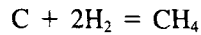
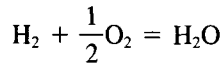
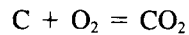
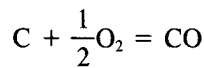


encountered such a special case, what we should do is only to change the initial values of H_2 and CO .

Simplicity of our method is to deal with the most fundamental equilibria, *i.e.*,



and to employ the popular Newton-Raphson method. We also showed an intuitive method to obtain a_C , avoiding the restriction mentioned above.

An advantage of the method proposed by Rao and Lee would be in formulation of the iteration, where it does not need to calculate the derivatives such as $\partial \bar{H}/\partial H_2$. However, in exchange for the advantage, their method has brought mathematical ambiguity of the convergence, which results in ambiguity in selecting the convergence coefficients (u, v, w) and sometimes sluggish convergence. As suggested by Kellogg (Reference 6 above), the convergence coefficients should be set to be smaller values (<1) depending on the gas composition. Their method gives not only simple formulation but also ambiguity of the coefficients.

On the other hand, the non-convergent behavior of the Newton-Raphson method is much more comprehensible than their method and does not occur in the vicinity of the real roots. We believe that both methods do not make great differences, if their method is found to be mathematically valid, and that simplicity would depend on preference of the users.

They criticized the fact that we did not use recent thermodynamic data of free energies. We agree that improved data should be used. However, we cannot find any significant differences between our results and theirs and there would not be any changes in the discussion in the paper.

We are grateful for their check of our results and constructive discussion.

The Effects of CO and CO_2 on the Rate of Na_2CO_3 Catalyzed Boudouard Reaction

M. ALAM and T. DEBROY

The reaction between carbon and CO_2 ,



has been the subject of extensive research in the last several decades. The large and proliferating literature on this topic is a testimony of both the importance and the complexity of

this reaction. The complexity arises from the frequent involvement of more than one of the large number of factors that influence the reaction rate. These factors include the concentration of active sites on the carbon surface, the pore structure and the crystallinity of carbon, and the nature and concentration of inorganic impurities in the coke.¹ Despite the large volume of existing literature on this reaction, the effects of catalytic additives in this reaction are still not clearly understood. The purpose of this article is to present experimental results on the effects of CO and CO_2 in the Na_2CO_3 catalyzed reaction between CO_2 and two different types of coke. The work reported here is a part of a continuing study^{2,3,4} aimed at understanding the Boudouard Reaction involving different commercial coke samples that have different reactivities on the Bethlehem Reactivity scale.⁵

Commercial grades of low and high reactivity coke, obtained from Koppers Company, were utilized for the present study. The characteristics of the cokes used in the present study are presented in Table I. It is clear from this table that the major difference in the properties of the two types of coke lies in the reactivity as measured on the Bethlehem Reactivity scale.

A thermogravimetric set-up consisting of a Cahn Model 1000 electrobalance which had a sensitivity of $0.5 \mu g$ was utilized to study the rates of reaction between coke samples and CO/CO_2 mixtures at 1173 K with and without the addition of a catalyst. The coke samples were shaped into discs of about 1.5×10^{-2} m diameter and 0.5×10^{-2} m thickness. The samples were suspended inside a mullite tube of 1.5 inch (3.7×10^{-2} m) internal diameter. The gas flow rate was 1 liter per minute (1.67×10^{-5} m³ per second) at room temperature and 1 atmosphere (1.01×10^5 N/m²)

Table I. Characteristics of Coke Samples

Characteristics	Low Reactivity	High Reactivity
A. Proximate Analysis (wt pct d.b.)		
Fixed carbon	92.57	91.20
Volatile matter	0.71	0.52
Ash	6.72	8.26
B. Ash Composition (pct)		
SiO ₂	49.60	50.92
Al ₂ O ₃	29.11	28.50
Fe ₂ O ₃	10.72	11.82
CaO	2.67	2.33
TiO ₂	1.57	1.37
MgO	1.52	1.46
Na ₂ O	0.77	1.05
K ₂ O	2.00	1.63
C. Physical Properties		
True specific gravity	1.92	1.79
Apparent specific gravity	0.98	0.91
Porosity (pct)	49.00	49.20
Mean pore size (microns)	80.00	88.80
Specific surface area (m ² /g)	0.40	0.45
D. Reactivity		
Bethlehem	17.40	24.80

