

was also applied to the results of Fraser *et al.*² for nickel, again taking χ in their experiments to be 1.33. This decreased their surface tension value of ~ 1960 dynes/cm to ~ 1790 dynes/cm at the melting point. For comparison purposes, the data listed by Lang⁵ for nickel at its melting temperature are in the range 1700 to 1820 dynes/cm. Once again the corrected results are in line with the data obtained by static methods, and again the levitation result lies near the upper bound of the data.

Summary. It has been demonstrated that the levitation method for surface tension measurement using oscillating droplets can yield results which are in agreement with existing data obtained by other methods. However, the levitation results are very sensitive to oscillation amplitude, as well as to other factors discussed in Ref. 6, and these factors, if left unaccounted for, can lead to anomalously high values of γ in metals. Based on measurements with liquid copper, an amplitude correction factor has been proposed, which, when applied to levitation data in the literature for iron and nickel, brings the high, apparent values of γ down to the range of presently accepted results obtained by static methods. More work is required both to verify the variation of B with χ in copper, as well as to measure B for other metals, but the success of Eq. [5] in dealing with data for copper, iron, and nickel suggests

that this approximate relationship is reasonably valid. Finally, it is worth restating that the levitation values for γ , even after correction for amplitude effects, still lie near the upper limits of the surface tension data in the literature. This may imply either that a small additional correction is called for, or that the levitation technique leads to the production of extraordinarily clean surfaces.

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The Reduction of Wustite Disks with Carbon Monoxide Over the Temperature Range 573 to 845°C

J. SZEKELY AND C. KARATAS

The purpose of this communication is to report experimental measurements on the rate of wustite reduction with carbon monoxide. The main motivation for this work was the need for kinetic information on this reaction in a study of the reaction between wustite and carbon, where the gaseous reduction step could be a component of the overall reaction scheme.

While the reduction of hematite with carbon monoxide has received a great deal of attention,¹⁻³ little work has been reported on the kinetics of wustite reduction. The activation energies found ranged from about 13 kcal/g mole to 37 kcal/g mole. These earlier workers used shrinking core type models for representing their measurements and one may well question the reliability of the rate constants thus obtained.⁴⁻⁷

In the present work, the apparatus was so constructed that wustite disks, suspended from a recording balance, could be reacted with a stream of carbon monoxide at controlled temperatures.⁸ The gas flow

rate was high enough so that external mass transfer was not rate controlling.

The carbon monoxide used was CP grade, with a minimum purity of 99.3 pct, supplied by the Union Carbide Corporation, Linde Division.

The wustite was prepared by reacting magnetite powder, supplied by the Fisher Scientific Co., with a gas mixture consisting of analytical grade 50 pct CO and 50 pct CO₂, at 900°C. The chemical formula of the wustite thus produced was determined, using a method recommended by the U.S. Bureau of Mines,⁹ as Fe_{0.923}O. This value was confirmed independently by both the weight loss in sample preparation, and by the weight loss in the subsequent reaction of the wustite thus produced.

The grain size of the wustite particles thus made was determined using a Quantimet TV Analysing Computer from the Union Carbide Corporation, Metals Division, of Niagara Falls, New York. The mean value obtained for the grain size was 3.52 μm , which was consistent with the values deduced from the examination of the scanning electronmicrographs. The true (skeletal) density of the wustite thus produced was 5.64 g/cm³, as obtained from its composition.¹⁰

The wustite powder was compressed at a pressure of about 700 atm into cylindrical disks, 28.58 mm in diam, with a half thickness of about 0.8 mm. The mean value of the porosity of these disks was about 0.38.

In a typical run, the solid sample was brought to the reaction temperature in a nitrogen stream and was then allowed to react with the carbon monoxide until the reaction was completed. This latter stage usually took some 5 to 15 min.

