq. (2) must be modified to

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

in order correctly to describe the reaction kinetics. This prediction was confirmed by performing three reduction tests (1% Cs, 910°C) with increasing carbon additions and observing that the reduction curves plotted according to Eq. (3) were linear and yielded the same value of k_s. Graphite additions corresponded to 1, 1.35, and 1.70 stoichiometric amounts; the corresponding f values were 1, 0.74, and 0.58, respectively. The k_s values derived from the linear plots were (min^{-1}): 0.024, 0.025, and 0.023, respectively.

Additional experimental evidence in support of this interpretation of the reaction Eq. (2) was the finding that the highest value of k_s was attained (at fixed temperature) when Cs was added in aqueous solution to graphite prior to reduction. This is just what is expected if the rate-limiting step is the gasification of carbon, the catalysis of which is presumably most efficient in the event of intimate contact between catalyst and carbon surface.

The temperature variation of this rate-limiting step in the presence of Cs, K, and Ba carbonates was investigated using stoichiometric additions of graphite ($f = 1$). For these reduction tests hematite was impregnated with nominal one molar percent concentrations of additive cations by evaporating aqueous solutions (or suspensions in the case of Ba) to dryness with weighed quantities of hematite. This method of making catalyst additions offered several advantages: greater control over the accuracy of the iron/cation ratio, even distribution of catalyst through the volume of the reduction mixture, and

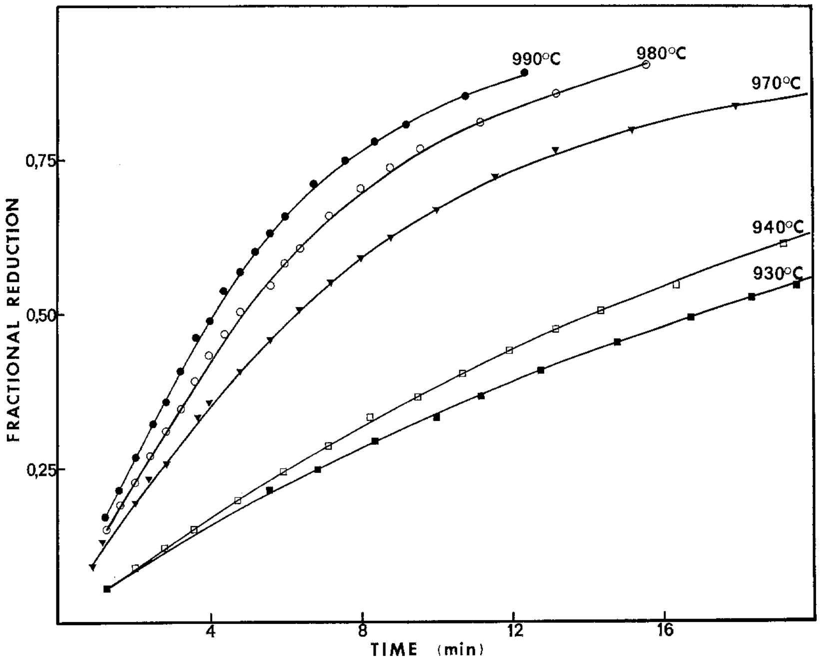

Fig. 6. The effect of temperature on the reduction of magnetite catalyzed by $BaCO_3$.

greater reproducibility of data. The temperature variation of the reduction curves with Ba addition is displayed in Fig. 6, and the corresponding surface reaction plots are shown in Fig. 7. The k_s values derived from the slopes of these plots are

