The Effect of Surfactants on the Interfacial Rates of Reaction of CO_2 and CO with Liquid Iron Oxide

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The $^{14}CO_2$-CO isotope exchange technique has been used to measure the rates of dissociation of CO_2 on liquid iron oxide containing the surface active components P_2O_5 or Na_2O, principally at 1673 K. The apparent first-order rate constant is found to decrease monotonically with small additions of P_2O_5 up to a factor of about 4 at 3.5 mol pct. Vaporization losses prevented detailed studies of the effect of Na_2O, but it is shown that there is probably a twofold increase in the rate constant at a concentration of about 0.2 wt pct and a fivefold increase at a concentration between 0.5 and 1.6 wt pct. A smoothed surface potential model, based upon the Vol'kenshtein model for catalysis by semiconductors, is developed, and it is shown that the required surface potential changes due to the segregation of P_2O_5 and Na_2O are physically reasonable.

I. INTRODUCTION

A series of studies[1,2,3] using the $^{14}CO_2$-CO isotope exchange technique has established interfacial rates and rate constants for the dissociation of CO_2 on liquid iron oxide, some binary and ternary melts of iron oxide with CaO and SiO_2, and silica-saturated manganese silicates. The apparent first-order rate constant, k_a, defined by the forward rate law

$$v = k_a p CO_2 \qquad [1]$$

was found to be a function of the state of oxidation of each melt. Incorporating the functional dependence, it was shown that rates of oxygen exchange with the melts in CO_2-CO mixtures would be given by the expression

$$v = k_a^\circ \left(p CO_2 a_O^{-x} - p CO a_O^{1-x} \right) \qquad [2]$$

over the experimentally accessible range of conditions, where a_O is the oxygen activity of the melt (standard state $p CO_2/p CO = 1$) and k_a° is a temperature-dependent constant for each melt. For the particular cases of ''FeO'', ''FeO''-CaO (sat), ''FeO''-SiO_2 (sat), and MnO-SiO_2 (sat), the rate law took the simple limiting form

$$v = k_a^\circ \left(p CO_2 a_O^{-1} - p CO \right) \qquad [3]$$

within the experimental error.

For the iron oxide-containing melts, a reasonably close correlation was found between values of k_a° at 1793 K and the basicities of the melts. The basicities were expressed as equilibrium Fe^{3+}/Fe^{2+} ratios at $p CO_2/p CO = 1$. This plot is shown in Figure 1, where the units for k_a° are mol m^{-2} s^{-1} Pa^{-1}. Also shown in Figure 1 are values of k_a° at 1573 K for ''FeO''-SiO_2 (sat), ''FeO'' (extrapolated), ''FeO''-CaO at Ca/Fe = 0.3, and ''FeO''-CaO (sat), in increasing order of basicity.

Nagasaka and co-workers[4–7] have carried out a series of studies of the rates of reduction of iron oxide-containing melts by CO and CO-CO_2 mixtures at iron saturation. They established the conditions where mass-transfer processes did not significantly affect the rates. They demonstrated that the reaction was first order with respect to $p CO$ and obtained values for the interfacial rate constants. As has been shown elsewhere,[2,5,8] the rate constants from these studies are in very close agreement with those deduced from the isotope exchange studies on the respective melts. Values of the rate constant, k, defined by the forward rate law

$$v = kp CO \qquad [4]$$

were obtained for binary melts of ''FeO'' with CaO, Na_2O, MgO, MnO, TiO_2, SiO_2, and P_2O_5; ternary melts of ''FeO'' and SiO_2 with CaO, Na_2O, MgO, and MnO; and a quaternary ''FeO''-SiO_2-CaO-P_2O_5 melt. With the marked exception of the ''FeO''-P_2O_5 melts, values of k were shown to be reasonably well correlated by the empirical expression

$$k = k^\circ \left(X_{FeO_{1.5}}^2 / X_{FeO}^3 \right)^{1/3} \qquad [5]$$

where $X_{FeO_{1.5}}$ and X_{FeO} are mole fractions of the ferric and ferrous oxides in the melt at iron saturation, and k° is a temperature-dependent constant with a value of 5.3×10^{-6} mol m^{-2} s^{-1} Pa^{-1} (5.3×10^{-5} mol cm^{-2} s^{-1} atm^{-1}) at 1673 K.

