

RECENT DEVELOPMENTS IN THE KINETICS AND MECHANISM OF THE DIRECT REDUCTION OF HEMATITE WITH SOLID CARBON

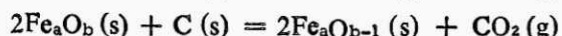
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Abstract: The rate of reaction of hematite fines ($\approx 10 \mu m$) with carbon particles was investigated in the temperature range $850^\circ C$ to $1087^\circ C$. The experimental method consisted of determining the weight loss sustained by a sample of the mixture when maintained at constant temperature under argon atmosphere. The respective effects of carbon particle size, the hematite to carbon proportion in the mixture and the addition of catalytic reagents were investigated. The reaction occurs by a two-stage mechanistic scheme consisting of (a) reduction of iron oxides by carbon monoxide and (b) oxidation of carbon by carbon dioxide, in other words, carbon passes through the intermediate stage of carbon monoxide formation prior to reacting with iron oxides. A chemical kinetic model developed on the basis of carbon solution-loss reaction, viz., stage (b), as rate-controlling represented the results reasonably well. Lithium oxide catalyst was found to enhance the rate of reaction; the addition of ferrous sulfide inhibited the reaction. These observations are consistent with the proposed mechanism because the carbon solution-loss reaction is known to be promoted by alkali metal salts and inhibited by sulfur-bearing compounds.

INTRODUCTION

That metallic iron can be produced by heating a mixture of hematite fines and carbon particles to a moderately high temperature ($\approx 850^\circ C$), under an inert gas blanket, is well established. The mechanism of reduction is not fully understood despite the numerous earlier studies on the subject¹⁻¹⁰. According to the "direct reduction" mechanism, carbon is presumed to react directly with iron oxide, producing CO along with a certain amount of CO_2 . Thus:



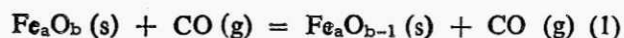
where $a = 1, 2, \text{ or } 3$

when $b = 1, 3, \text{ or } 4$

The "direct reduction" is considered to begin at the points of contact between iron oxide and carbon particles. The product of reaction, viz.,

solid iron, forms a shell around the still unreacted oxide core. Further conversion of oxide takes place by the diffusion of carbon through the shell to the iron/oxide interface. The interfacial reaction which consumes carbon and releases CO and CO_2 is usually assumed to occur rapidly so that the diffusion process becomes the rate-controlling step. Indeed the theories proposed by Baukloh and Durrer¹ and Yun⁷ maintain that diffusion through iron shell is the critical process in the overall "direct reduction" process.

The gaseous products of reaction, i.e., CO and CO_2 , if not removed from the reaction system as soon as these are produced tend to participate in the reduction process as outlined below:



'a' and 'b' have the same values as specified earlier. Arkharov et al⁶, Baukloh and Durrer¹, and Yun⁷ performed direct reduction experiments under vacuum to eliminate the effects of CO and CO₂. In Figure 1, the direct reduction kinetics determined by different investigators are shown. The results are plotted according to Jander's equation¹¹, reproduced below:

$$[1 - (1 - f)^{1/3}]^2 = \frac{Kt}{r^2} \quad (3)$$

where 'r' is the initial radius of the oxide particle and 'f' is the fraction reacted at time 't'. Eqn. (3) was derived on the assumption that the reduction is controlled by the rate of diffusion through the product layer. Although the results of Baukloh and Durrer¹ appear to be in good agreement with the predicted linear behavior, concern has been voiced in the literature^{3,4,13} about the accuracy of these authors' experimental method. Furthermore, working with more stringent experimental conditions, particularly a high vacuum of 5×10^{-4} mm, Yun⁷ obtained direct reduction kinetic data which, as shown in Figure 1, deviates considerably from the predicted linear behavior. The disagreement between these two studies suggests that secondary reduction effects produced by CO and CO₂ might have overshadowed the "true" direct reduction kinetic effects.

The present study was begun with the aim of investigating the kinetics of the overall reduction process—not only the solid/solid reaction but also the gas/solid interactions—in the hematite+carbon mixture heated to a high temperature. Insight into the mechanism of the reduction process was gained by investigating the effects of catalytic additives.