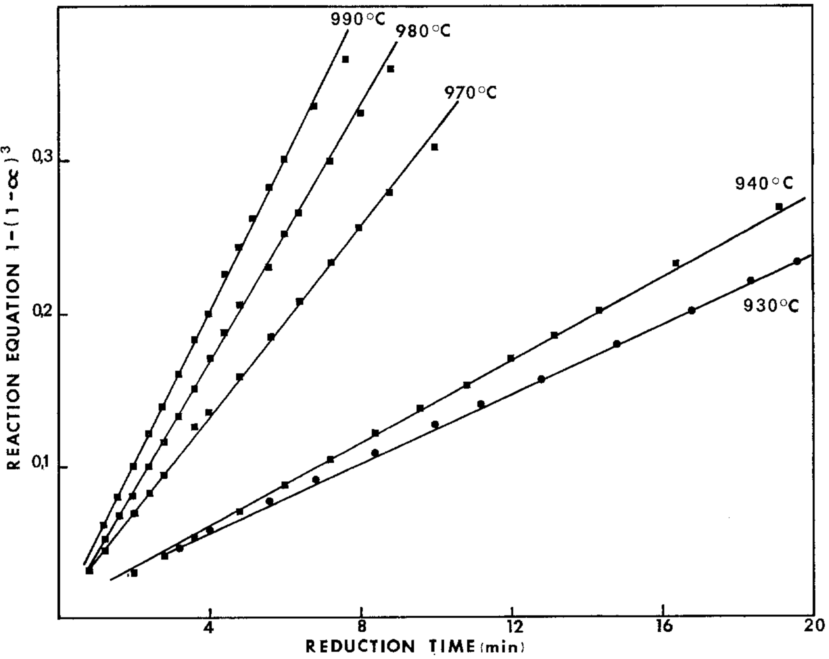

Fig. 7. $BaCO_3$ catalyzed reduction of magnetite plotted according to the surface reaction equation at various temperatures.

TABLE 2

Temperature Variation of Surface Reaction Rate k_s in the Presence of K, Cs, Ba Carbonates

Temperature (°C)	k_s (min^{-1})		
	K	Cs	Ba
880	—	0.014	—
890	0.012	0.017	—
900	0.018	0.020	—
910	0.021	0.023	—
920	—	0.028	—
930	0.032	—	0.011
935	—	—	0.014
940	0.047	0.036	0.016
950	0.056	—	0.025
970	0.075	—	0.039
980	—	—	0.042
990	—	—	0.053

listed in Table 2 together with the values of K and Cs additions derived in an analogous manner. The data are displayed on Arrhenius-type plots in Fig. 8. The activation energies of reduction were derived from linear regression analyses of the slopes and are indicated in Fig. 8 together with the 1σ error ranges.

DISCUSSION

Graphite

The results of the reduction of magnetite by graphite suggest that catalysis of the reduction is explicable in terms of the catalysis of the Boudouard reaction. The catalytic effects of small amounts of metals, particularly of transition metals, on the gasification of carbon have been extensively reported (*12*). That alkali metals may also act as catalytic entities was demonstrated by Bach and Lewitin (*13*) in studies on the burning rate in CO_2 of graphite impregnated with K vapors. Taylor and Neville (*14*) reported that Na and K carbonates are good catalysts for the Boudouard reaction, the latter being more effective, while it is apparent from the work of Rao (*3*) that Li_2O (in large amounts) also exerts a catalytic effect on this reaction. The alkaline earth metals have been reported to catalyze the combustion of carbon in air (*15*).

In their review of the catalysis of carbon gasification, Walker *et al.* (*12*) noted that while a number of conjectures have been made in regard to explaining observed accelerating effects of additive salts, there have been few attempts to substantiate any particular mechanism by a detailed kinetic study of a limited number of closely comparable catalysts. They divided the diverse theories into two broad categories: an oxygen-transfer mechanism involving an oxidation–reduction cycle of the catalyst, and an electron transfer mechanism which postulates that catalysts act as donor or acceptor centres for the π-electrons of graphite. It will be demonstrated by thermodynamic arguments that the experimental evidence on the reduction of magnetite in the presence of alkaline earth carbonates is compatible with the oxygen-transfer mechanism. This mechanism is, however, unable to account for the catalysis of reduction by alkali carbonates, the interpretation of which probably requires a variant of the electron-transfer mechanism.