For melts containing P_2O_5, the lowering of the rate constant as a function of P_2O_5 concentration was found to be significantly more than expected from changes in the ratio of ferric to ferrous iron at iron saturation. In Figure 2(a), which is adapted from Nagasaka et al.,[7] the measured rate constants for reduction at 1643 K of the quaternary with CaO/SiO_2 = 1.5 and total iron oxide content of 80 mol pct are compared with the behavior that would be expected from the composition dependence in Eq. [5]. The results for ''FeO''-P_2O_5 melts at 1673 K are compared with the expected behavior in Figure 2(b). Since P_2O_5 is known to be strongly surface active in some oxide melts,[9] the depression of the rate beyond that expected from the effect of P_2O_5 on the bulk basicity may be reasonably attributed to the segregation of phosphate to the surface.

Pal et al.[10,11] have studied the effect of P_2O_5 on the rates of reduction by hydrogen of PbO-SiO_2 melts (Pb/Si = 3) at 1173 K. They concluded that the decrease in the values

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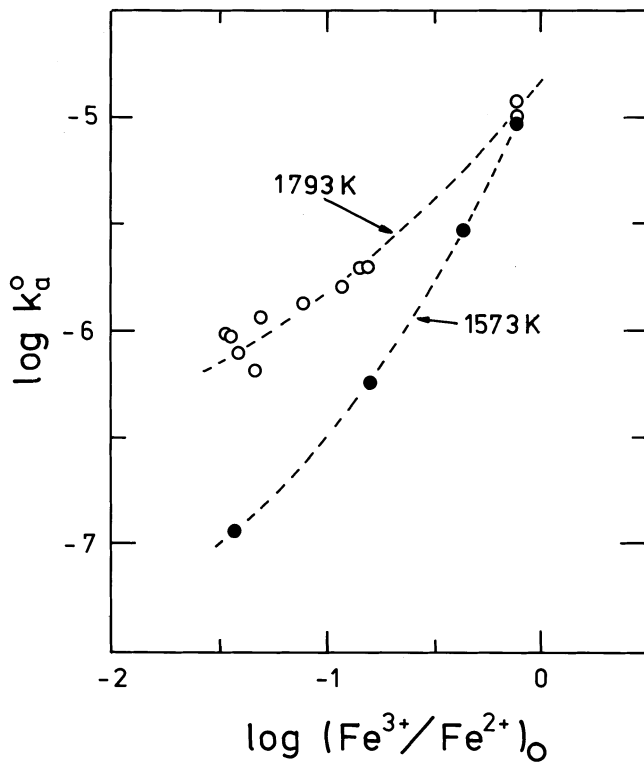Manuscript submitted October 3, 1996.

