

The Reduction of Nickel Oxide Disks with Carbon Monoxide

J. SZEKELY AND C. I. LIN

The purpose of this paper is to report experimental measurements on the rate of nickel oxide reduction with carbon monoxide over the temperature range 847 to 1099°C. The main motivation for the work was provided by the need for kinetic information in this temperature range in conjunction with an investigation aimed at the study of the reaction between solid nickel oxide and solid carbon, where the gaseous reduction step could be a component of the overall reaction scheme.¹ While the reaction between NiO and CO has been studied, at temperatures below 796°C,²⁻⁸ the behavior of this system at higher temperatures has not yet been investigated.

The apparatus was so constructed that nickel oxide disks, suspended from one arm of a recording balance in a wire mesh basket, could be reacted with a stream of carbon monoxide at controlled temperatures. The gas flow rate was fast enough that external mass transfer was not rate limiting and the progress of the reaction was monitored by recording the weight change of the sample. Further details of this standard experimental arrangement are available elsewhere.¹

The carbon monoxide used was CP grade, supplied by the Union Carbide Corporation; the nickel oxide was Fisher certified grade. The mean diameter of the nickel oxide powder, as determined by X-ray diffraction¹ was 0.102 μ and the true density was 6.88 g/cm³. The nickel oxide was reacted in the form of circular disks, 28.58 mm in diam, the thickness of which varied from 1.8 mm to 2.6 mm. The initial porosity of the unsintered pellets was ranged from 0.474 to 0.518. The actual experimental procedure was similar to that reported in earlier papers dealing with gas-solid reactions.⁹

The sample was brought to the reaction temperature in a helium stream and then the solid disk was allowed to react with carbon monoxide until the reaction was completed. In a typical run the preparatory stage took some 2 to 3 h, while the reaction itself was completed in about 3 to 7 min, depending on the experimental conditions. After the completion of the reaction the solid product was examined and no evidence was found of carbon deposition.

In measurements involving gas-solid reactions it is customary to determine the chemical rate constant by conducting experiments under such conditions that neither external mass transfer nor pore diffusion play a role in determining the overall rate.⁹ In the present study, the resistance due to external mass transfer could be eliminated by using a gas flow rate in excess

of 16,000 cc/min as is illustrated in Fig. 1. The effect of pore diffusion was difficult to eliminate in spite of very thin pellet used. For this reason, the chemical rate constant was deduced from the measurements of the initial rate, when the contribution of pore diffusion was at its minimum.

The interpretation of the rate data was carried out using the grain model.^{9,10} If we assume first order reaction, slablike geometry for the disk (which is reasonable, because of the small value of the ratio: thickness/diameter) and postulate, furthermore, that the grains are spherical in shape, the conservation equations describing the system may be written as:

$$De_{CO} = \frac{d^2 C_{CO}}{dR^2} - \frac{3(1-\epsilon)k}{r_{NiO}} \left(\frac{r}{r_{NiO}} \right)^2 C_{CO} = 0. \quad [1]^*$$

*For the definition of the symbols see the nomenclature.

Since initially $r = r_{NiO}$, at the initial stage we may rewrite Eq. [1] in the following form:

$$\frac{d^2 C_{CO}}{dR^2} = \left(\frac{3(1-\epsilon)k}{De_{CO} r_{NiO}} \right) C_{CO}. \quad [2]$$

The conservation of the solid reactant is written as:

$$-\rho_{NiO} \frac{dr}{dt} = k C_{CO}. \quad [3]$$

The initial and boundary conditions are given as:

$$\text{At } t = 0, r = r_{NiO}. \quad [4]$$

$$\text{At } R = R_p, C_{CO} = C_{CO_s}. \quad [5a]$$

$$\text{At } R = 0, \frac{dC_{CO}}{dR} = 0. \quad [5b]$$

In the interpretation of the measurements it is convenient to use ζ , the effectiveness factor, which is frequently employed in heterogeneous catalysis.¹² In essence the effectiveness factor designates the fraction of the total surface area within the porous solid which participates in the reaction. When the overall rate is chemically controlled, $\zeta = 1$; when diffusion contributes to the overall resistance, $\zeta < 1$.