In kinetic studies, it is customary to perform ex-

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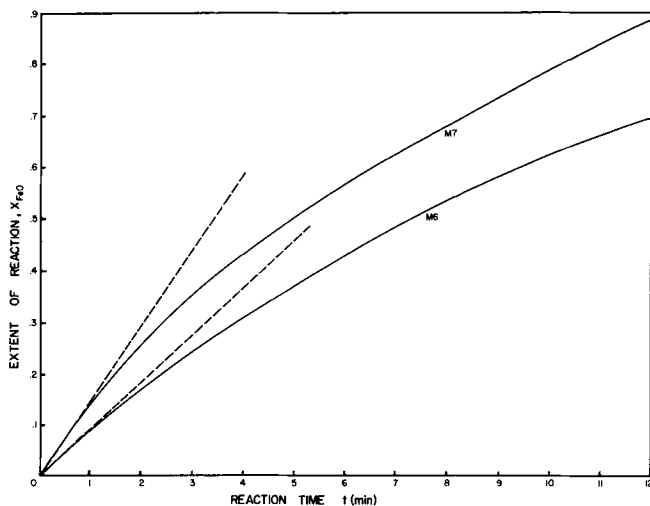


Fig. 1—Plots of the extent of reaction of the pellets *vs* time at 573 and 656°C.

periments such that both the resistances associated with external mass transfer and with pore diffusion are eliminated. In the present case, the effect of external mass transfer could be eliminated by using high enough gas flow rates (in excess of 16,000 cm³/min), giving a pellet Reynolds number of about 85 at 900°C. However, the effect of pore diffusion was difficult to eliminate, even by using very thin pellets. For this reason, the chemical reaction rate constant was deduced from the initial rate measurements, when the contribution from pore diffusion was at its minimum.

The reaction between wustite and carbon monoxide is reversible, with a standard free energy change of:

$$\Delta G^\circ = -4300 + 5.24 T \text{ (Ref. 11)*}$$

*This expression provides a better agreement with the experimental measurements obtained in this investigation and also by Darken¹⁶ than does the alternative relationship cited by Kubaschewski *et al.*¹⁷.

Figure 1 shows a plot of the extent of reaction against time for two typical runs, together with the tangents drawn at $t = 0$, which denote the initial rates. Key parameters characterizing a selection of the experimental runs are summarized in Table I.

While the equilibrium conditions would have allowed carbon deposition due to the decomposition of CO, in fact, no carbon deposition was found until the reaction approached completion. The absence of carbon deposition in the initial stages was confirmed by independent X-ray diffraction measurements, and by the scanning electromicrographs of the partially reacted specimens. Furthermore, even at 50 pct reduction, the

measured weight loss agreed within 3 to 5 pct of the values found by chemical analysis of the partially reacted specimen.

This absence of carbon deposition is consistent with findings reported by Turkdogan,¹ Osman *et al.*,² and by Krasuk and Smith¹⁸ and Szekely and Lin,¹⁹ the latter two for the reduction of nickel oxide with CO. Since only the initial rates were used in the interpretation of the data, the effect of carbon deposition was not taken into account in the analysis.

In the interpretation of the measurements, we shall use the grain model.^{12,13} If we assume isothermal behavior, slab-like geometry for the pellet (which is reasonable, because of the small value of the ratio: thickness per diameter) and postulate that the grains are spherical, the conservation of the gaseous reactant may be written as:

$$De_{CO} \frac{d^2 C_{CO}}{dR^2} - \frac{3(1-\epsilon)k}{r_{FeO}} \left(\frac{r}{r_{FeO}} \right)^2 \left(C_{CO} - \frac{C_{CO_2}}{K_E} \right) = 0. \quad [1]$$

The conservation of the solid reactant is given as:

$$-\rho_{FeO} \frac{dr}{dt} = k \left(C_{CO} - \frac{C_{CO_2}}{K_E} \right). \quad [2]$$

The boundary conditions are:

$$r = r_{FeO} \quad \text{at } t = 0 \quad [3]$$

$$C_{CO} = C_{CO_s} \quad \text{at } R = R_P \quad [4]$$

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

In the analysis of gas-solid reaction systems, it was found that $\hat{\sigma}$, the gas-solid reaction modulus, plays an important role.

$$\hat{\sigma} = R_P \sqrt{\frac{(1-\epsilon)k}{2De_{CO}r_{FeO}} \left(1 + \frac{1}{K_E} \right)}. \quad [6]$$

When $\hat{\sigma} < 0.3$ the overall rate is chemically controlled, and when $\hat{\sigma} > 3$ the overall rate is controlled by pore diffusion.¹³

In the very initial stages, when the grain size has not altered appreciably, the solution of Eq. [1] may be approximated by:

$$C_{CO}(R) \approx C_{CO_s} \frac{\cosh \left(\sqrt{6} \frac{R}{R_P} \frac{r}{r_{FeO}} \hat{\sigma} \right)}{\cosh \left(\sqrt{6} \hat{\sigma} \right)}. \quad [7]$$

Table I.

