Interfacial Rates of Reaction of CO_2 with Liquid Iron Silicates, Silica-Saturated Manganese Silicates, and Some Calcium Iron Silicates

S. K. EL-RAHAIBY, Y. SASAKI, D. R. GASKELL, and G. R. BELTON

Measurements of the rates of dissociation of CO_2 have been made by the $^{14}CO_2$-CO isotope exchange technique on liquid iron silicates, calcium iron silicates, and silica-saturated manganese silicates as functions of temperature and imposed equilibrium CO_2/CO ratio. It is shown that the rates of reduction of the liquid iron silicates and an iron oxide-rich slag in CO-CO_2 atmospheres are consistent with the rates of isotope exchange, indicating a common rate determining step. The dependences of the apparent first order rate constant on the oxygen activity for the dissociation of CO_2 on silica-saturated iron silicates and an equimolar "FeO"-CaO-SiO_2 melt are found to be closely consistent with the ability to transfer two charges to the adsorbing or dissociating CO_2 molecule, as was previously found for liquid iron oxide and lime-saturated calcium ferrites. Apparent rate constants at fixed oxygen activity are found to increase generally with the basicities of the melts.

I. INTRODUCTION

In a recent paper,[1] an experimental technique was described for the measurement of the rate of the $^{14}CO_2$-CO isotope exchange reaction on oxide melts held as thin films on an inductively heated platinum susceptor. Values for the apparent first order rate constant for the dissociation of CO_2, k_a, were obtained for reaction with liquid iron oxides and CaO-saturated calcium ferrites at temperatures from near the melting points to about 1550 °C under conditions where the melts were in *chemical* equilibrium with the gas. For both melts, k_a was found to be essentially inversely proportional to the value of the CO_2/CO ratio of the gas over the range of values studied ($\sim$0.4 to 12). Thus, within the limits of the experimental scatter, rates were given by the expression:

$$v = k_a pCO_2 = k_a^\circ pCO_2(pCO_2/pCO)^{-1} \qquad [1]$$

where k_a° is a temperature dependent constant for each melt.

For dissociation of CO_2 as the rate determining step, it was shown that the rates of oxidation (or reduction) of these melts in CO_2-CO atmospheres should be given by the simple expression:

$$v = k_a^\circ(pCO_2 a_O^{-1} - pCO) \qquad [2]$$

where a_O is the oxygen activity of the melt, expressed as the CO_2/CO ratio which would be in equilibrium with the melt, and k_a° is the rate constant for the dissociation of CO_2 on the particular melt at $a_O = 1$. It was shown that values of k_a° which were derived from the isotope exchange experiments were in excellent accord with data[2] for the rates of reduction of liquid droplets of iron oxide in CO. Calculated values of the rate of oxidation of CaO-saturated liquid calcium ferrites, extrapolated beyond the range covered by the experiments, were shown to be in reasonably good agreement with rates of oxidation of high CaO content calcium ferrites measured by Strachan and Grieveson.[3]

New results[14] which have become available on the rates of reduction of liquid iron oxides in CO and CO-CO_2 mixtures have been shown elsewhere[4] to be in close agreement with the isotope exchange results and the form of Eq. [2]. Similarly, new measurements of the rates of reduction of unsaturated calcium ferrites have been shown[4] to be in accord with interpolated rates from the isotope exchange studies.

Correlation of the behavior represented by Eq. [1] with the probable variation in surface constitution with oxygen activity deduced from available surface tension studies[5,6] proved inconclusive. It was suggested that the inverse dependence of the apparent first order rate constant on the oxygen activity arises from the need to transfer two electrons to the adsorbing CO_2 molecule or to an activated complex which contains one molecule of CO_2. Thus, if the rate determining step is *formally* represented by:

$$CO_2^{2-}(ad) \rightarrow CO(g) + O^{2-} \qquad [3]$$

the surface concentration of CO_2^{2-}, $\Gamma_{CO_2^{2-}}$, may be assumed to be given in terms of pCO_2 and the concentrations of electron donors and acceptors through virtual redox equilibria of the form:

$$CO_2(g) + 2Fe^{2+} = CO_2^{2-}(ad) + 2Fe^{3+} \qquad [4]$$

as

$$\Gamma_{CO_2^{2-}} = KpCO_2(Fe^{2+}/Fe^{3+})^2 \qquad [5]$$

where K is a temperature dependent constant for a given system, low surface coverage is assumed, and the redox couple is ideal.

The expected forward rate law would be:

$$v = kpCO_2(Fe^{2+}/Fe^{3+})^2 \qquad [6]$$

where k is a rate constant. For the liquid iron oxide and CaO-saturated calcium ferrites, it was shown that the avail-

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Manuscript submitted August 28, 1985.

able equilibrium data[7,8,9] were in close accord with the relationship:

$$(Fe^{3+}/Fe^{2+})^2 \propto pCO_2/pCO \qquad [7]$$

over the range of conditions of the kinetic measurements. Substitution of Eq. [7] in Eq. [6] recovers the observed rate law, Eq. [1].

The principal aims of the present work were to extend the measurements to other systems relevant to metallurgical slags and to examine the effect of silica on both the value of the rate constant and the dependence of the rate constant on the state of oxidation of the melt. Accordingly, measurements have been made of the rate of the $^{14}CO_2$-CO exchange reaction on iron oxide-silica melts, silica-saturated manganese oxide melts, and some melts in the system SiO_2-CaO-"FeO".

II. EXPERIMENTAL DETAILS

The experimental arrangement and procedure were essentially identical to those described earlier.[1] In summary, a small sample ($\simeq$0.5 g) of slag was held as a molten film in a 13 mm diameter shallow well in an inductively heated Pt/Rh alloy susceptor which was held within a silica tube. A refractory containment tube was inserted into the well to prevent exposure of the Pt/Rh surface to the reaction gases which were passed to within 5 mm of the surface of the melt through a coaxially held alumina tube of about 3 mm ID. All tubes were held by an appropriate system of O-ring sealed end caps. Temperature measurement was by a noble metal thermocouple inserted in the susceptor.

All melts were equilibrated at temperature under a flowing CO_2-CO mixture of the desired composition for at least 30 minutes before $^{14}CO_2$ was introduced into the gas mixture without changing the CO_2/CO ratio. After at least a further 30 minutes, the flow of the reacted gas was diverted from waste to pass through a molecular sieve (Linde 13x) and Ascarite to strip out the CO_2. The CO was then oxidized to CO_2 over CuO at 300 °C.

As in the previous study,[1] two methods of counting the ^{14}C content of the initial or resulting CO_2 were used. The internal Geiger-Müller tube method[10,11] was used to count samples of CO_2 which were taken by freezing into gas bottles cooled by liquid nitrogen. Alternatively, CO_2 was absorbed from the gas stream into 0.2 ml of Carbo-Sorb II (an organic amine produced by United Technologies Packard). This was then dissolved in 10 ml of Scint-O aryl hydrocarbon scintillation cocktail (also United Technologies Packard) contained in a standard counting vial. Counting was then carried out in a model 4530 Tri-Carb liquid scintillation spectrometer. No systematic differences could be detected between results obtained by the two methods.

CaO was prepared by calcining reagent grade $CaCO_3$. "FeO" was prepared by melting reagent grade Fe_2O_3 in an iron crucible and quenching onto a steel plate. Samples of melts of the required compositions were prepared by premelting these and other reagent grade oxides in either silica (for SiO_2-saturated melts) or platinum crucibles and then quenching and crushing. Containment tubes were of fused quartz for the experiments with silica-saturated melts, lime for those with CaO-saturated melts, and yttria-stabilized zirconia, lime-stabilized zirconia, or single crystal sapphire for those with nominally unsaturated melts. The internal diameters of the tubes, which were freshly cut and ground for each experiment, varied between 0.95 and 1.08 cm.