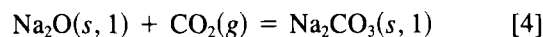
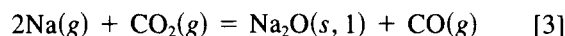
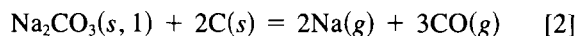
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Manuscript submitted October 20, 1983.

total pressure. At this flow rate the diffusion of CO and CO₂ through the external gas boundary layer did not control the rate of reaction.⁴ The rate of oxidation of coke was determined from the slope of the weight loss vs time plots. These plots were essentially linear for all the experiments during the period of measurement. The experimental conditions were such that Na₂CO₃ did not decompose during the experiments. Care was exercised during selection of coke pieces from which samples were made. In particular, coke pieces with structural discontinuities or visual appearances uncharacteristic of the lot were discarded. All coke samples were preheated at 413 K for three hours to eliminate moisture. The samples were cooled in a desiccator for one hour, weighed, and subsequently dipped in an aqueous solution of Na₂CO₃ for a predetermined length of time. After soaking the samples were dried at 413 K for 15 hours, cooled, and weighed. The concentrations of Na₂CO₃ in the coke samples were determined from the weight gain of the samples. The experimental details of various runs are presented in Table II.

The rate of reaction of both low and high reactivity coke at different P_{CO_2} values are plotted in Figure 1 as a function of Na₂CO₃ concentration in the coke. The figure indicates that the higher the Na₂CO₃ concentration, the higher the reaction rate for both low and high reactivity coke.

A number of alternative mechanisms have been proposed in the past to explain the catalytic behavior of alkali metal carbonates in the C-CO₂ reaction. The vapor cycle mechanism⁶ consists of the following steps:



Since Na(g) is highly reactive, it is unlikely that reaction [3] is the slowest step in the catalysis. The roles of the other two steps can be examined utilizing the experimental data. It is observed from Figure 2(a) that the higher the partial pressure of CO₂, the higher the difference between the rates

Table II. Summary of Experimental Data for the Reaction of Low and High Reactivity Coke at 1123 K in CO-CO₂-Ar Mixtures at a Total Pressure of 1.0133 × 10⁵ N/m²

S. No.	Weight of Sample (kg × 10 ⁴)	Na ₂ CO ₃ (Wt Pct)	P_{CO} (N/m ² × 10 ⁻⁵)	P_{CO_2} (N/m ² × 10 ⁻⁵)	Weight Loss (kg × 10 ⁶)	Time (s × 1.67 × 10 ⁻²)
L-C1	8.304	2.06	0.05	0.55	22.55	40
L-C2	6.821	2.05	0.10	0.55	18.80	48
L-C3	8.304	2.06	0.20	0.55	7.50	45
L-C4	8.304	2.06	0.30	0.55	4.20	40
L-C5	7.617	2.00	0.00	0.3	20.00	23
L-C6	6.821	2.05	0.00	0.55	18.70	17
L-C7	7.506	1.99	0.00	0.8	21.12	14
L-C8	9.244	1.99	0.00	1.0	21.00	12
L-C9	7.809	1.31	0.00	0.3	20.6	30
L-C10	8.571	1.32	0.00	0.55	23.4	26
L-C11	7.539	1.30	0.00	0.8	20.7	19
L-C12	7.336	1.32	0.00	1.0	20.55	17
L-1	8.476	0.00	0.05	0.55	4.65	120
L-2	8.620	0.00	0.10	0.55	3.00	120
L-3	8.476	0.00	0.20	0.55	2.20	120
L-4	8.476	0.00	0.30	0.55	2.00	120
L-5	7.313	0.00	0.00	0.3	3.10	38
L-6	8.107	0.00	0.00	0.55	5.75	40
L-7	8.006	0.00	0.00	0.8	7.50	40
L-8	7.175	0.00	0.00	1.0	9.50	40
H-C1	7.956	2.05	0.10	0.55	15.35	40
H-C2	8.871	2.03	0.20	0.55	9.325	39
H-C3	8.871	2.03	0.30	0.55	4.2	42
H-C4	7.527	1.99	0.00	0.30	20.65	31
H-C5	7.956	2.05	0.00	0.55	22.45	23
H-C6	8.104	1.99	0.00	0.30	23.35	18
H-C7	8.272	2.01	0.00	1.00	22.80	16
H-C8	7.520	2.81	0.00	0.30	20.65	31
H-C9	9.863	2.88	0.00	0.55	22.45	23
H-C10	8.701	2.87	0.00	0.80	22.35	18
H-C11	0.491	2.88	0.00	1.00	22.8	16
H-1	7.304	0.00	0.10	0.55	2.9	120
H-2	8.925	0.00	0.20	0.55	2.5	120
H-3	7.956	0.00	0.30	0.55	2.0	120
H-4	8.861	0.00	0.00	0.30	3.70	40
H-5	8.836	0.00	0.00	0.55	6.25	42
H-6	8.782	0.00	0.00	0.80	7.45	37
H-7	8.707	0.00	0.00	1.00	9.1	35