Experimental Number	T°C	$R_P \times 10^{-2}$, cm	Wt, gr	$De_{CO} \times 10^{-2}$, cm ² /s	$De_{CO_2} \times 10^{-2}$, cm ² /s	$\frac{dx}{dt} \Big _{t=0}$, (1/s) × 10 ⁻³ , observed	$\hat{\sigma}$	k , cm/s × 10 ⁻³	K_E
M12	845	8.80	2.874	12.34	11.30	3.508	1.33	5.332	0.496
M11	806	8.85	2.950	11.74	10.78	3.145	1.16	4.017	0.530
M10	752	8.80	2.392	10.90	10.05	2.860	0.99	2.963	0.590
M9	726	8.92	3.038	10.50	9.699	2.645	0.94	2.531	0.625
M8	701	8.95	2.540	10.11	9.358	2.518	0.87	2.197	0.660
M7	656	8.98	2.210	9.418	8.745	2.258	0.77	1.679	0.736
M6	573	8.89	1.700	8.143	7.612	1.501	0.52	0.756	0.925

Then the effectiveness factor, η , is given as:

$$\eta = \frac{1}{2R_P C_{CO_s} - R_P} \int_0^{R_P} C_{CO}(R) dR = \frac{\tanh(\sqrt{6} \hat{\sigma})}{\sqrt{6} \hat{\sigma}} \quad [8]$$

here

$$\eta = \frac{\text{surface area used for reaction}}{\text{total surface area within the porous reactant}} \quad [9]$$

In the chemically controlled regime, $\eta \approx 1$, but when pore diffusion controls, $\eta \ll 1$.

In the chemically controlled regime,

$$X = 1 - \left(1 - \frac{k(C_{CO_s} - \frac{C_{CO_2s}}{K_E})t}{\rho_{FeO} \cdot r_{FeO}} \right)^3 \quad [10]$$

The effectiveness factor may also be expressed in terms of the experimental data, *viz*:

$$\eta = \frac{\left. \frac{dx}{dt} \right|_{t=0, \text{observed}}}{\left. \frac{dx}{dt} \right|_{t=0, C_{CO} = C_{CO_s}}} = \frac{\left. \frac{dx}{dt} \right|_{t=0, \text{observed}}}{\frac{3k(C_{CO_s} - \frac{C_{CO_2s}}{K_E})}{\rho_{FeO} r_{FeO}}} \quad [11]$$

Upon combining Eqs. [8] and [11] and after some manipulation, we obtain the following expression:

$$\begin{aligned} [\tanh(\sqrt{6} \hat{\sigma}) \sqrt{k} = \frac{dx}{dt} \Big|_{t=0, \text{observed}} \cdot x] \\ \times R_P \left[\frac{1 - \epsilon}{De_{CO}} \left(1 + \frac{1}{K_E} \right) \right]^{1/2} \\ \times \rho_{FeO} \sqrt{r_{FeO}} / \sqrt{3} \left(C_{CO_s} - \frac{C_{CO_2s}}{K_E} \right) \end{aligned} \quad [12]$$

which has to be solved for k by trial and error.

For a given application, all the terms in Eq. [12] are known, except De_{CO} , which was calculated from the molecular diffusivities and the Knudsen component, using the "dusty gas" model and the Bosanquet interpolation formula.^{14,15} The tortuosity was assumed to be equal to the reciprocal of porosity.

As seen in Table I, $0.52 < \hat{\sigma} < 1.33$, indicating that under the experimental conditions, pore diffusion played an important role in the reaction.

Figure 2 shows an Arrhenius plot deduced from the measurements. The activation energy obtained (13 kcal/g mole) is very close to the result of Bicknese and Clark,⁶ who found a value of 13.9 kcal/g mole over the temperature range 980 to 1165°C.