III. RESULTS

As discussed earlier,[1] the overall isotope exchange reaction:

$$^{14}CO_2 + {}^{12}CO = {}^{14}CO + {}^{12}CO_2 \qquad [8]$$

may be supposed to occur by consecutive steps involving the dissociation and reforming of CO_2 molecules at the surface. Apparent first order rate constants (with respect to pCO_2) for the dissociation step are given by the following expression which does not depend on the detailed mechanism:[1,12]

$$k_a = \frac{\dot{V}}{ART}\frac{1}{1+B}\ln\left[\frac{1}{1 - N(1+B)/N'B}\right] \qquad [9]$$

where $\dot{V}$ is the total volume flowrate of the gas mixture exposed to an area A of the melt, B is the value of the CO_2/CO ratio, and N' and N are the counting rates of the ingoing CO_2 and the CO_2 which results from the conversion of CO after the reaction, respectively.

In the present work, values of N' were varied between about 2000 and 20,000 min^{-1} above background. Values for N were predominantly in the range 50 to 3000 min^{-1}. Experiments with silica-saturated calcium silicate melts at 1520 to 1570 °C at a CO_2/CO ratio of 1 and at flowrates typical of all the experiments gave no measurable exchange.

A. *Liquid Iron Silicates*

The dependence of the apparent rate constant on the applied CO_2/CO ratio for silica-saturated iron silicates was examined at 1240 and 1400 °C. Flowrates were within the range 200 to 300 ml min^{-1} (STP) for the measurements at 1400 °C and within the range 140 to 260 ml min^{-1} for the measurements at 1240 °C. Apparent rate constants, in units of mol cm^{-2} s^{-1} atm^{-1}, are presented as a function of the CO_2/CO ratio in logarithmic form in Figure 1.

Within the experimental scatter, the data are consistent with the represented slope of -1. Accordingly, as in the case of liquid iron oxide and liquid CaO-saturated calcium ferrites, we may write:

$$k_a = k_a^\circ (pCO_2/pCO)^{-1} \qquad [10]$$

where k_a° is a temperature dependent constant.

Results obtained as a function of temperature for a fixed CO_2/CO ratio of 0.85 are presented as the open circles in Figure 2. Values interpolated from the data of Figure 1 are shown as the closed circles. Taking all data into account, the best straight line is given by the equation:

$$\log k_a = -11100/T + 1.22 \qquad [11]$$

and values of k_a° would be given by the equation:

$$\log k_a^\circ = -11100/T + 1.15 \qquad [12]$$

Experiments with unsaturated iron silicates were carried out in the temperature range 1240 to 1480 °C at gas flowrates of 150 to 280 ml min^{-1} at a CO_2/CO ratio of approximately 1 (0.96 to 1.07). Both lime-stabilized and yttria-stabilized zirconia containment tubes were used. Neither

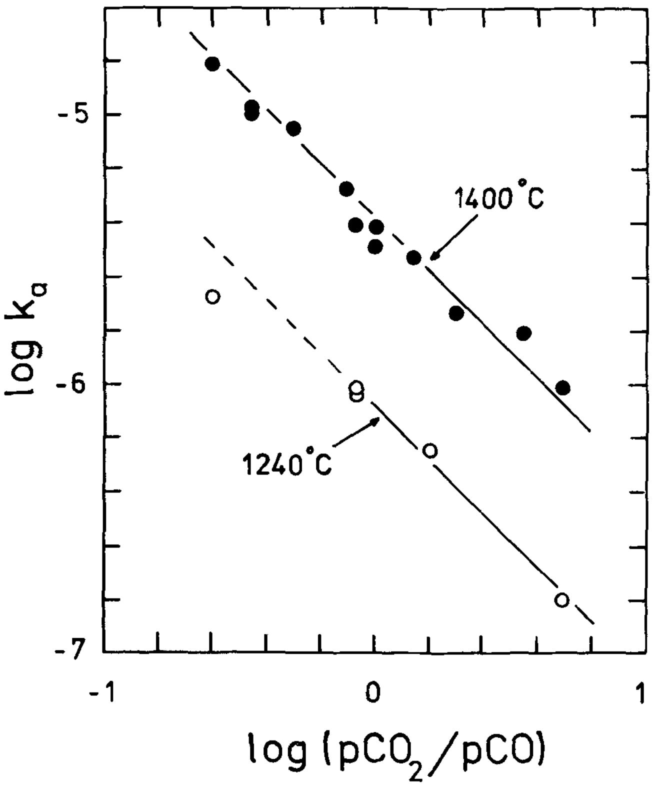

Fig. 1 — Apparent first order rate constants for the dissociation of CO_2 on SiO_2-saturated liquid iron silicates as a function of the equilibrium CO_2/CO ratio. Lines are drawn with a slope of -1.

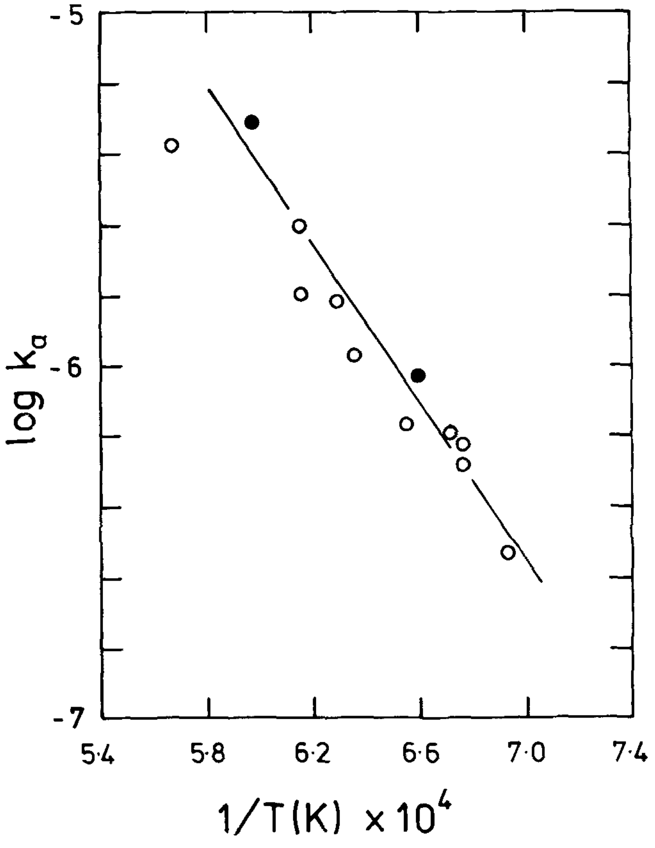

Fig. 2 — Arrhenius plot of the apparent rate constants for SiO_2-saturated liquid iron silicates at an equilibrium CO_2/CO ratio of 0.85.

showed obvious attack, and no effect of the type of tube on the results could be detected. Relationship [10] was assumed to hold and all the experimental data are presented as values of the apparent rate constant at unit CO_2/CO ratio, k_a°, in Figure 3. Best straight lines through the data are given by:

$$\log k_a^\circ = -7800/T - 0.45 \qquad [13]$$

for 10 wt pct (11.8 mol pct) SiO_2,

$$\log k_a^\circ = -8700/T - 0.03 \qquad [14]$$

for 20 wt pct (22.1 mol pct) SiO_2,

$$\log k_a^\circ = -10{,}200/T + 0.75 \qquad [15]$$

for 30 wt pct (34.0 mol pct) SiO_2, and

$$\log k_a^\circ = -9900/T + 0.49 \qquad [16]$$

for 36 wt pct (40.3 mol pct) SiO_2.