It was found that the value of $\hat{\sigma}$, gas-solid reaction modulus,

$$\hat{\sigma} \equiv R_p \sqrt{\frac{(1-\epsilon)k}{2De_{CO} r_{NiO}}} \quad [6]$$

plays an important role in determining the controlling rate mechanism.¹¹ When $\hat{\sigma} < 0.3$ the reaction is largely chemically controlled; when $\hat{\sigma} > 3$, the overall rate is largely diffusion controlled.

It is seen in Fig. 6.7 of Ref. 12 that when $\zeta < 1/2$, its value may be approximated by the following relationship:

$$\zeta = \frac{1}{\sqrt{6} \hat{\sigma}} \quad [7a]$$

$$\zeta = \frac{1}{R_p} \left(\frac{r_{NiO} De_{CO}}{3(1-\epsilon)k} \right)^{1/2}. \quad [7b]$$

Upon recalling that in the chemically controlled regime the extent of reaction is related to time by the

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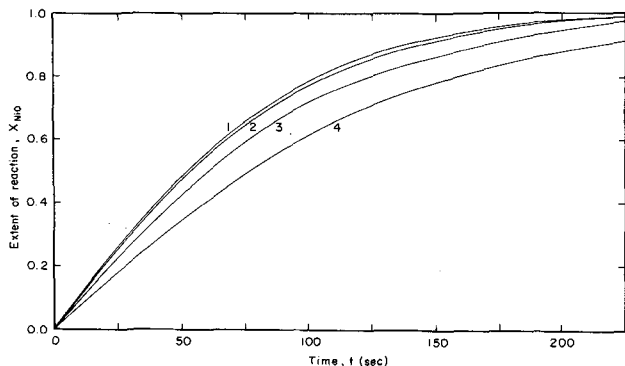


Fig. 1—Conversion vs reaction time. The effect of gas flow rate. Notation:

| Curve Number | Gas Flow Rate cm ³ /min |
|--------------|---------------------------------------|
| 1 | 16,000 |
| 2 | 20,000 |
| 3 | 10,000 |
| 4 | 5,000 |

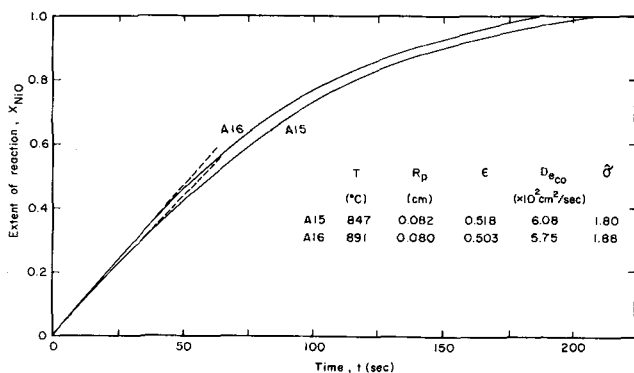


Fig. 2—Conversion vs reaction time.

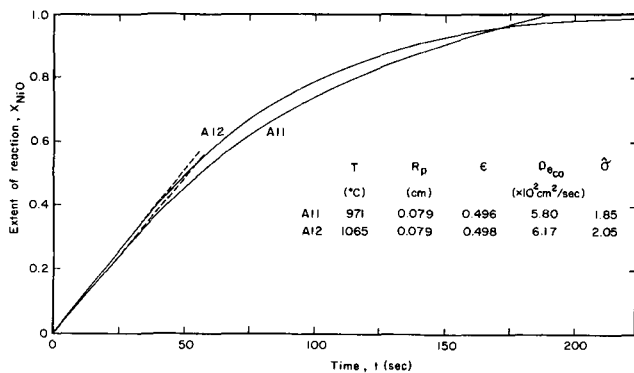


Fig. 3—Conversion vs reaction time.