The essential requirement of the oxygen-transfer mechanism is that the catalyst be capable of undergoing a cycle between two oxidation states. The cycle may be represented for carbonates as (M being metal):

$$MO + CO_2 = MCO_3, \quad (4)$$

$$MCO_3 + C = MO + 2CO. \quad (5)$$

To the extent that the reduction of carbonates by carbon results in enhanced rates of CO generation, the catalytic effects of alkaline earth carbonates are predictable on thermodynamic grounds. Data for the standard free energies of formation of the compounds in reactions (4, 5) for Ca, Sr, and Ba taken from Barin and

Knacke (*16*) were used to calculate the standard free energies of the reactions, their equilibrium constants and equilibrium pressures of CO and CO_2 at 1200 and 1300 K (see Table 3).

It is informative to compare the equilibrium values of P_{CO} in Table 3 with the values in equilibrium with Fe_3O_4/FeO and FeO/Fe phases calculated on the assumption that P_{CO}, P_{CO_2} together constitute one atmosphere pressure. These values serve to define the limits of P_{CO} between which the reduction of magnetite to wustite (but not iron) is permitted. The range (atm) is 0.18 to 0.69 at 1200 K and 0.14 to 0.72 at 1300 K (*9*). A consideration of the P_{CO} values of Table 3 leads to several conclusions.

(i) The formation of $CaCO_3$ according to reaction (4) at reduction temperatures and at one atmosphere reaction pressure is thermodynamically prohibited. It follows that the formation of $MgCO_3$ is even more unfavorable as its decomposition temperature is lower than that of $CaCO_3$. Thus the operation of the oxidation–reduction cycle is precluded. This is in accord with the experimental observation that these carbonates are catalytically inert for the reduction of magnetite.

(ii) Both reactions of the cycle are thermodynamically feasible for Sr under pressures of CO and CO_2 prevailing during the reduction of magnetite. Reaction (4) requires $P_{CO_2} > 0.135$ and reaction (5) requires $P_{CO} < 1.35$. Both these requirements are met simultaneously by the range of CO–CO_2 pressures for which the reduction of magnetite to wustite is possible.

(iii) Reaction (4) is also possible for Ba. Thermodynamics does not, however, yield a completely unambiguous conclusion on the feasibility of reaction (5) at the low end of the temperature range considered. At 1200 K the maximum value of P_{CO} for which the reaction can proceed in the forward direction is very close to the

TABLE 3

Standard Free Energies of Reaction,[a] Equilibrium Constants and Equilibrium CO, CO_2 Pressures[b] for Reactions (4) and (5)

Metal	Reaction (4)						Reaction (5)					
	ΔG°_{1200}	ΔG°_{1300}	K_p^{1200}	K_p^{1300}	$P_{CO_2}^{1200}$	$P_{CO_2}^{1300}$	ΔG°_{1200}	ΔG°_{1300}	K_p^{1200}	K_p^{1300}	P_{CO}^{1200}	P_{CO}^{1300}
Ca	+ 2.74	—	0.317	—	3.15	—	−12.16	—	167	—	12.9	—
Sr	− 8.15	− 4.78	30.2	7.45	0.033	0.135	− 1.27	−8.78	1.7	29.5	1.3	5.4
Ba	−17.57	−14.44	1580	269	6.3×10^{-4}	3.7×10^{-3}	+ 8.15	+0.88	3.3×10^{-2}	0.71	0.18	0.84

[a] kcal/mole (= 4.184×10^3 J).

[b] Standard atmosphere (= 101 325 N m^{-2}).