B. *Silica-Saturated Liquid Manganese Silicates*

The dependence of the apparent rate constant on the applied CO_2/CO ratio was examined for this system at 1500 °C and with gas flowrates in the range 280 to 320 ml min^{-1}. The results are presented in logarithmic form in Figure 4. Again, within the limits of the experimental scatter, the data are consistent with a slope of -1.

Results obtained as a function of temperature over the interval 1390 to 1560 °C at a fixed CO_2/CO ratio of 1 are presented in Figure 5. Values of k_a° are closely represented by the equation:

$$\log k_a^\circ = -7200/T - 0.93 \qquad [17]$$

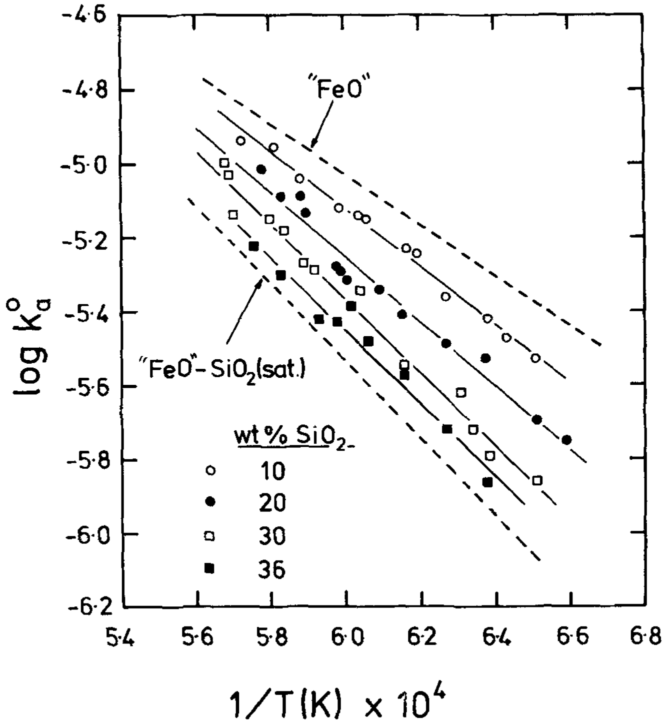

Fig. 3 — Arrhenius plot of the apparent rate constants for unsaturated liquid iron silicates at an equilibrium CO_2/CO ratio of 1.

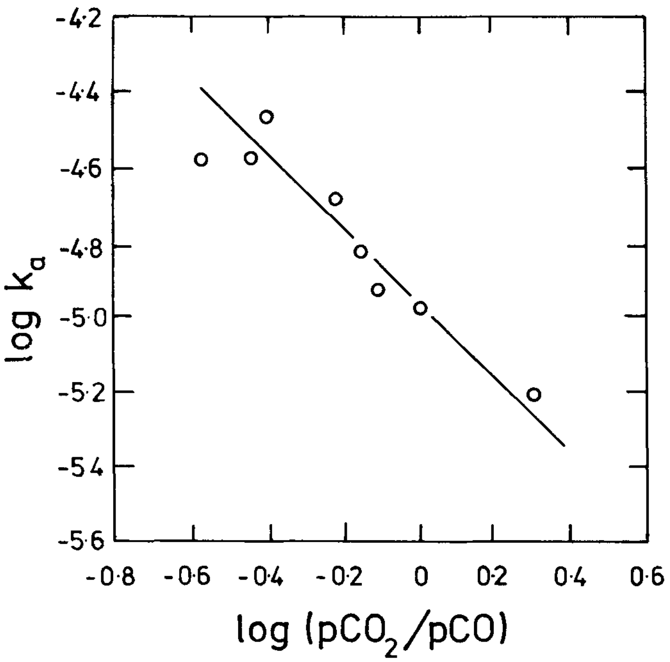

Fig. 4—Apparent rate constants as a function of the CO_2/CO ratio for SiO_2-saturated liquid manganese silicates at 1500 °C. The line is drawn with a slope of −1.

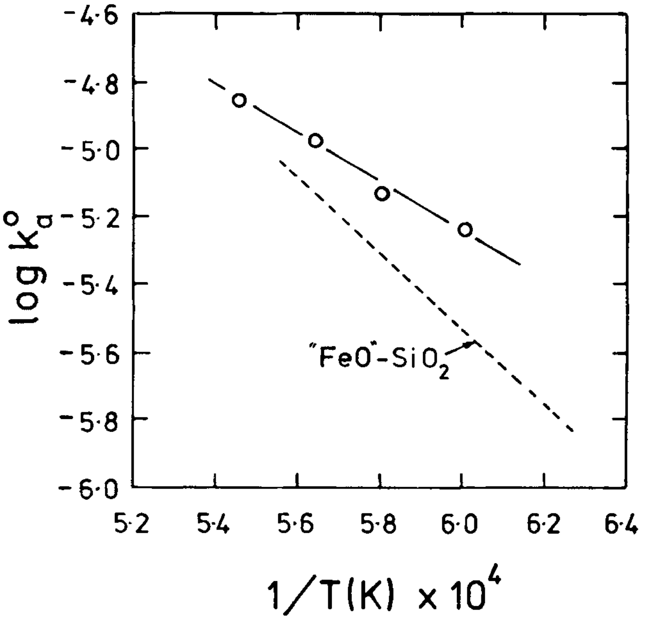

Fig. 5—Arrhenius plot of the apparent rate constants for SiO_2-saturated liquid manganese silicates at an equilibrium CO_2/CO ratio of 1.

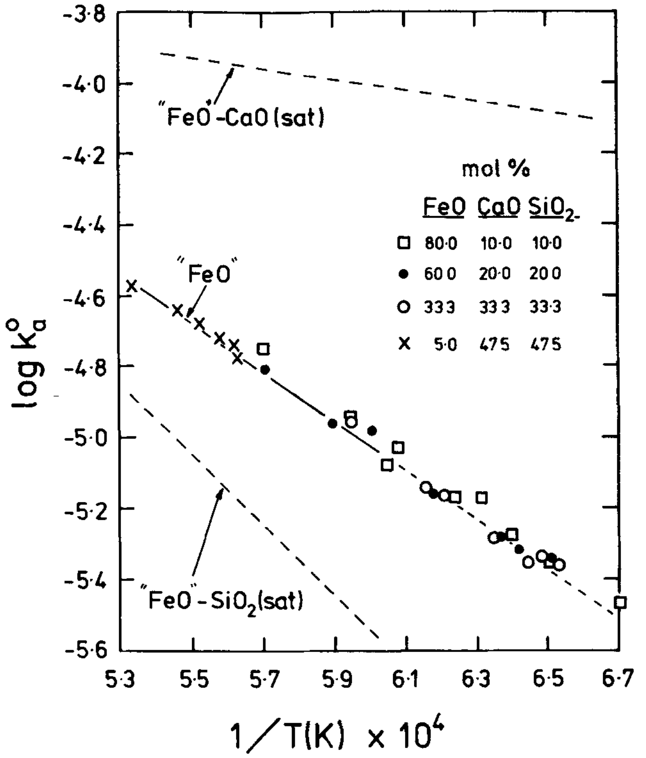

Fig. 6—Arrhenius plot of the apparent rate constants for pseudo ternary melts containing equal mole fractions of CaO and SiO_2 at an equilibrium CO_2/CO ratio of 1.