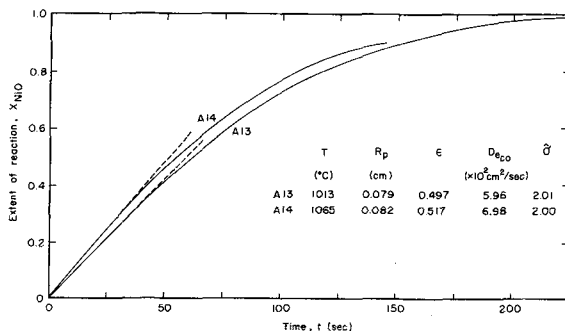


Fig. 4—Conversion vs reaction time.

following expression:¹⁰

$$X = 1 - \left(1 - \frac{k C_{CO_s}}{\rho_{NiO} r_{NiO}} t \right)^3 \quad [8]$$

and that the effectiveness factor may also be expressed in terms of the experimental data, viz:

$$\zeta = \frac{\frac{dX}{dt} \Big|_{t=0, \text{observed}}}{\frac{dX}{dt} \Big|_{t=0, C_{CO} = C_{CO_s}}} \quad [9]$$

after some manipulation we obtain the following expression for the reaction rate constant, in terms of the experimentally determined initial rate:

$$k = \left[\frac{\frac{dX}{dt} \Big|_{t=0, \text{observed}}}{\left(\frac{1}{\rho_{NiO} R_p} \right)} \right]^2 \times \left[\frac{r_{NiO} (1 - \epsilon)}{3 C_{CO_s}^2 D_{eCO}} \right] \quad [10]$$

For a given application, all the terms appearing in Eq. [10] are known, except for D_{eCO} , the effective diffusivity. The method of estimating the value of D_{eCO} is similar to that discussed in Ref. 9 except that the tortuosity was assumed to be equal to the reciprocal of porosity.

Figs. 2 to 4 show typical plots of the extent of reaction against time. To calculate the extent of reaction, the following equation was employed.

$$X_{NiO} = \frac{\text{Measured weight loss at time } t}{\text{Theoretical total weight loss}} \quad [11]$$

It is seen in the captions that the gas-solid reaction

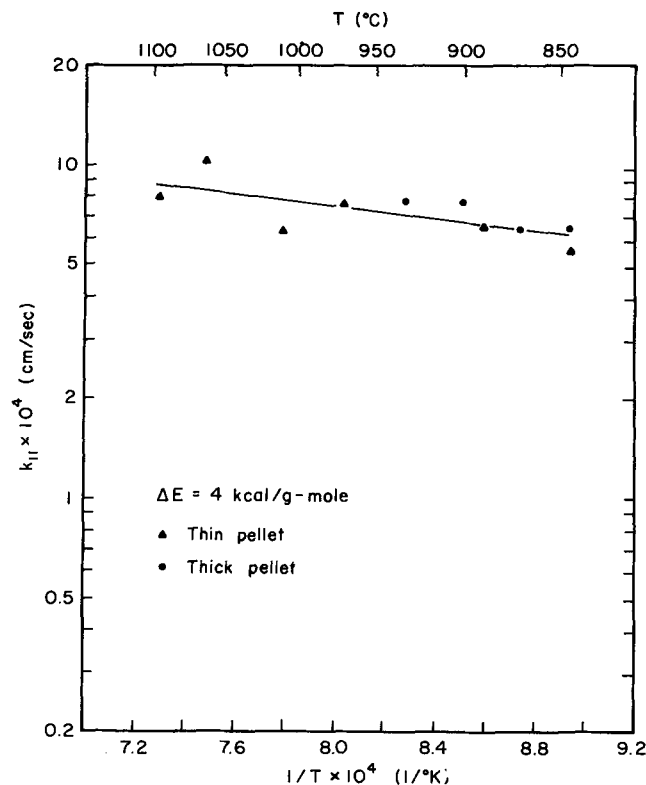


Fig. 5—Temperature dependence of the rate constant of the reaction of nickel oxide with carbon monoxide.

modulus was larger than 1.8 in all cases, which indicates that pore diffusion would play an important role in the (complete) reaction for the experimental conditions.

Fig. 5 shows an Arrhenius plot of the reaction rate constant deduced from the measurements, which indicates an appreciable scatter. The apparent activation energy is seen to be quite small, of the order of about 4 Kcal/g mole. This finding seems consistent with that reported by Krasuk and Smith³ who found a zero activation energy for the same reaction over the temperature range 682 to 796°C.