Fig. 1—Apparent first-order rate constants for the dissociation of CO_2 on high iron oxide content melts as a function of the basicity, expressed as the Fe^{3+}/Fe^{2+} ratio in equilibrium with $pCO_2/pCO = 1$. The data are from Refs. 1 through 3.
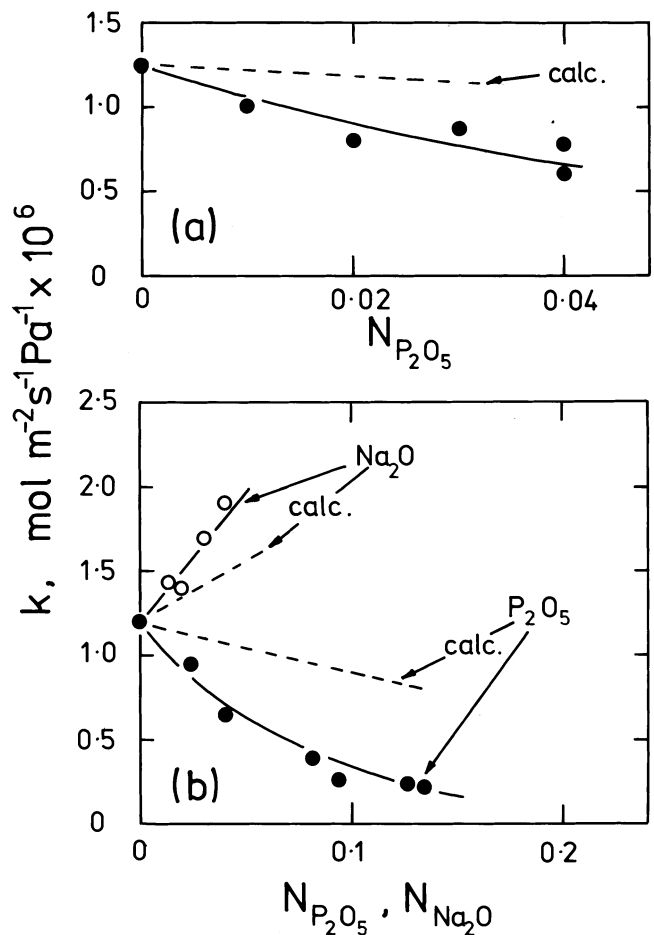

Fig. 2—Values for the first-order rate constant for the reduction by CO of (a) an "FeO"-CaO-SiO_2 melt as a function of the mol fraction of P_2O_5 at 1643 K and (b) "FeO" at 1673 K as a function of the mol fraction of Na_2O or P_2O_5. The data are from Nagasaka et al.[4–7]

of the rate constant as a function of the concentration of P_2O_5 (up to 4 mol pct) was consistent with ideal (Langmuir) adsorption of phosphate groups and negligible rate of reaction over the covered sites.

Of the metallurgically common solutes in liquid iron oxide, only P_2O_5 and Na_2O are markedly surface active, *i.e.*, cause a strong depression of the surface tension.[9] The third most surface active common solute, SiO_2, depresses the surface tension by only about 4 mN m^{-1} mol pct^{-1}, and it has been shown[12] that even at bulk saturation with solid silica (about 50 mol pct at 1673 K), the surface coverage by silica is probably only about 70 pct. Na_2O shows an initial depression of the surface tension of about 30 mN m^{-1} mol pct^{-1} at about 1673 K.[9]

The effect of Na_2O on the kinetics of reduction of iron oxide melts by CO was included in the work of Nagasaka et al.,[7] and their measured rate constants for 1673 K are shown as a function of the *initial* Na_2O concentration in Figure 2(b). If the variation of the equilibrium Fe^{3+}/Fe^{2+} ratio with the Na_2O concentration at iron saturation is taken to be the same as that established by Ban-ya et al.[14] at 1883 K and higher oxygen potential ($pCO_2 = 1$ atm), the expected behavior would be that shown by the dashed line, if Eq. [5] is assumed to hold.

Thus, there is good evidence that the surface-active acidic solute P_2O_5 *decreases* the rate constant and that the surface-active basic solute Na_2O *increases* the rate constant, both beyond what would be expected from their effects on the bulk basicity of the melt. The same general conclusion would be reached if the variation of the rate constant with the Fe^{3+}/Fe^{2+} ratio at $pCO_2/pCO = 1$ shown in Figure 1

(interpolated for 1673 K) were to be taken for the comparison rather than the empirical dependence of Eq. [5].

The present[14] CO_2-CO isotope exchange study was undertaken to confirm these effects and to obtain more detailed information on the composition dependence of the rate of dissociation of CO_2 on liquid iron oxide at low concentrations of P_2O_5 and Na_2O. This has been achieved for melts containing up to about 3.5 mol pct P_2O_5. More limited information has been obtained for Na_2O-containing melts because of high rates of volatilization of sodium.