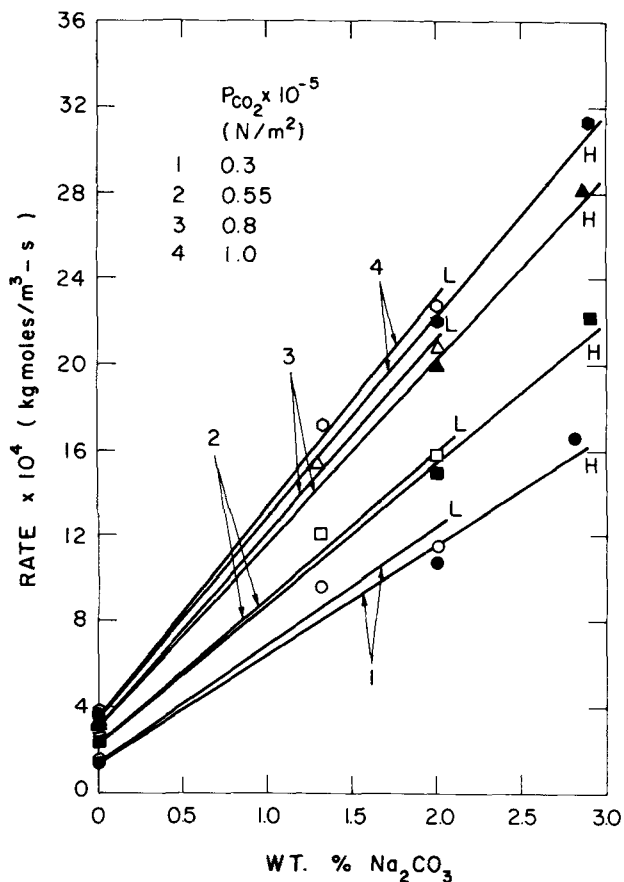
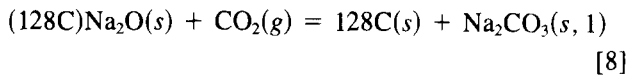
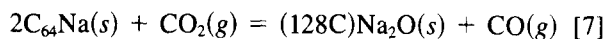
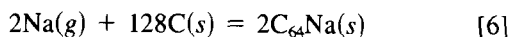
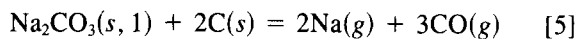


Fig. 1—Effect of Na_2CO_3 on the rate of reaction of low and high reactivity coke at different P_{CO_2} values, in absence of CO. The symbols L and H on the diagram indicate lines for the low and the high reactivity coke, respectively.

of the catalyzed and the noncatalyzed reactions. This is to be expected if reaction [4] plays an important role in the catalysis. Similarly, the reduction in the influence of catalysis with the increase in the partial pressure of CO (Figure 2(b)) is in agreement with the fact that reaction [2] also plays an important role in the catalysis.