C. *Liquid Calcium Iron Silicates*

Four series of experiments were carried out on melts which initially contained 5 to 80 mol pct iron oxide and equal molar concentrations of CaO and SiO_2. Yttria-stabilized zirconia containment tubes were used, and these appeared to show no significant attack by the melts. Results for unit CO_2/CO ratio and gas flowrates of 250 to 340 ml min^{-1} are presented in Arrhenius form in Figure 6.

Surprisingly, the results show no resolvable dependence on composition and are in close accord with the previously obtained results for liquid iron oxide[1] which are indicated by the continuous line in Figure 6 and are closely described by the equation:

$$\log k_a^o = -6900/T - 0.88 \qquad [18]$$

At the average temperature of about 1400 °C, the rate constant for these melts is a factor of about 10 lower than that for lime-saturated calcium ferrites and a factor of about 3 higher than that for silica-saturated iron silicates.

Results obtained as a function of temperature for a melt containing 21 mol pct CaO and 57 mol pct SiO_2, using an yttria-stabilized zirconia and single crystal sapphire containment tubes, a gas flowrate of 450 to 480 ml min^{-1}, and a CO_2/CO ratio of 1 are shown in Figure 7. No effect of the containment tube is apparent and the data are closely represented by the equation:

$$\log k_a^o = -9600/T + 0.14 \qquad [19]$$

The apparent rate constants for this melt, which is near to silica-saturation, are close to those observed for the silica-saturated iron silicates.

Measurements at unit CO_2/CO ratio and at a gas flowrate of 360 ml min^{-1} were also made on a melt with the initial composition: 5 mol pct SiO_2, 45 mol pct CaO, and 50 mol pct FeO. This composition was chosen to lie in the small region where the liquid solution is the single phase at about 1450 °C between saturation by solid CaO and solid Ca_2SiO_4.[13] Since a lime containment tube was used, it is likely that the results refer to a CaO-saturated melt with an FeO/SiO_2 ratio of 10. Apparent first order rate constants were determined to be 1.3, 1.6, and 1.5 × 10^{-4} mol cm^{-2} s^{-1} atm^{-1} at 1450, 1515, and 1580 °C, respectively. These values are about 30 pct higher than the average values obtained for CaO-saturated liquid calcium ferrites[1] but lie within the experimental uncertainty.

Studies of the dependence of the apparent rate constant on the equilibrium CO_2/CO ratio were carried out on three "ternary" melts. Initial compositions in mol pct FeO, CaO, and SiO_2 were: 5.0, 47.5, 47.5; 1.0, 37.5, 61.5; and 33.3, 33.3, 33.3. Results obtained for the first two melts at 1520 °C with gas flowrates of 260 to 340 ml min^{-1} and using an yttria-stabilized zirconia containment tube are presented in logarithmic form in Figure 8. The best straight lines through the data give slopes of -0.86 and -0.84 with calculated uncertainties (two standard deviations) of about ± 0.09. However, particularly in the case of the 5 mol pct FeO melt, a slope of -1 would still be in reasonable accord with the data. This is illustrated by the dashed line in the same figure. Experiments with the equimolar melt were carried out at the lower temperature of 1420 °C, using an yttria-stabilized zirconia containment tube and gas flowrates of 430 to 505 ml min^{-1}. The results are presented in logarithmic form in Figure 9 when the best straight line shown drawn through the data has a slope of -0.75 with a calculated uncertainty of ± 0.06. This is strong evidence that the simple inverse dependence of the apparent rate constant on the imposed CO_2/CO ratio does not hold for all iron oxide-containing melts.

IV. DISCUSSION

A. *Rates of Oxidation and Reduction of Liquid Iron Silicates and Iron Calcium Silicates*

No direct measurements have been made of the interfacial rate of oxidation of liquid iron silicates by CO_2. However, Ban-ya, Iguchi, and Nagasaka[14] have recently measured the rates of reduction in Ar-CO mixtures at high enough gas flowrates to avoid mass transfer restrictions in the gas. Their results for 1400 °C and three concentrations of silica are reproduced in Figure 10. At low pressures of CO, when the rates are sufficiently low to avoid diffusional limitations in the melt, the rates are directly proportional to pCO, *i.e.*, they are given by the expression:

$$v = k' p\mathrm{CO} \qquad [20]$$

where k' decreases with increasing silica concentration. Values of k' for 1320 and 1400 °C, in the practical units of g-oxygen cm^{-2} s^{-1} atm^{-1}, are presented in Figure 11 as the open circles.

In the present work, the apparent first order rate constant for the dissociation of CO_2 on silica-saturated iron silicates has been found to be inversely proportional to the oxygen activity within experimental error. Accordingly, and as discussed earlier, if the rate determining step for the dissociation is the same as that for the oxidation reaction, rates of reaction in CO_2-CO atmospheres should be given by Eq. [2], *i.e.*, k' in Eq. [20] should be given by the value of k_a^o from Eq. [12]. Similarly, the value of k' for liquid iron oxide should be given by the previously obtained equation for k_a^o for liquid iron oxide, Eq. [18].[1] If it is assumed that the inverse dependence of the apparent rate constant for the dissociation of CO_2 on oxygen activity also holds for the unsaturated iron silicate melts at given silica contents, values of k' for these melts may be equated with values of k_a^o from Eqs. [13] through [16]. All the derived values, converted to the appropriate practical units, are shown as the filled circles in Figure 11.

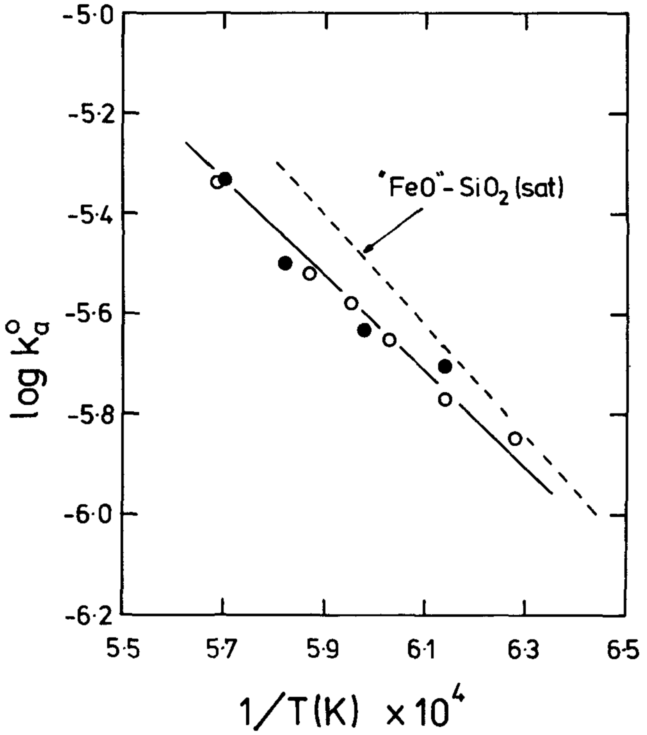

Fig. 7 — Arrhenius plot of the apparent rate constants for melts containing 22 mol pct "FeO", 21 mol pct CaO, and 57 mol pct SiO_2. Open circles are for measurements using an yttria-stabilized zirconia containment tube; closed circles are for data with a single crystal sapphire tube.