EXPERIMENTAL

The materials used in this study were Baker reagent grade hematite powder (99.5 + wt.%) and high purity carbon, the latter supplied by Ultra Pure Carbon Co., Bay City, Michigan. To determine the effect of the particle size on reduction kinetics three different size-fractions of carbon were employed: a fine-sized fraction (-325 mesh), a medium-sized fraction (-100 to + 115 mesh) and a coarse-sized fraction (-48 to + 60 mesh). The average hematite particle size was found to be about 1 μ m; only one size-fraction was employed in this work.

The samples were prepared by mixing hematite and carbon powders in the designated proportion. Samples weighing about 1 g. were taken from the prepared mixtures for carrying out the weight-loss measurements. Pelletized samples, 5/16" x 1/2", were also used in some experiments. The details of the experimental procedure are omitted here as a clear account of it has been published earlier¹⁷. The weight-loss sustained by the sample when held at constant temperature in an argon atmosphere, was determined at several time intervals. Based on these weight-loss measurements, the "fractional reaction" values were computed using the following relationship.

$$f = (100 \Delta W_t / NW_o) \quad (4)$$

where $(100 \Delta W_t / W_o)$ is the weight loss percent at time 't' and N is the weight loss percent corresponding to complete reduction. N was determined experimentally for each mixture; and N = 38.7, 37.0, 39.5 and 30.8, respectively, for mixtures Fe₂O₃ + 3C, Fe₂O₃ + 1.5C, Fe₂O₃ + 2.25C and Fe₂O₃ + 9C.

RESULTS

The experimental data is presented in the form of "fractional reaction" vs "time" plots in Figure 2 through 6.