The intercalation mechanism⁷ consists of the following steps:



It is known⁹ that the intercalation compound (C_{64}Na) is unstable in the presence of a small amount of CO_2 and reaction [7] is not the slowest reaction step in the catalysis. Since both the partial pressures of CO and CO_2 influence the extent of catalysis significantly, the experimental data can be explained by this mechanism if reactions [5] and [8] are important in the catalysis.

According to the electrochemical mechanism^{8,10} molten Na_2CO_3 forms a thin layer of electrolyte over the carbon

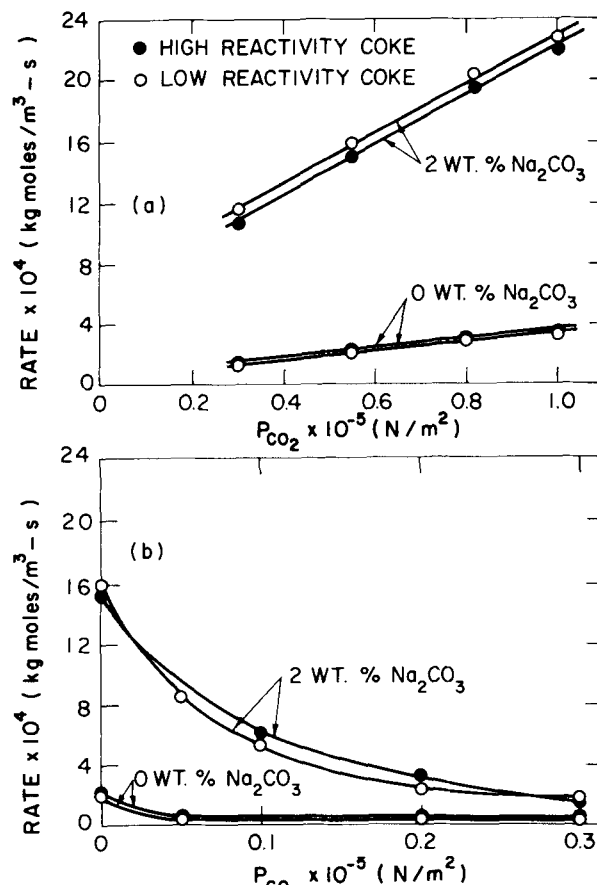
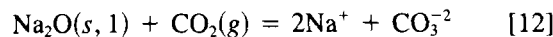
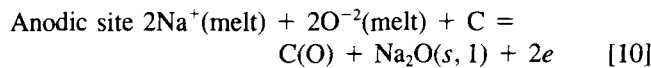
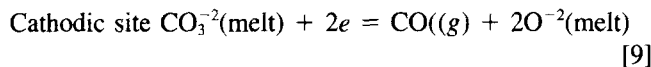


Fig. 2—(a) Effect of CO_2 on the extent of catalysis of low and high reactivity coke in absence of CO. (b) Effect of CO on the extent of catalysis of low and high reactivity coke ($P_{\text{CO}_2} = 0.55 \times 10^5 \text{ N/m}^2$).

surface and reactions occur at both gas/melt and melt/carbon interfaces.



Since both the partial pressures of CO and CO_2 affect the extent of catalysis, the experimental data are in agreement with the view that reaction [12] together with one or more of the reactions [9] and [11] influence the catalytic process significantly.

The experimental data can be explained on the basis of any one of the mechanisms discussed here. Furthermore, catalysis can also result due to any combination of the three mechanistic schemes discussed here. However, irrespective of the mechanistic scheme the following conclusions can be drawn from this study:

(a) The rate of the catalytic reaction is controlled by more than one of the several constituent steps involved in any mechanistic scheme.

(b) One of the slower steps in the catalysis is the regeneration of the Na_2CO_3 catalyst.