The agreement between the rate constants from the reduction studies and those calculated from the isotope exchange studies is very close. Accordingly, rates of oxidation of *silica-saturated* liquid iron silicates, over the range of conditions of the present experiments, may be taken to be given by the equation:

$$v = (p\mathrm{CO}_2 a_{\mathrm{O}}^{-1} - p\mathrm{CO}) \cdot \exp(-25600/T + 2.65) \text{ mol cm}^{-2}\text{ s}^{-1} \qquad [21]$$

obtained by appropriate combination of Eq. [2] and Eq. [12]. It appears likely that rates of reaction with unsaturated liquid iron silicates can be described by similar combination of Eq. [2] with Eqs. [13] through [16].

Fine, Meyer, Janke, and Engel[15] have studied the rates of reduction of FeO-CaO-SiO_2-MgO melts in CO at 1600 °C. For a starting composition of 67.7 wt pct FeO, 14.2 wt pct CaO, 12.4 wt pct SiO_2, and 5.7 wt pct MgO, they established the conditions where the rates were independent of the flowrate of the gas and observed an approximately constant rate until about half of the FeO had been consumed. Beyond this point the rate decreased, but after interrupting the experiments (by passing argon for a short period) higher rates were observed for a short time. This suggests that diffusional limitations in the melt were influencing the rates in the later stages of the experiments. Their results for a CO flowrate of 1670 ml min^{-1} (STP) impinging on a 2 g sample of slag contained in a magnesia crucible of 14.4 mm internal diameter are presented in Figure 12 as the fraction of the initial FeO content reacted *vs* time.

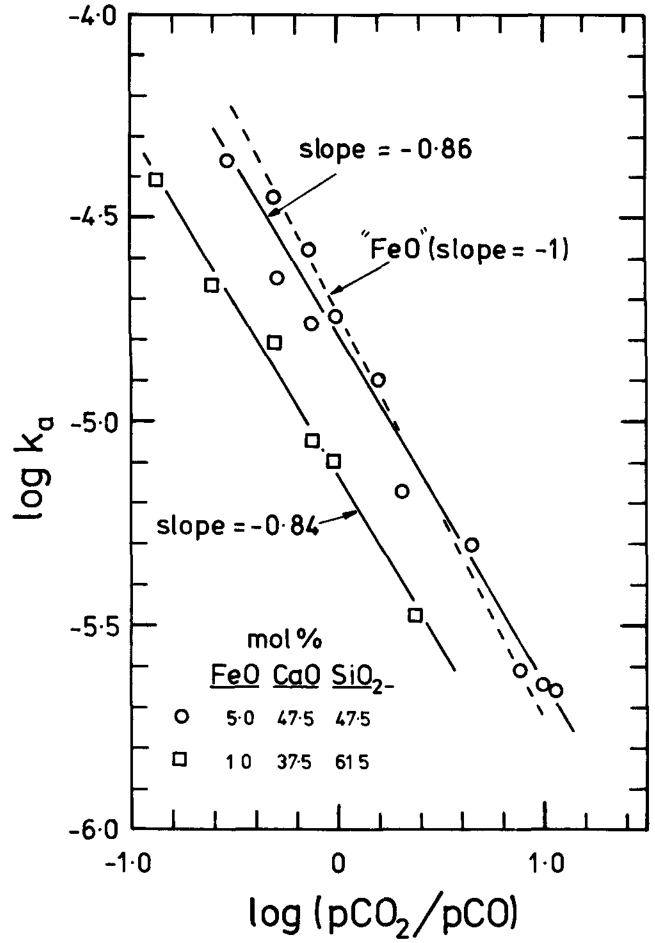

Fig. 8 — Apparent rate constants as a function of the CO_2/CO ratio for two calcium iron silicates at 1520 °C.

Taking the value of k_a° from Eq. [18], the expected initial rate equation for the reduction of liquid *iron oxide* at 1600 °C would be:

$$\frac{dX}{dt} = 2.7 \times 10^{-5} pCO \frac{A}{n} \, s^{-1} \qquad [22]$$

where X is the fraction of iron oxide reacted, A is the area of the melt in cm^2, and n is the initial number of moles of FeO. This calculated rate is shown in Figure 12 to describe closely the measured rate until about half of the iron oxide is reduced from the melt. This agreement is good evidence that the rate-determining steps in the isotope exchange and reduction reactions are the same for such melts at high iron oxide content in view of the observation in the present work that equimolar additions of CaO and SiO_2 to liquid iron oxide have little effect on the rate of isotope exchange.

For melts where the simple inverse dependence of k_a on a_O is not followed, the rate constant for reduction in CO, k', cannot be simply identified with k_a°. For the case where

$$k_a = k_a^\circ a_O^{-y} \qquad [23]$$

it follows that the rate of oxidation in CO_2-CO atmospheres should be given by:

$$v = k_a^\circ (pCO_2 a_O^{-y} - pCO a_O^{1-y}) \qquad [24]$$

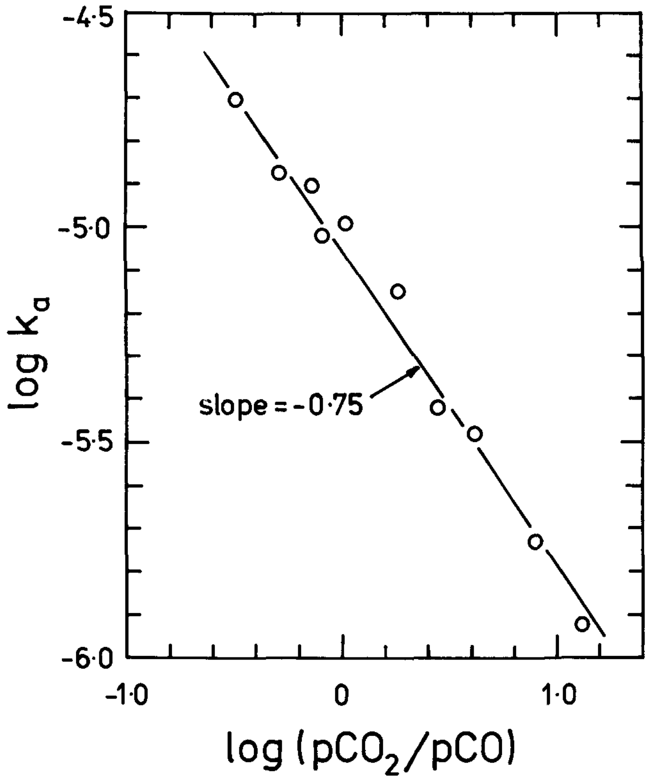

Fig. 9 — Apparent rate constants as a function of the CO_2/CO ratio for the equimolar calcium iron silicate at 1420 °C.

if the rate determining steps for isotope exchange and reaction are the same. The apparent first order rate constant for reduction in CO atmospheres would then be given by:

$$k' = k_a^\circ a_O^{1-y} \qquad [25]$$

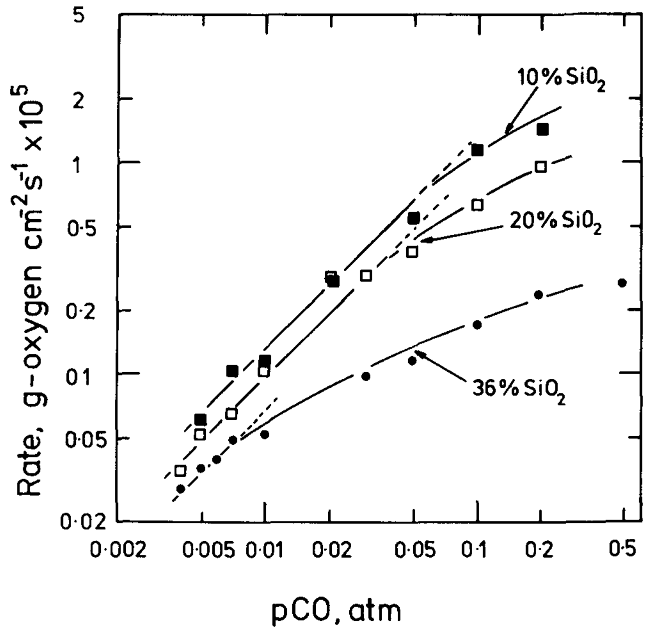

Fig. 10 — Rates of reduction of liquid iron silicates at iron saturation at 1400 °C in CO-Ar mixtures observed by Ban-ya, Iguchi, and Nagasaka.[14]