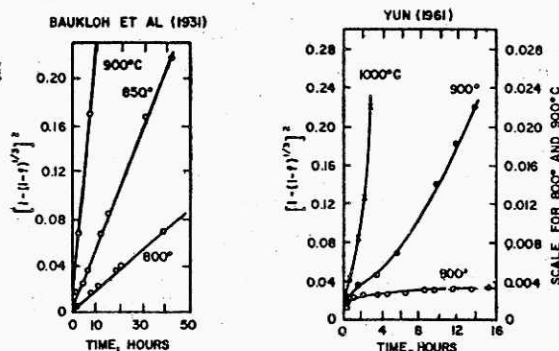


FIG. 1 DIRECT REDUCTION OF Fe₂O₃ BY CARBON; RESULTS PLOTTED ACCORDING TO JANDER'S EQUATION

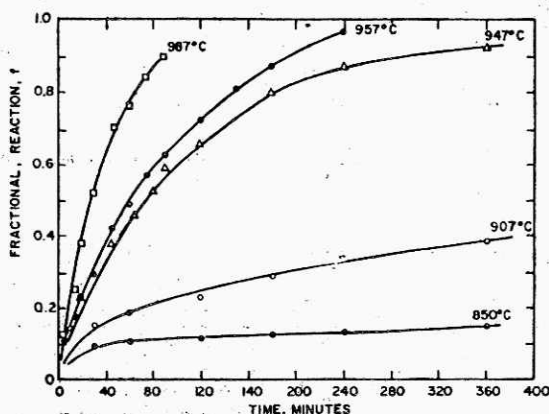


FIG. 2 THE EFFECT OF TEMPERATURE ON THE REDUCTION OF HEMATITE BY CARBON

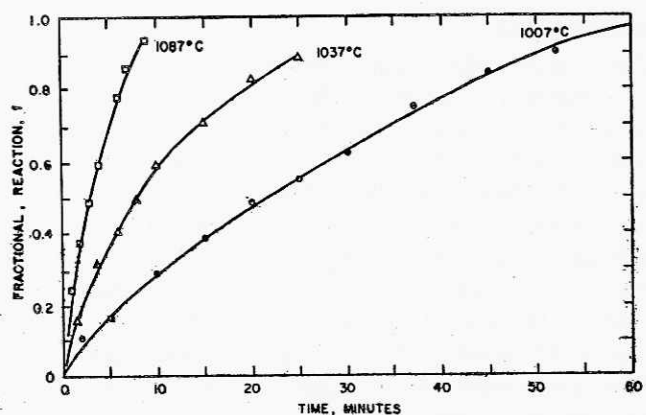


FIG. 3 THE EFFECT OF TEMPERATURE ON THE REDUCTION OF HEMATITE BY CARBON

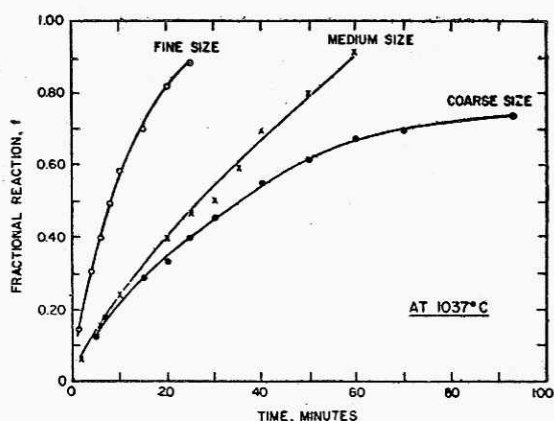


FIG. 4 THE EFFECT OF PARTICLE SIZE OF CARBON ON THE REDUCTION OF HEMATITE

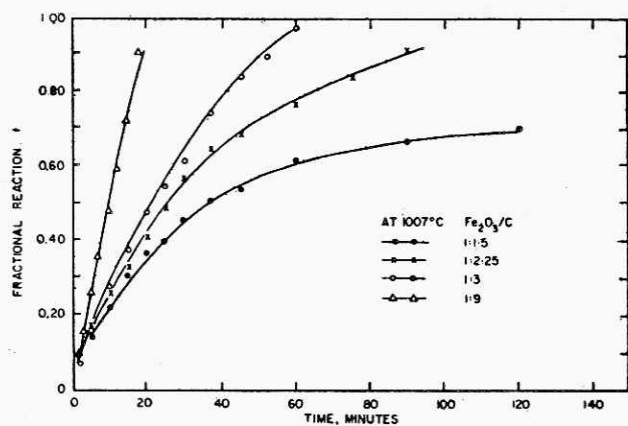


FIG. 5 THE EFFECT OF THE "Fe₂O₃/C" RATIO OF THE MIXTURE ON THE REDUCTION OF HEMATITE

The effect of temperature on the reduction kinetics is shown in Figures 2 and 3; only the fine-sized carbon was used. In Figure 4, the influence of carbon particle size is demonstrated. The proportion of Fe₂O₃ to C was maintained the same at 1 to 3 in the foregoing experiments. The results of experiments performed with mix-

tures having different Fe₂O₃ /C ratios are given in Figure 5. The rate promotion caused by the addition of 5% by wt. Li₂O and the rate inhibition resulting from the presence of 5% by wt. FeS are shown in Figure 6.

DISCUSSION:

As no attempt was made in this study to withdraw the gaseous products from the site of reaction, it is surmised that both CO and CO₂ fully partake in additional reactions as given by eqns. (1) and (2). It has been proposed 5,9,10,17 that reactions (1) and (2) together account for the entire reduction occurring in a mixture of iron oxide and carbon heated to an elevated temperature. During the initial stage of the reduction process, CO is formed by one or more of the following mechanisms: (1) Oxygen of the air entrapped in the porous sample combines with carbon (2) Oxygen chemisorbed on carbon surfaces liberated as CO (3) Carbon reacts with oxygen released by the dissociation of iron oxides and (4) direct reduction occurring at the points of contact between carbon and oxide particles.

Carbon monoxide thus generated attacks hematite particles and reduces them to lower oxides and metallic iron.

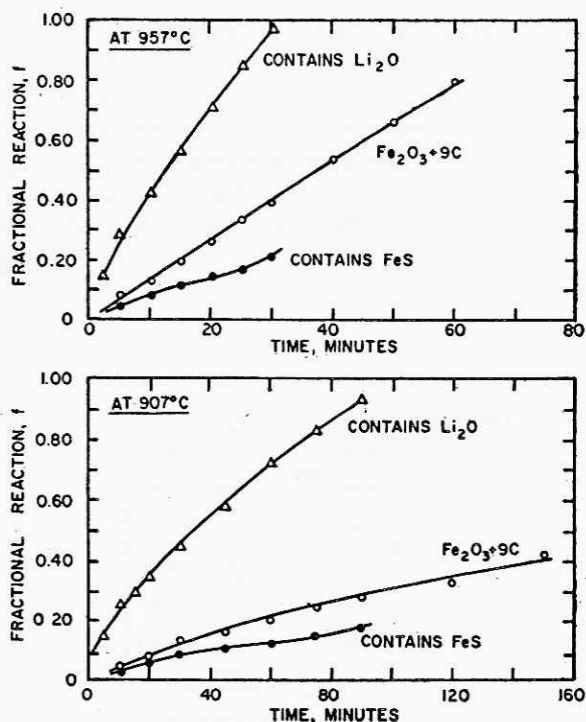
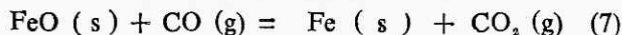
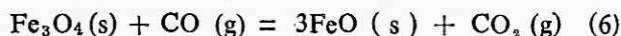
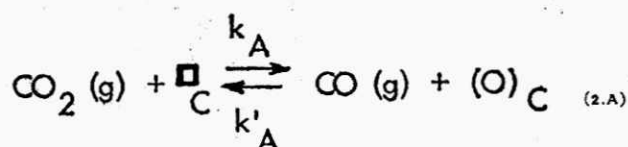