We note that the activation energies reported for the reduction of hematite with CO range from about 8 to 10 kcal/g mole.^{2,3} Since the overall rate of reaction (in the chemically controlled regime) is thought to be limited by the rate of wustite reduction, the findings in the present paper are consistent with the earlier work. If, in these previous studies, no full allowance was made for the diffusional effects, then the resultant activation energies would have been lower than the intrinsic values, which may well be the case.

Figure 3 depicts a plot of the gas-solid reaction modulus $\hat{\sigma}$ against temperature. It is seen that $\hat{\sigma}$ tends

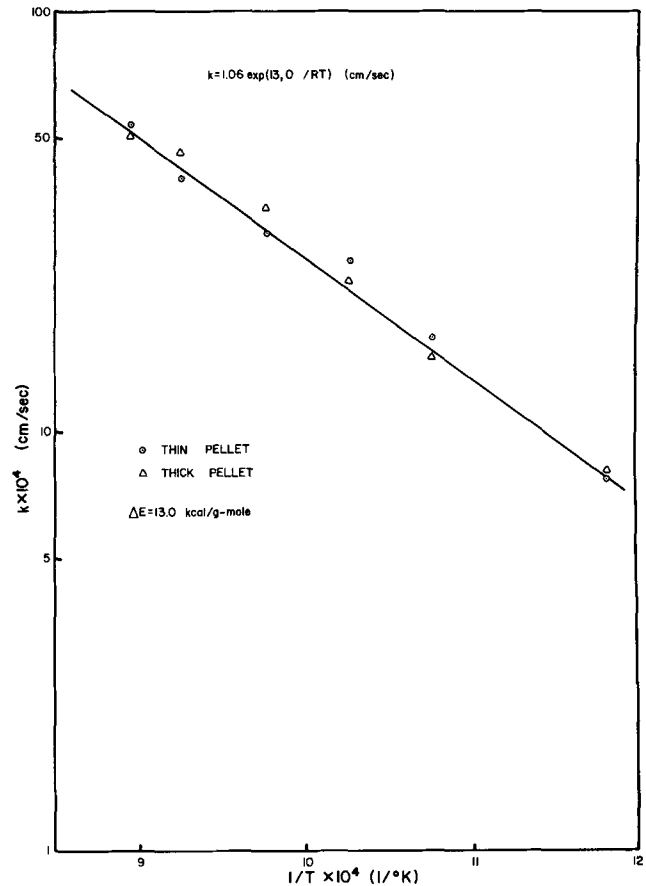


Fig. 2—Arrhenius plot of the intrinsic reaction rate constant k .

to increase with increasing temperature.

Finally, Fig. 4 shows a scanning electromicrograph of an unreacted wustite pellet, which indicates that the assumption of $F_P = 3$ (spherical pellets) was not unreasonable.

Nomenclature

C_{CO}, C_{CO_2}	Molar concentration of carbon monoxide and carbon dioxide, respectively, g mole/cm ³ ,
C_{CO}, C_{CO_2s}	molar concentration of carbon monoxide and carbon dioxide at pellet surface, respectively, g mole/cm ³ ,
De_{CO}	effective diffusivity of carbon monoxide, cm ² /s,
A_{FeO}	surface area of wustite grain, cm ² ,
V_{FeO}	volume of wustite grain, cm ³ ,
F_{FeO}	shape factor of wustite grain (= 3 for spheres),
k	reaction rate constant, cm/s,
R	pellet coordinate, cm,
R_P	pellet half-thickness, cm,
r	grain coordinate, cm,
r_{FeO}	grain radius of wustite, cm,
K_E	equilibrium constant,
t	reaction time, s,
T	temperature, K,
ΔG°	standard free energy change, cal/mole, and
X_{FeO}	extent of reaction.