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The Law of Additive Reaction Times Applied to the Hydrogen Reduction of Porous Nickel-Oxide Pellets

H. Y. SOHN and DAESOO KIM

Until recently, the models for the reaction of a porous solid with a fluid have, for conceptual simplicity, generally assumed the solid to be made up of grains with a well-defined, basic geometry, namely that of a flat plate, a long cylinder, or a sphere. Furthermore, the grains have been assumed to react according to the shrinking-core model.^{1,2}

Sohn^{3,4} extended this grain model to incorporate other types of kinetics for the solid. This study showed that the following approximate solution obtained for the earlier idealized version of the grain model^{5,6} is very likely to remain valid regardless of the type of rate dependence on the amount of solid reactant remaining unreacted:

Time required to attain a certain conversion	Time required to attain the same conversion if the intrapellet diffusion were infinitely fast	+	Time required to attain the same conversion if the reaction of individual grains were infinitely fast (rate control by product-layer diffusion)
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[1]

This relationship is valid for an isothermal fluid-solid reaction in which a coherent layer of solid product is formed and the effective diffusivity remains unchanged.

The reactions of many finely-sized solid particles follow the nucleation and growth kinetics characterized by

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Manuscript submitted August 29, 1983.

S-shaped conversion-vs-time relationships.^{7,8,9} The experimental data for the hydrogen reduction of nickel oxide exhibit this characteristic.^{10,11,12}

A simplified form of the nucleation and growth kinetics attributed to Erofeev⁷ is as follows:

$$[-\ln(1-x)]^{1/n} = bk_N C_{Ab} t \quad [2]$$

Incorporating this kinetics expression, Eq. [1] can be written as³

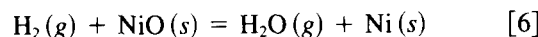
$$t_N^* = [-\ln(1-x)]^{1/n} + \hat{\sigma}_N^2 \cdot p_{Fp}(x) \quad [3]$$

where

$$t_N^* \equiv bk_N C_{Ab} t \quad [4]$$

$$\hat{\sigma}_N = \frac{V_p}{A_p} \sqrt{\frac{F_p k_N \alpha_B \rho_B}{2D_e}} \quad [5]$$

It is the purpose of this communication to present the results of applying Eq. [3] to the experimental data of the hydrogen reduction of porous nickel-oxide pellets reported previously.¹⁰ The reaction can be expressed as



The data reported therein are most suitable for the stated purpose because experiments were carried out to obtain separately information on intrinsic kinetics and on effective diffusivity, as required for the application of Eq. [1]. Data were also taken in the intermediate regime. In the original paper, the intrinsic kinetics of the reaction of the grains were interpreted based on the shrinking-core scheme for a long cylinder. Since the shrinking-core model does not yield an S-shaped conversion curve, the leading tail at low conversions representing the induction period had to be replaced by an induction time obtained by extrapolating the portion of the curve for higher conversions to zero conversion.

We have reinterpreted these intrinsic data using Eq. [2]. This equation allows the inclusion of both the low- and high-conversion regions of the conversion curve, which could not be done using the shrinking-core equation.¹⁰ The determination of the intrinsic rate parameters based on Eq. [2], by eliminating the mass transfer effects, closely follows the procedure described in Reference 10. A typical example is shown in Figure 1(a), which has been obtained by replotting the data of Figure 5(a) in Reference 10. It is seen that a much better representation of the entire range of conversion is obtained by the use of Eq. [2] in lieu of the shrinking-core model. The intercepts of these lines with $\ln t = 0$ axis yield the apparent values (including small effects of diffusion) of $bk_N C_{Ab}$, and the slopes give the values of n . The intrinsic values of $bk_N C_{Ab}$ unaffected by diffusion can be obtained by plotting the apparent values against R_p^2 and extrapolating to zero thickness. The theoretical basis of this extrapolation procedure is given in References 5 and 10. Figure 1(b) illustrates this. The value of n remained quite constant (=2.804 to 2.856) at this fixed temperature for thin pellets of various thicknesses; thus, an average of these n values was used for the case of $R_p = 0$.

From the values of $bk_N C_{Ab}$, k_N can be computed because C_{Ab} is known from the experimental conditions ($p_{\text{H}_2} = 1$ atm) and the stoichiometry coefficient b is unity for this system. Using the values of k_N and n we can draw a straight line according to Eq. [2], which would correspond