FIG. 6 THE EFFECT OF PROMOTIVE (Li₂O) AND INHIBITIVE (FeS) AGENTS ON THE REDUCTION OF HEMATITE

Incidentally, eqns. (5) through (7) can be generated from eqn. (1) by substituting appropriate values for the suffixes 'a' and 'b' respectively.

The gaseous product of reduction, i.e., CO₂ reacts with carbon particles and produces carbon monoxide, according to eqn. (2). This is the so-called solution-loss or Boudouard reaction. Since the rate of consumption of CO gas, by reactions (5) through (7), is much faster than its regeneration by reaction (2), the gas-phase within the porous sample becomes progressively less reducing until a steady-state is reached; whereupon the overall reduction process occurs at much the same rate as the solution-loss reaction. There have been a number of investigations¹²⁻¹⁶ to elucidate the mechanism of the reaction between carbon and carbon dioxide. The overall reaction is considered to occur by a sequence comprised of two elementary reactions.

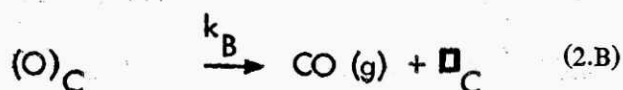
1. Reversible oxygen-exchange reaction involving transfer of oxygen from CO₂ to carbon surface.



where \square_{C} and $(\text{O})_{\text{C}}$ denote a "free reaction site" and a "chemisorbed oxygen atom" on the carbon surface; and

$$\Sigma_{\text{C}} = \square_{\text{C}} + (\text{O})_{\text{C}}$$

2. The chemisorbed oxygen combines with a carbon atom which is liberated as carbon monoxide.



The rate equation for reaction (2) can be written as¹⁶,

$$-\frac{1}{W_{\text{C}}} \frac{dW_{\text{C}}}{dt} = \frac{[720 k_A \Sigma_{\text{C}}] P_{\text{CO}_2}}{1 + (k'_A/k_B) P_{\text{CO}} + (k_A/k_B) P_{\text{CO}_2}} \quad \text{g/g of C - min} \quad (8)$$

In eqn (8), W_{C} denotes the mass of carbon at any time 't', Σ_{C} is the total number of reaction sites on carbon in g. mole/g. of C., k_A , k'_A and k_B are specific rate constants and P_{CO_2} , P_{CO} are the partial pressures of CO₂ and CO in the gas-phase.

The possibility of freshly reduced iron, produced by reaction (7), catalyzing the carbon solution cannot be disregarded. The investigations of King and Jones¹⁹, Walker and co-workers²⁰ and Turkdogan and Vinters²¹, have established that iron, in amounts as small as a few parts per million, greatly enhances the rate of reaction between carbon and carbon dioxide. The rate promotion by the iron catalyst may be attributed to a substantial increase in the number of reaction sites, i.e., Σ_{C} near the iron/carbon contact points. An increase in Σ_{C} according to eqn. (8), results in an enhanced rate of reaction. Much of the catalytic activity of iron, however, is destroyed when it alloys with carbon or forms wustite.

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CHEMICAL KINETIC MODEL :

The kinetic data was interpreted in the light of the two-stage reaction mechanism discussed earlier. The reduction of iron oxides by CO, i.e., eqns. (5) through (7), occurs rapidly so that one may assume the gas-phase within the porous sample to be in virtual equilibrium with "FeO" and Fe. As the penetration of argon gas is bound to be limited to the superficial layers of the sample, the gas-phase may be assumed to consist of CO and CO₂ only. The values of the equilibrium $P_{\text{CO}_2}/P_{\text{CO}}$ ratio for reaction (7) are listed in Table 122. The principal resistance to the overall reduction process stems from the chemical kinetics of the solution-loss reaction which constitutes the chief mode of CO generation within the sample.