II. EXPERIMENTAL DETAILS

The experimental technique was similar to that used in previously reported work.[1–3] Slag samples of about 0.5 g were contained in a shallow well in a platinum-rhodium susceptor which was inductively heated with an RF (radio frequency) (450 kHz) generator. A sharp-edged refractory containment tube (7- to 11-mm i.d.) was inserted into the slag well, forming a confined reaction zone. Inside this tube, a second tube (3-mm i.d. alumina) was coaxially held about 5 mm above the melt surface for gas delivery. Three types of containment tube were used: lime-stabilized zirconia, recrystallized alumina, and thin-walled transparent single-crystal alumina (referred to hereafter as sapphire).
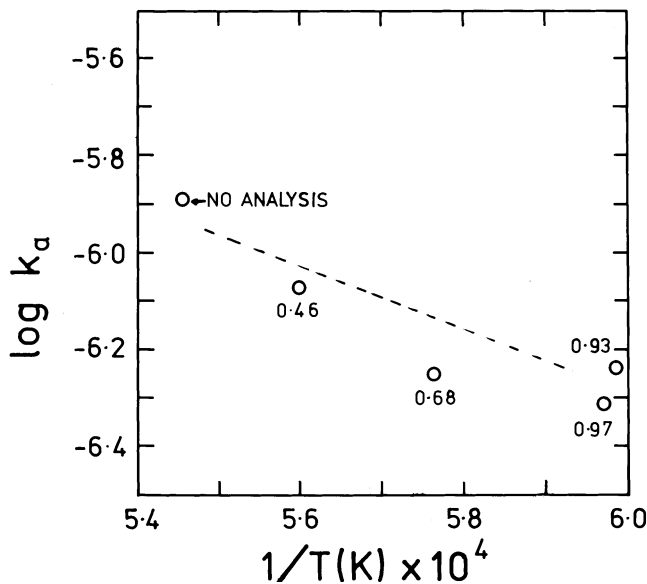
Fig. 3—Arrhenius plot of the apparent first-order rate constants at $pCO_2/pCO = 1$ for melts with an initial P_2O_5 content of 0.93 mol pct. The numbers next to the datum points are the final concentrations of P_2O_5 in mol pct.
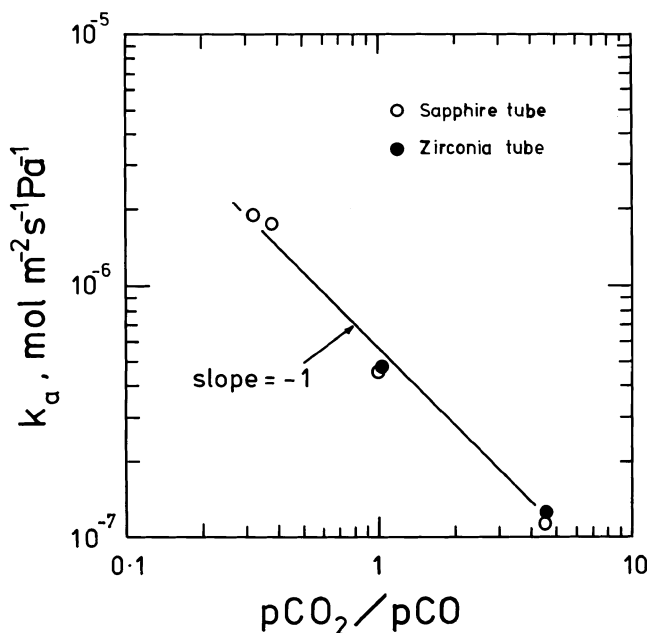

Fig. 4—Dependence of the apparent first-order rate constant on the equilibrium CO_2/CO ratio for liquid "FeO" containing about 1.6 mol pct P_2O_5 at 1673 K.