NOMENCLATURE

| | |
|----------------|--|
| A_{NiO}, A_p | Surface areas of nickel oxide grain and pellet, respectively, cm^2 |
| C_{CO} | Molar concentration of carbon monoxide, g-mole/ cm^3 |
| C_{CO_s} | Molar concentration of carbon monoxide at pellet surface, g-mole/ cm^3 |
| De_{CO} | Effective diffusivity of carbon monoxide, cm^2/s |
| F_{NiO}, F_p | Shape factors of nickel oxide grain and pellet, respectively |
| k | Reaction rate constant, cm/s |
| R | Pellet coordinate, cm |
| R_p | Pellet half-thickness, cm |
| r | Grain coordinate, cm |
| r_{NiO} | Grain radius of nickel oxide, cm |
| V_{NiO}, V_p | Volume of nickel oxide grain and pellet, respectively, cm^3 |
| t | Reaction time, s |
| X | Extent of reaction. |

GREEK LETTERS

| | |
|--------------|---|
| ϵ | Porosity |
| ζ | Effectiveness factor, defined in Eqs. [7a] and [7b] |
| ρ_{NiO} | Density of nickel oxide, mole/ cm^3 |
| δ | Gas-solid reaction modulus, defined in Eq. [6]. |

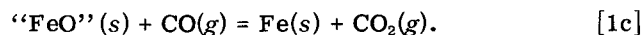
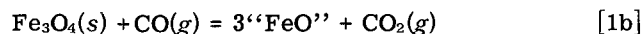
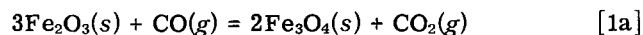
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Reactions Between Particulate Solids: Viscous Flow and Knudsen Diffusion

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Reactions between solid oxide particles and carbonaceous material underlie the direct reduction processes for iron-making and the carbothermic reduction process for the manufacture of zinc. Careful studies of the mechanism have established that the reduction of oxide particles by solid carbon occurs, for the most part, via gaseous intermediates CO and CO₂. The reduction of hematite by carbon proceeds in three successive stages.



The gasification of carbon particles by the internally generated CO₂ gas proceeds simultaneously but at a relatively lesser speed as compared to Reactions [1a] to [1c].



Reaction [2] restores the reduction potential of the gas-phase.

The "chemical kinetic" model due to Sohn and Szekely¹ and the "physicochemical" model formulated by Rao² have been applied with varying degrees of success to the interpretation of available data on the kinetics of reduction in the Fe₂O₃ + 3C system. The present communication reports a modified "physicochemical" model which considers i) heterogeneous Reactions [1] and [2]; ii) Knudsen diffusion and iii) the viscous flow of gases, all of these occurring simultaneously within a compact of iron oxide and carbon. One of the objectives of this work has been to demonstrate the significant effect of viscous flow of gaseous species on the pressure profiles of CO₂ within the compact. The mass-transfer of gases CO and CO₂ through the pores of the compact is expressed by the Kozeny-Carman law.^{3,4} Assuming that the diffusivities of CO and CO₂ are nearly equal,

$$-J_{CO} = \frac{B_1(1+K)}{RT} \left[\frac{\partial P_{CO}^2}{\partial Z} \right] + \frac{D_K}{RT} \left[\frac{\partial P_{CO}}{\partial Z} \right] \quad [3a]$$

and

$$-J_{CO_2} = \frac{B_1(1+K)}{RTK} \left[\frac{\partial P_{CO_2}^2}{\partial Z} \right] + \frac{D_K}{RT} \left[\frac{\partial P_{CO_2}}{\partial Z} \right]. \quad [3b]$$

Mass balances for CO and CO₂ provide the following relationships.^{2,4}

$$\frac{B_1(1+K)}{RT} \left[\frac{\partial^2 P_{CO}^2}{\partial Z^2} \right] + \frac{D_K}{RT} \left[\frac{\partial^2 P_{CO}}{\partial Z^2} \right]$$

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