Let $n^{\circ} \text{CO}_2$ and $n^{\circ} \text{CO}$ denote the number of moles of CO₂ and CO within the porous sample at any time 't'. Subsequently, the occurrence of reaction (2) over a time-span of 'dt' results in the consumption of 'x' g. moles of CO₂ and simultaneous production of '2x' g. moles of CO gas. Let 'β' be the fraction of CO gas which is utilized in the iron oxide reduction according to eqn. (7).

$$2x[\beta \text{FeO}(\text{s}) + \beta \text{CO}(\text{g}) = \beta \text{Fe}(\text{s}) + \beta \text{CO}_2(\text{g})]$$

As a result of these reactions, the number of moles of CO₂ and CO within the sample now become n_{CO_2} and n_{CO} respectively. By molar balance,

$$n_{\text{CO}_2} = n^{\circ}_{\text{CO}_2} - x + 2x\beta \quad (9.A)$$

and

$$n_{\text{CO}} = n^{\circ}_{\text{CO}} + 2x - 2x\beta \quad (9.B)$$

Since "near" equilibrium conditions are assumed to prevail with respect to reaction (7),

for an isothermal sample of a given volume,

$$\frac{n_{\text{CO}_2}^0}{n_{\text{CO}}^0} = \frac{n_{\text{CO}_2}}{n_{\text{CO}}} = K_e \quad (10)$$

where $K_e (=P_{\text{CO}_2}/P_{\text{CO}})$ is the equilibrium constant for reaction (7). From eqns. (9) and (10).

$$\beta = 1 - (1/2 + 2 K_e) \quad (11)$$

The values of β at various temperatures are listed in Table I.

The rate at which carbon is gasified is given by eqn. (8). At a given temperature, the magnitude of the right side of this equation is determined by (1) The values of the specific rate constants k_A , k_A' and k_B and (2) the composition of the gas-phase, i.e., P_{CO_2} and P_{CO} for the heterogeneous equilibrium "FeO"/Fe/ $\text{CO}_2 + \text{CO}$. To a good approximation the variation in the P_{CO_2} and P_{CO} values (Table 1) may be regarded

as negligible over the temperature range investigated here. Thus,

$$-\frac{1}{W_c} \frac{dW_c}{dt} = R_c' \text{ min}^{-1} \quad (12)$$

where R_c' is the rate constant defined by eqns. (8) and (12). The total weight loss, $\Delta W_c'$ sustained by the mixture over a time-span 't' can be computed from the rate of carbon solution-loss reaction.

Equation (12) is integrated using the boundary conditions $W_c = W_c^0$ at $t = 0$ and $W_c = W_c \text{ at } t = t$. This gives

$$W_c = W_c^0 \exp. (-R_c t) \quad (13)$$

The amount of carbon gasified during time-span 't' is

$$\Delta W_c = W_c^0 - W_c = W_c^0 [1 - \exp. (-R_c t)] \quad (14)$$

As per the stoichiometry of reaction (2), for 12 gms. of carbon gasified, 2 g. moles of CO are

TABLE 1 : Values of utilization factor ' β '

$\frac{1000}{T \text{ K}}$	$K_e = \frac{P_{\text{CO}_2}}{P_{\text{CO}}}$	at $\frac{P}{T} = 1 \text{ atm}$		* β	** λ
		P_{CO_2}	P_{CO}		
1123	0.619	0.382	0.618	0.691	1.352
1180	0.551	0.355	0.645	0.678	1.335
1220	0.511	0.338	0.662	0.669	1.323
1230	0.502	0.334	0.666	0.667	1.321
1260	0.487	0.327	0.673	0.664	1.317
128	0.460	0.315	0.685	0.657	1.309
1310	0.438	0.304	0.696	0.652	1.303
1360	0.405	0.288	0.712	0.644	1.292

* $\beta = 1 - (1/2 + 2 K_e)$

** $\lambda = 0.475 (1 + 2.67 \beta)$, for $\text{Fe}_{203} + 3\text{C}$ mixture

produced; of which $2\beta g$ moles are utilized in iron oxide reduction. In other words, $2\beta g$ atoms of oxygen are extracted. Thus the weight loss sustained by oxide in the sample is given by

$$\Delta W_{ox} = \frac{32}{12} \beta \Delta W_c \quad (15)$$

The total weight loss during time-span 't' is

$$\Delta W_t = \Delta W_c (1 + 2.67 \beta) \quad (16)$$

From eqns. (14) and (16)

$$\Delta W_t = W_c^0 (1 + 2.67 \beta) [1 - \exp(-R_c t)] \quad (17)$$

For $Fe_2O_3 + 3C$ mixture, $W_c^0 = (36/195.7) W_0$, where W_0 is the initial weight of the mixture.