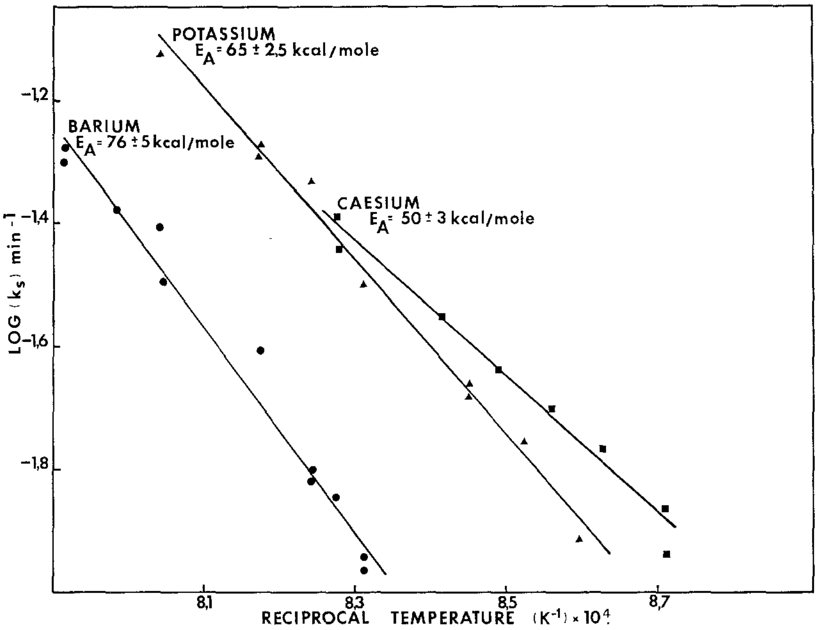

FIG. 8. Arrhenius plot of surface reaction rate constants for the determination of the energy of activation for catalyzed and uncatalyzed reduction of magnetite. The preexponential terms (min^{-1}) are: Ba, 1.1×10^{12}; K, 2.1×10^{10}; Cs, 4.8×10^{7}.

minimum value of P_{CO} required for the reduction of magnetite. It is pertinent to note in this regard that the lowest temperature at which the effect of $BaCO_3$ was examined on the reduction for the purpose of establishing the temperature variation of k_s (Table 2) was very close to 1200 K (930°C). Below this temperature the data could no longer be fitted to the surface reaction equation. The data of Table 3 indicate that at higher temperatures the limiting value of P_{CO} for the occurrence of reaction (5) rises rapidly and at 1300 K it is well in excess of the maximum permitted value for the reduction of magnetite to wustite. Thus, except for some uncertainty at 1200 K, reaction (5) is feasible, and the oxidation–reduction cycle can operate in the presence of $BaCO_3$.

Rao (*3*) invoked the reaction cycle (4, 5) to explain the observed catalysis of the reduction of hematite to iron by Li_2O. That this mechanism is of restricted validity emerges when the equilibrium value of P_{CO} for reaction (5) is considered. The value of $P_{CO} < 0.48$ (1200 K) obtained implies that this mechanism cannot function during the reduction of wustite which requires higher CO concentrations at this temperature. It follows that the results of Rao, which clearly indicate that the FeO/Fe reduction step is well catalyzed at 1180 and 1230 K, are not fully explicable in terms of this mechanism. The restriction on the validity of the oxygen transfer mechanism in respect of Na_2CO_3 are even more grave. Reaction (5) requires $P_{CO} < \sim 10^{-3}$ for which the reduction of magnetite to wustite could not occur. Furthermore, the low thermal stabilities of the heavy alkali oxides (*17*) make the operation of the cycle seem most unlikely. K_2O, for instance, decomposes well below reduction temperatures. These considerations strongly suggest that catalysis of magnetite reduction requires an alternative mechanism for its explanation.

It is suggested that the catalytic effect of alkalis is a consequence of the formation of intercalation compounds of graphite. Such compounds are formed by the accommodation of foreign atoms in the interplanar spaces between parallel hexagonal network planes of carbon (*18*). That graphite reacts spontaneously and very readily with potassium, rubidium, and cesium is well established (*19, 20*); in contrast, it was believed for a long time that sodium and lithium do not form intercalation compounds of the same structure. However, the existence of these compounds was later shown to be possible (*21, 22*). The formation of intercalate compounds involves charge transfer between intercalate species and graphite; alkalis donate electrons into the conduction band formed by π-electron orbitals (*23, 24*). In the event that this charge transfer results in the catalysis of the Boudouard reaction, it may reasonably be surmised that the ionization potentials of the alkalis are of significance to the catalysis.