Temperature measurement was by means of an alumina-sheathed Pt/Pt-13 pct Rh thermocouple inserted into the base of the susceptor.

The methods used for the preparation of $^{14}CO_2$-enriched CO_2-CO mixtures, the collection of ^{14}CO-enriched CO after reaction, conversion of this gas to CO_2, and the counting of the relative ^{14}C contents by internal Geiger–Muller tube techniques were as described in detail elsewhere.[1] Reaction-gas flow rates were between 200 and 330 cm^3 min^{-1} STP, and samples of the reacted gas were taken after a period of 5 to 20 minutes.

Master slags were prepared by melting laboratory rea-

gent-grade oxides in a heavy iron crucible and quenching on a stainless-steel plate. The major impurities in these master slags were CaO $\approx$ 0.1 wt pct, SiO$_2$ $\approx$ 0.2 wt pct, Al$_2$O$_3$ < 0.02 wt pct, and ZrO$_2$ < 0.01 wt pct. Analyses of the solidified slag films after reaction showed some dissolution of the containment tube into the melt. For the sapphire tubes, the resulting Al$_2$O$_3$ was about 6 wt pct. For the narrow-bore alumina tubes, the Al$_2$O$_3$ content varied between 6 and 15 wt pct. Accurate analyses were not possible for the melts with zirconia containment tubes due to difficulties in separating small fragments of the tube from the solidified film. The lowest measured ZrO$_2$ content was 3.8 wt pct, which suggests that the amount dissolved in the melt was very low, as previously observed[3] for "FeO"-CaO melts. Changes in the concentration of P$_2$O$_5$ and Na$_2$O will be discussed in Section III.

III. RESULTS

Results are reported as values of the apparent first-order rate constant, k_a, for the dissociation of CO$_2$ calculated from the equation

$$k_a = \frac{\widetilde{V}}{ART(1 + B)} \ln \frac{1}{1 - C(1 + B)/C'B} \qquad [6]$$

where A is the reaction area, $\tilde{V}$ is the volumetric flow rate of the reaction gas at temperature T, B is the ratio pCO_2/pCO, and C' and C are the counting rates for the initial labeled CO$_2$ and the CO$_2$ resulting from conversion of CO from the reacted gases, respectively. All concentrations of P$_2$O$_5$ and Na$_2$O are reported as mol pct in the apparent binary system with FeO, $i.e.$, all iron is assumed to be in the ferrous form, and the small variable effect of dissolved Al$_2$O$_3$ and ZrO$_2$ is ignored.

Rate constants measured at $pCO_2/pCO = 1$ for melts with an initial P$_2$O$_5$ content of 0.93 mol pct and using a zirconia containment tube are presented in Arrhenius form in Figure 3. The numbers near each datum point are the final concentrations of P$_2$O$_5$. No final concentration is given for the point at 1833 K since this result was obtained prior to and with the same sample as that at 1786 K. Over the temperature range of the measurements, the apparent rate constants are approximately a factor of 2 lower than for P$_2$O$_5$-free iron oxide, but in view of the losses of P$_2$O$_5$, no significance can be given to the temperature dependence. Within experimental error, no loss of P$_2$O$_5$ occurred at about 1673 K. Accordingly, all subsequent studies were restricted to this temperature.

Results obtained at 1673 K for melts initially containing 1.66 mol pct P$_2$O$_5$ are presented as a function of pCO_2/pCO in logarithmic form in Figure 4. Two solidified films were subsequently analyzed. P$_2$O$_5$ contents were determined to be 1.60 mol pct for an experiment with $pCO_2/pCO = 0.38$ and 1.47 mol pct for $pCO_2/pCO = 1.04$. Within experimental error, the data are consistent with the indicated slope of -1. Thus, it may be reasonably concluded that for an essentially constant P$_2$O$_5$ content of about 1.6 mol pct, the dependence of the apparent first-order rate constant on oxygen activity is the same as that for P$_2$O$_5$-free iron oxide.[1]