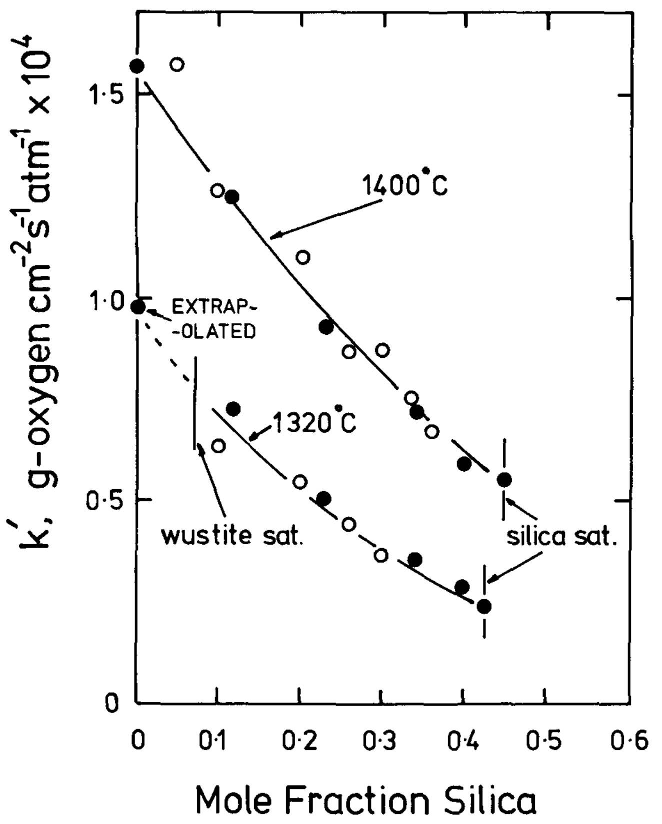

Fig. 11 — Comparison of the practical first order rate constants for the reduction of liquid iron silicate melts at iron saturation due to Ban-ya *et al.*[14] (open circles) with values from the isotope exchange measurements on liquid iron oxide and iron silicates.

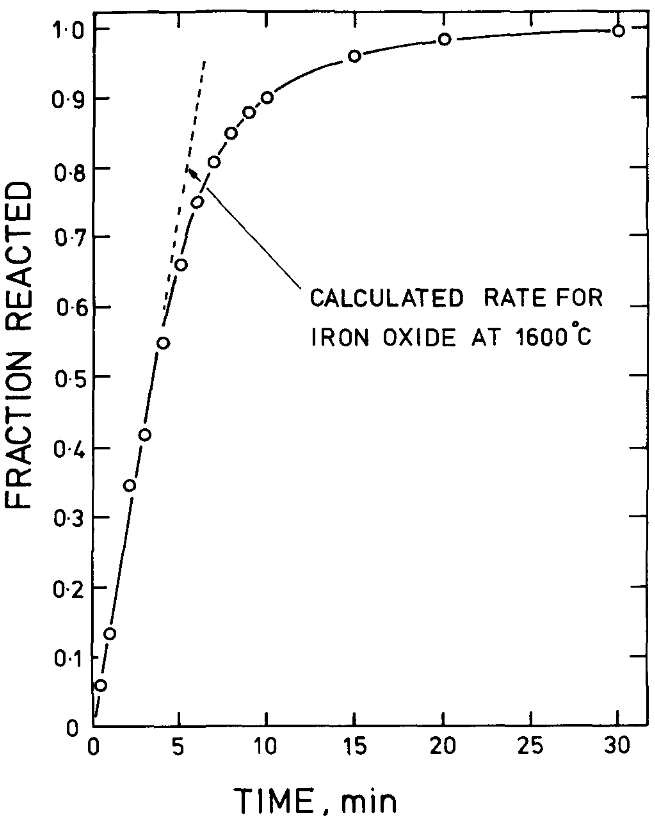

Fig. 12 — Results of Fine *et al.*[15] for the rate of reduction of an iron oxide-containing slag under flowing CO at 1600 °C in comparison with the calculated rate for liquid iron oxide from the isotope exchange studies, Eq. [22]. The composition of the slag, in wt pct, is FeO, 67.7; CaO, 14.2; SiO_2, 12.4; MgO, 5.7. The nominal surface area is 1.63 cm^2.

For equimolar FeO-SiO_2-CaO melts, the data in Figure 9 are consistent with:

$$k_a = k_a^\circ a_O^{-0.75} \qquad [26]$$

at 1420 °C. Accordingly, the apparent first order rate constant for the reduction of such a melt to metallic iron in a CO atmosphere should be given by:

$$k' = k_a^\circ (a_O)_e^{0.25} \qquad [27]$$

where $(a_O)_e$ is the value of the CO_2/CO ratio which would be in equilibrium with the melt and metallic iron, and provided that relationship [26] holds for the short extrapolation to equilibrium with iron. From the assessment of Timucin and Morris,[16] the value of $(a_O)_e$ at 1450 °C is about 0.13. Substitution in Eq. [27] gives:

$$k' \simeq 0.6 k_a^\circ \qquad [28]$$

Since the value of k_a° for the equimolar melt is essentially identical with that for liquid iron oxide, we would thus expect only a small decrease in rates of reduction as equimolar additions of CaO and SiO_2 are made to liquid iron oxide. This is closely consistent with unpublished results of Nagasaka[17] who has studied the rates of reduction of such melts in CO-Ar atmospheres at 1400 °C.

B. *The Dependence of the Apparent Rate Constant on the State of Oxidation of the Melt*

Within the limits of experimental error, the apparent rate constant for silica-saturated iron silicate melts is inversely proportional to the equillibrium CO_2/CO ratio (Figure 1). Michal and Schuhmann[18] have measured the equilibrium ferric and ferrous ion contents of silica-saturated iron silicate melts between 1250 and 1350 °C as a function of the CO_2/CO ratio. As is shown in Figure 13, there is a linear relationship between $(Fe^{3+}/Fe^{2+})^2$ and pCO_2/pCO. Accordingly, and through Eqs. [3] through [7], the behavior of the apparent rate constant for the silica-saturated iron silicates is fully consistent with the charge transfer model.

There is some evidence from the surface tension studies of Popel and Esin[6] that the ferric or a ferrite ion is surface active in liquid iron silicates. However, no information is available for silica-saturated melts, and the other experimental data are too few to allow a quantitative analysis of whether or not changes in surface constitution with the state of oxidation could account for the observed dependence of the apparent rate constant. In the case of manganese silicate melts, the work of Sharma and Philbrook[19] has shown that at high silica concentrations the surface tension, and hence the surface constitution, is *not* a strong function of oxygen potential. It appears reasonable to attribute the essentially inverse dependence of the apparent rate constant on oxygen activity, shown in Figure 4, to charge transfer effects; however, no data are available on the variation of Mn^{3+}/Mn^{2+} ratios in the system and further analysis is not possible.