Evidence for this view is provided by the observation that it is possible to relate the surface reaction rates k_s (Table 1) to the ionization potentials V_I(eV). The relationship takes the form

$$k_s(\mathrm{M}) = 44.4 \exp\{-1.39\, V_I(\mathrm{M})\},$$

where the coefficients have been derived from a least squares analysis of the plot $\ln k_s(\mathrm{M})$ vs V_I (Fig. 9). Harker (*25*) has correlated the decrease of the ignition point in air of coconut charcoal in the presence of admixtures of alkali carbonates to the ionization potentials.

TABLE 4

Activation Energies for the Reduction of Magnetite Catalyzed by Alkalis Compared to Ionization Energies

Catalyst	E_A (kcal/mole)	$E_I - E_A$ (kcal/mole)
Na	73 ± 9	46 ± 9
K	65 ± 2.5	35 ± 2.5
Rb	60 ± 9	36 ± 9
Cs	50 ± 3	40 ± 3

Additional evidence in support of the importance of ionization potentials is provided by the observation that the activation energies of alkali catalyzed reduction can be related to the ionization energies. In order to confirm this, additional tests were carried out with Na_2CO_3 (6.3 molar%) and $RbNO_3$ (1 molar%). The results are

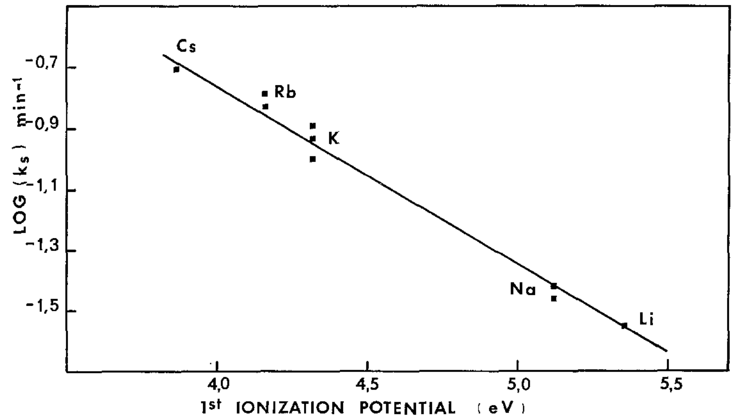

FIG. 9. The relationship between the surface reaction rate constant and first ionization energy of catalyst cation.

summarized in Table 4. E_I denotes the first ionization energy. It is seen that within the 1σ error range, the E_A values differ from E_I by an amount of approximately 37 kcal/mol in all cases. (The pre-exponential terms for Na and Rb are 2.4×10^{11} and 1.1×10^9 min^{-1}, respectively).

It follows from the above considerations that it may be possible to interpret the catalytic effect of alkalis in terms of their enhancement of the free electron density of graphite.

A large amount of evidence has accumulated (*26*) which shows that one of the steps involved in a gas–carbon reaction is chemisorption of the gas on the carbon surface; in particular, it is well established that carbons are capable of retaining oxygen at certain surface sites by chemical bonding. One of the requirements for chemisorption is that the surface atoms must have free valence electrons in order to form chemical bonds with gas molecules or atoms.

The intrinsic rates of C–CO_2 reaction are generally interpreted by the mechanism (*27*)

$$CO_2(g) + f_c \xrightarrow{k_1} CO(g) + (O)_c \qquad (6)$$

and

$$(O)_c \xrightarrow{k_2} CO(g) + f_c, \qquad (7)$$

where f_c and $(O)_c$ are, respectively, free and occupied reaction sites on the carbon surface. The total number of reaction sites is conserved (*27*):

$$\sum_c = \sum f_c + \sum (O)_c = \text{constant}.$$

The forward reaction step of (7) is considered to proceed relatively slowly and the intrinsic rate constant is given by the product $k_2 \sum_c$ (*27*). If the reaction sites f_c may be identified with chemisorption sites, then in terms of this mechanism for the Boudouard reaction, alkalis catalyze the reaction by increasing the magnitude of $\sum_c$. The temperature dependence of the rate is then determined by the rate of creation of additional chemisorption sites in the presence of each alkali as a function of temperature.

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