From eqns. (4) and (17):

$$f = \frac{(36)(1+2.67\beta)}{(0.387)(195.7)} [1 - \exp(-R_c t)] \quad (18)$$

Rearranging the terms:

$$\log(\lambda - f) = - (R_c / 2.303) t + \log \lambda \quad (19)$$

$$\lambda = 0.4753 (1 + 2.67 \beta) \quad (20)$$

The values of ' λ ' at different temperatures are given in Table 1.

The experimental data was recast into " $\log(\lambda - f)$ " vs. " t " plots as shown in figures 7 and 8. The agreement with the model is reasonably good at temperatures ranging from 957 to 1087 deg. C. At lower temperatures, i.e. at 907 deg. and 947 deg. C, the plots exhibit three different stages; each of which occurs at a slower rate than the preceding one. As discussed in an earlier publication¹⁷, this behaviour may be attributed to the relative ease with which the iron catalyst gets deactivated (through reoxidation) at lower temperatures. Furthermore, the gas-phase composition, which has been assumed to remain constant over the entire time, might change at the completion of the $Fe_2O_3 \rightarrow FeO$ conversion.

The values of the rate constant " R_c " evaluated from the steepest slopes of these plots are listed in Table II. The enthalpy of activation was

TABLE II: Values of Rate Constant " R "
c

T °K	Rmin ⁻¹ c'	Published data 23		(k _A M _C) [*]	4 10/T	-log R _c	-log (k _A M _C)
		k/k _A B	k'/k _A B				
1123	1.152x10 ⁻⁴	3.06	1973	5.12x10 ⁻⁴	8.905	3.9385	3.2910
1180	8.356x10 ⁻⁴	2.65	531.4	1.13x10 ⁻³	8.475	3.0780	2.948
1220	5.890x10 ⁻³	2.41	227.7	3.65x10 ⁻³	8.197	2.2300	2.438
1230	6.910x10 ⁻³	2.36	185.8	3.65x10 ⁻³	8.130	2.1600	2.438
1260	1.565x10 ⁻²	2.21	103.1	4.72x10 ⁻³	7.937	1.8050	2.326
1280	2.233x10 ⁻²	2.12	70.5	4.92x10 ⁻³	7.812	1.6510	2.308
1310	4.788x10 ⁻²	2.00	40.9	6.58x10 ⁻³	7.634	1.3200	2.182
1360	0.134 2	1.82	17.4	8.99x10 ⁻³	7.353	0.8720	2.046

*

$$k_A M_C = (R_c / 720 P_{CO_2}) [1 + (k'/k_A) P_{CO} + (k/k_A) P_{CO_2}]$$

The units of k_A M_C are g. mole/g. of C - atm. - sec.

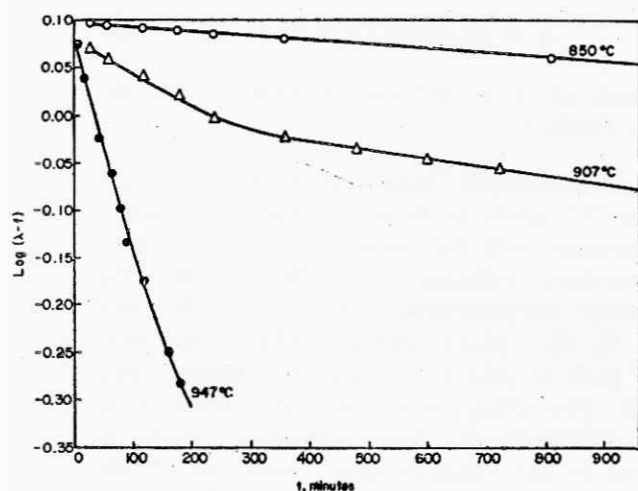


FIGURE 7: RESULTS REPLOTTED ACCORDING TO EQUATION (17)