Ferric and ferrous ion concentrations in iron calcium silicates at various oxygen activities have been determined by Timucin and Morris.[16] Derived values for the Fe^{3+}/Fe^{2+} ratio for melts containing 30 wt pct SiO_2 with 20 and

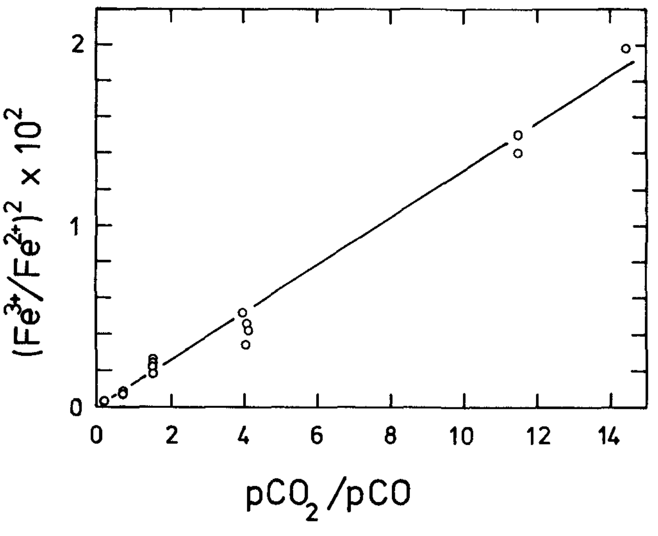

Fig. 13—Measured equilibrium values of the ratio $(Fe^{3+}/Fe^{2+})^2$ as a function of the CO_2/CO ratio for silica-saturated iron silicates at 1250 to 1350 °C, from the data of Michal and Schuhmann.[18]

30 wt pct CaO at 1450 °C are presented in logarithmic form *vs* the oxygen activity in Figure 14. Treating both sets of data together, the best straight line has a slope of about 0.4; hence, we may write:

$$(Fe^{3+}/Fe^{2+})^2 \propto (pCO_2/pCO)^{0.8} \qquad [29]$$

Substitution in Eq. [6] gives:

$$v = kpCO_2(pCO_2/pCO)^{-0.8} \qquad [30]$$

for the expected form of the forward rate law for the dissociation of CO_2 on the melts when two charges are transferred to the dissociating molecule. Accordingly, the apparent rate constant should be given by:

$$k_a = k_a^\circ(pCO_2/pCO)^{-0.8} \qquad [31]$$

This agrees with the dependence found for the equimolar melt at 1450 °C; namely,

$$k_a = k_a^\circ(pCO_2/pCO)^{-0.75(\pm 0.06)} \qquad [32]$$

More experimental rate data on other melts, together with the appropriate thermodynamic data, are required before broad conclusions can be drawn, but this is good evidence that the charge transfer model, expressed in terms of the *concentrations* of donors and acceptors, is closely followed for the nonideal equimolar melt.

C. *The Effect of Bulk Composition on the Value of the Rate Constant*

In view of the apparent importance of charge transfer in determining the dependence of the rate constant on the state of oxidation of a given melt, differences in the value of the rate constant among melts might be expected to result from differences in the propensity of such melts to transfer charge, *i.e.*, related to the basicity. In addition, it is known that silica is surface active in oxide melts and it might be speculated that at high activities of silica the rate is depressed by the enhanced coverage of the surface by adsorbed silica.

The strong influence of silica content on the apparent rate constant for calcium iron silicates is illustrated in Figure 15, where derived values of k_a° at about 1480 °C are shown as a function of the concentration of SiO_2 for melts which contain equal mole fractions of CaO and "FeO". The effect of silica in the binary iron silicates is less marked, the value of the rate constant at 1400 °C for the silica-saturated melt being about one-third of the value for liquid iron oxide.

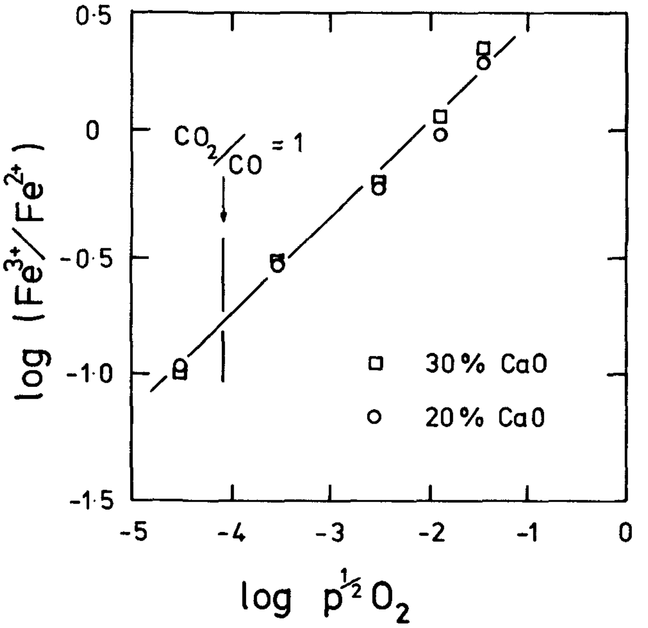

Fig. 14—Logarithmic plot of the equilibrium Fe^{3+}/Fe^{2+} ratio as a function of oxygen pressure at 1450 °C for calcium iron silicates containing 30 wt pct SiO_2 with 30 and 20 wt pct CaO, from the data of Timucin and Morris.[16]

We consider firstly the surface constitution of the silica-containing melts. Richardson[20] has analyzed the available surface tension data for liquid binary iron silicates at

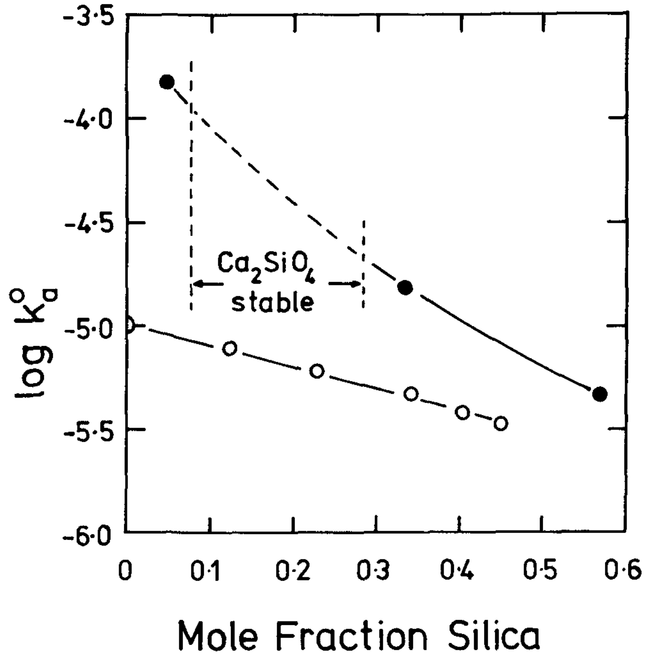

Fig. 15—The influence of silica content on the apparent rate constant at unit CO_2/CO ratio for calcium iron silicates with CaO/"FeO" = 1 at 1480 °C (closed circles) and iron oxide at 1400 °C (open circles).

1420 °C and has shown that at bulk saturation with solid silica the surface is still unsaturated. The surface coverage by SiO_2 was deduced to be about 70 pct. Cooper and McCabe[21] reached a similar conclusion in an independent analysis. Thus we might expect the apparent rate constant for a silica-saturated iron silicate melt to be about 30 pct of that for liquid iron oxide if significant reaction can occur only on the fraction of surface not covered by adsorbed silica and the reaction rate at remaining sites is unaffected by changes in bulk composition. The observed reduction in the apparent rate constant at about 1400 °C agrees with this expectation.