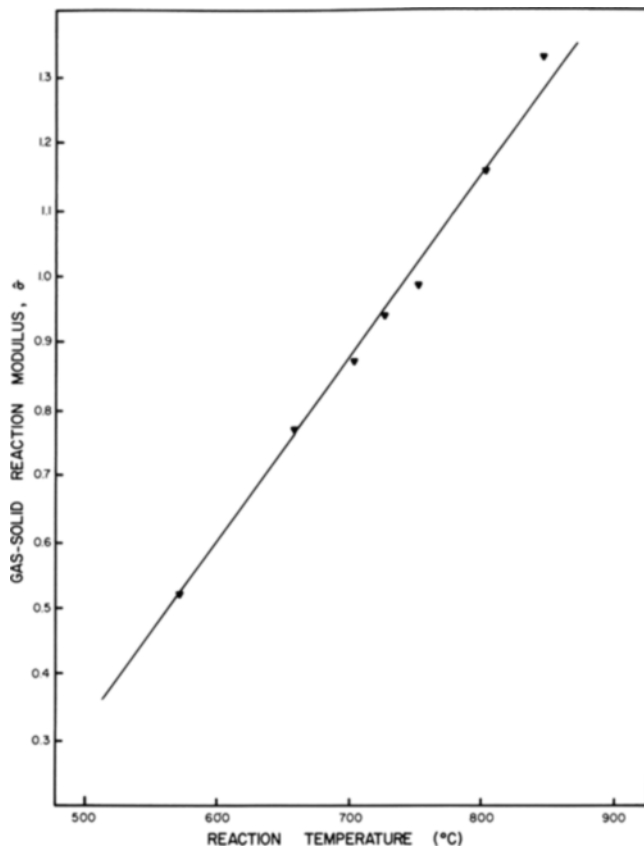


Fig. 3—Plot of gas-solid reaction modulus $\hat{\phi}$ vs reaction temperature.

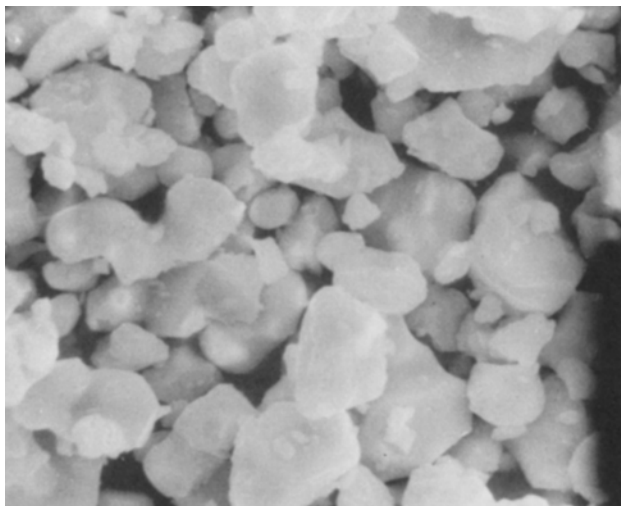


Fig. 4—Scanning electromicrograph of the unreacted wustite pellets at a magnification of 2370 times.

(Defines the ratio: $\frac{\text{Measured weight loss at time } t}{\text{theoretical total weight loss}}$).

Greek Letters

ϵ	Porosity,
η	effectiveness factor, defined in Eqs. [9] and [10],
ρ_{FeO}	density of wustite, mole/cm ³ , and
$\hat{\sigma}$	gas-solid reaction modulus, defined in Eq. [7].

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Inverse Segregation in Al-10 pct Cu

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Inverse segregation in Al-Cu alloys has been shown to occur as a result of enriched interdendritic flow toward the chill face due to volume shrinkage on cooling and solidification. Experimental observations of the solute concentration at the chill face have been shown to agree well with calculated values determined from a mathematical model of the process.^{1,2} Solute concentrations away from the interface also showed good agreement between experiment and model calculations.² The agreement between experiment and calculations appear to confirm the assumptions in the model and allow the model to be extended to other aspects of segregation.³

Solute segregation resulting from inverse segregation is difficult to measure. This is due to exudations on the surface; the small increase in concentration which occurs; the short distances at the chill face involved, and the microsegregation which is also present in the same region. The purpose of the present investigation was to repeat the measurements on Al-10 pct Cu alloy, the alloy giving the largest segregation at the chill face, using radioactive tracer techniques. With these techniques it was hoped to obtain more

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