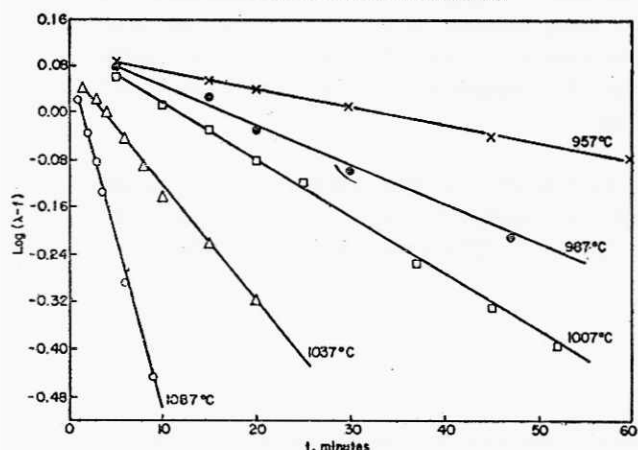


FIGURE 8: RESULTS REPLOTTED ACCORDING TO EQUATION (17)

determined by constructing a "log R_c " versus "10,000/T" plot, as shown in Figure 9. Within the temperature range 957 deg. to 1087 deg. C the enthalpy of activation was found to be 72 ± 4 k. cal./mole. Over the lower temperature range, value of 110 ± 5 k. cal./mole. This larger the enthalpy of activation has a much larger value, it must be emphasized, includes the combined effects of (1) temperature itself, (2) the catalyst action of iron which is markedly influenced by temperature and (3) gas-phase composition which is also a function of temperature. A clear-cut separation between the effect of temperature and the effects of other parameters on the rate constant, R_c is not possible. As a result, no definitive conclusions may be drawn at this stage concerning the derived activation enthalpies.

A better understanding of the reaction mechanism can be gained by reinterpreting the rate constant (R_c) data in the light of experimental data of Wu, reported by Reif²³, for k_A/k_B and k'_A/k_B . The values of " $k_A \Sigma_c$ " were calculated at different temperatures using these data and the PCO_2 , PCO values listed in Table

1. The results are summarized in Table II. The Arrhenius plot, " $\log k_A \Sigma_c$ " vs "10,000/T", exhibits two distinct regions, as shown in Figure 9. In the high temperature region, i.e., from 947 deg. to 1087 deg. C, the activation enthalpy was found to be 23 ± 4 k. cal./mole. A value of 55 ± 6 k. cal./mole was obtained for the lower temperature region.

In general, a catalyzed reaction is believed to manifest a much weaker temperature-dependence as compared to the uncatalyzed reaction. For the uncatalyzed carbon solution-loss reaction, Mentser and Ergun²⁴ reported a value of 53 k. cal./mole as the activation energy associated with the forward specific rate constant, " $k_A \Sigma_c$ ". By comparing this value with the present data, two conclusions may be drawn: (1) at lower temperatures the catalysis of solution-loss reaction by iron catalyst is much less significant than previously realized; and the decrease in the rate of the reduction process may simply be due to a change in gas-phase composition. Therefore, the derived activation enthalpy of 55 k. cal./mole, within experimental error, may be regarded as the true activation energy for the forward reaction rate constant, " $k_A \Sigma_c$ ". (II) the considerable lowering of the activation enthalpy (almost 30 k. cal./mole) for the high temperature region points out that in this range the iron catalyst