Cooper and Kitchener[22] analyzed their surface tension data for calcium silicate melts at 1600 °C and showed that the mole fraction of silica in the surface should approach unity before bulk saturation, *i.e.*, SiO_2 is more strongly adsorbed on calcium silicate melts than on iron silicate melts. Swisher and McCabe,[23] Ono *et al.*,[24] and Gunji and Dan[25] have since obtained surface tension data which agree very closely with those of Cooper and Kitchener, particularly at high silica concentration. Accordingly, their deductions can be accepted with some confidence. The limited amount of data which is available for calcium iron silicates[26,27] is consistent with a relatively smooth variation in the dependence of surface tension on silica concentration across the system from the iron silicate binary to the calcium silicate binary. It is reasonable to expect, therefore, that the adsorption behavior of silica in the ternary melts lies between the behaviors in the two binaries; *i.e.*, for the melt with equal mole fraction of "FeO" and CaO we would expect a higher coverage at bulk saturation than for iron silicates. To account fully for the observed reduction in the rate constant at 1480 °C, the coverage at bulk saturation would need to be about 97 pct. This appears high, but cannot be ruled out on the available evidence from the surface tension studies.

Generally, the apparent rate constant at a given oxygen potential increases with the basicity of the melt. Values of k_a° at 1520 °C for all the calcium iron silicates are shown plotted logarithmically against the CaO/SiO_2 ratio in Figure 16. There is a good correlation with this practical measure of basicity; however, this measure cannot be used for the CaO- or SiO_2-free melts.

If the ratio of the activity coefficients of the Fe^{2+} and Fe^{3+} ions is not a strong function of the bulk compositions of the melts, the value of the Fe^{3+}/Fe^{2+} ratio at fixed oxygen potential can be taken as a measure of the ease with which charge can be transferred from the Fe^{2+} ion to the oxygen anions and, accordingly, to other anionic species. In Figure 17, values of log k_a° at a common temperature of 1520 °C from the present and previous work[1] are shown as a function of log $(Fe^{3+}/Fe^{2+})_O$, where $(Fe^{3+}/Fe^{2+})_O$ is the value at $pCO_2/pCO = 1$. For some of the ternary melts, values of the ratio have been extrapolated from the data of Larson and Chipman[8] and Timucin and Morris.[16] Literature values are taken for other melts.[7–9,16,18,28]

There is a broad trend of increasing apparent rate constant with this particular measure of the propensity to transfer charge which suggests that the effects due to changes in surface constitution may be relatively minor. This is supported by the observation that k_a° is essentially constant for melts with $CaO/SiO_2 = 1$ (Figure 6). The data of Larson and Chipman[8] indicate that $(Fe^{3+}/Fe^{2+})_O$ is nearly independent of the iron oxide content of these melts but, clearly, the surface constitution of the 5 mol pct "FeO" melt is unlikely to be the same as that of pure "FeO".

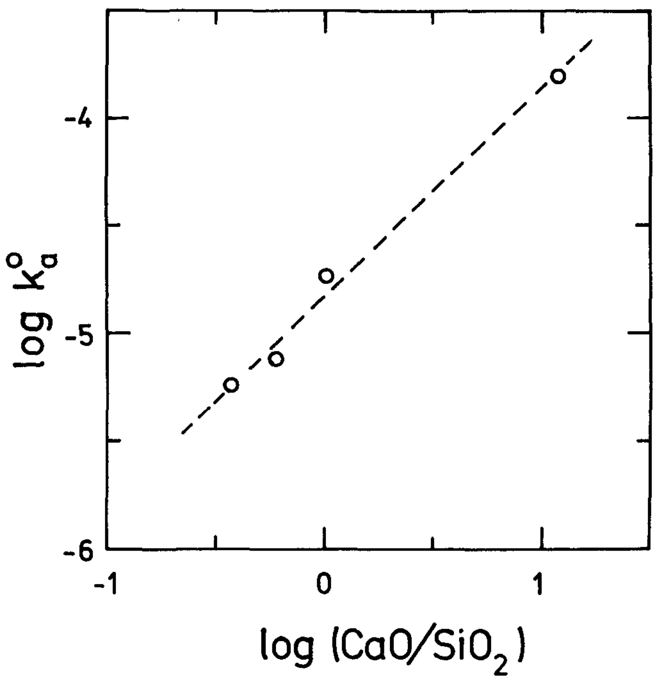

Fig. 16—The dependence of the apparent rate constants at unit CO_2/CO ratio on the CaO/SiO_2 ratio for calcium iron silicates at 1520 °C.

The relative roles of the bulk composition and surface constitution might be usefully investigated through measurements of the rate on melts containing small amounts of P_2O_5. This solute is strongly surface active in liquid iron oxide[29] at concentrations which should have a negligible effect on the basicity or state of oxidation of the melt.

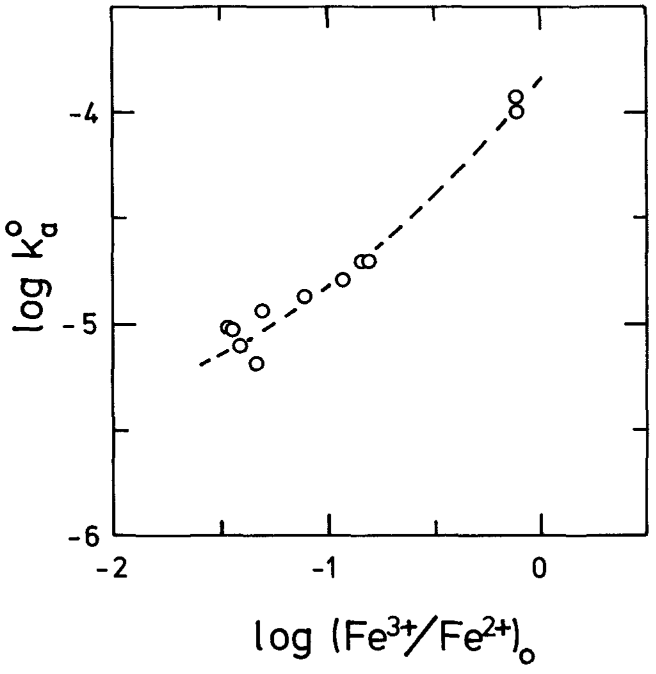

Fig. 17—The dependence of the apparent rate constants at unit CO_2/CO ratio on the value of Fe^{3+}/Fe^{2+} at unit CO_2/CO ratio for iron oxide-containing melts at 1520 °C.

An important observation of the present work is that the rate constants for the 1 mol pct "FeO" melt (Figure 8) are of similar order and show a similar oxygen potential dependence to those for melts with much higher iron oxide content. As the concentration of the oxidizable solute decreases, a situation must eventually be reached where the rate of the redox reaction becomes sufficiently slow to control the rate of dissociation, unless a parallel mechanism for CO_2 dissociation exists. Blank experiments[1] on CaO-saturated calcium silicates with no iron oxide additions showed negligibly low reaction rates. Thus it may be supposed that the observed trend in the value of the apparent rate constant with slag basicity applies only when the concentration of the oxidizable solute exceeds some system-dependent low value. Rate measurements on appropriate melts as a function of the concentrations of different oxidizable solutes at varying low concentrations would be useful in the interpretation.

ACKNOWLEDGMENTS

The authors acknowledge the support of this work by the National Science Foundation under Grant Nos. CPE-8215459 and CPE-8411266 and by The Broken Hill Proprietary Co. Ltd.

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