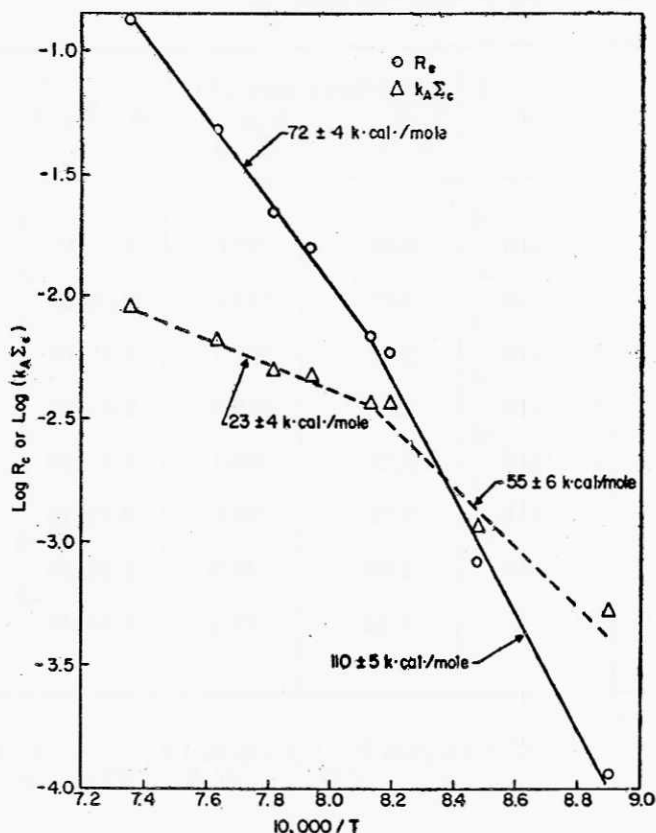


FIGURE 9: ARRHENIUS PLOT

actively partakes in the enhancement of the rate of solution-loss reaction.

VALIDITY OF THE PROPOSED MECHANISM:

That carbon solution-loss reaction governs the overall reduction process emerges as the central feature of the proposed mechanism. Recent studies^{25,26} from this laboratory have dealt with the general problem of catalysis of carbon-gas reactions. The results of these studies, given in Figure 10, clearly show that the addition of 1.5% by wt. Li_2O considerably enhances the rate of solution-loss reaction. These observations are in complete accord with the results reported here, i.e., Figure 6, on the effect of lithium oxide on the rate of reduction process.

Chufarov and Antonova²⁷ reported that sulfur-bearing compounds tend to retard the rate of carbon solution-loss reaction. The addition of ferrous sulfide does indeed produce rate-inhibition as indicated in Figure 6.

SUMMARY AND CONCLUSIONS:

(1) The direct reduction of hematite fines by solid carbon occurs via gaseous intermediates CO and CO_2 . (2) The reduction kinetic data can be meaningfully interpreted by means of a chemical kinetic model, developed on the basis that carbon solution-loss reaction controls the overall rate. (3) The observed effects of Li_2O and FeS are in agreement with the reported effects of these reagents on the carbon solution-loss reaction.

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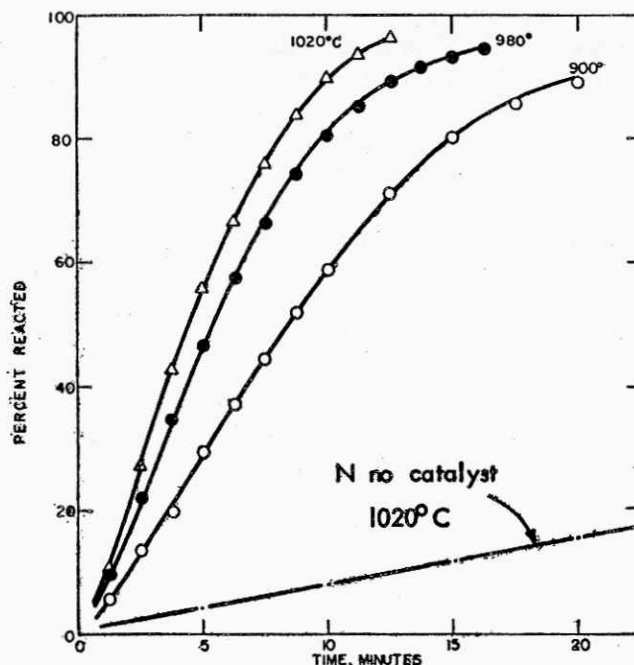


FIG. 10 EXPERIMENTAL RESULTS FOR CATALYST-DOPED CARBON PELLETS; CATALYST CONCENTRATION: 1.5% Li_2O

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**SESSION II - SPONGE IRON - FUNDAMENTAL ASPECTS,
PRESENT STATUS AND FUTURE DEVELOPMENT**

Monday, 19 February, 1973

The Session was convened at 2.30 P. M. The Chairman was Dr. Samir Taher, Chairman & Managing Director of Delta Steel Mill Co., Cairo, Egypt, the Co-Chairman was Mr. H. Chr. Andersen, Manager, Metallurgical Department, Elkem-Spigerverket A/S, Oslo, Norway and the Rapporteur was Dr. A. B. Chatterjea, Deputy Director, National Metallurgical Laboratory, Jamshedpur.