In Figure 5, values of the apparent rate constant at 1673 K and $pCO_2/pCO = 1$ are shown as a function of the con-

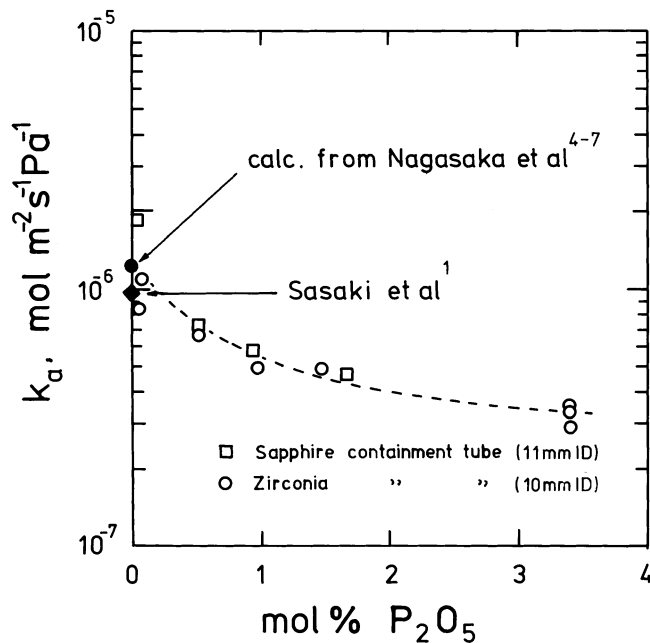Fig. 5—Apparent first-order rate constants at $pCO_2/pCO = 1$ as a function of P_2O_5 concentration at 1673 K, obtained from the experiments with wide-bore containment tubes.

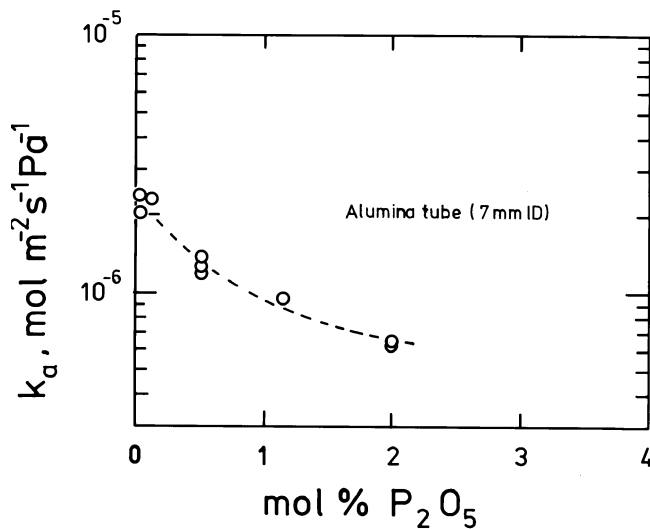Fig. 6—Apparent first-order rate constants at $pCO_2/pCO = 1$ as a function of P_2O_5 concentration at 1673 K, obtained from the experiments with narrow-bore containment tubes.

centration of P_2O_5 for a series of experiments using sapphire and zirconia containment tubes. Actual values of pCO_2/pCO varied between 0.93 and 1.03. Accordingly, small corrections to the values of the rate constants were made by assuming the dependence in Figure 4 to hold. Large losses of P_2O_5 were observed when experiments were attempted at high P_2O_5 concentrations, and the results shown plotted at the analyzed final concentration of 3.4 mol pct were from experiments with initial concentrations of 6.5 and 10.5 mol pct. Initial and final concentrations for the experiments at less than 1.7 mol pct P_2O_5 differed by less that 13 pct of the initial value. Also shown in Figure 5 is the value of the apparent rate constant for essentially P_2O_5-free iron oxide obtained by Sasaki et al.[1] and that
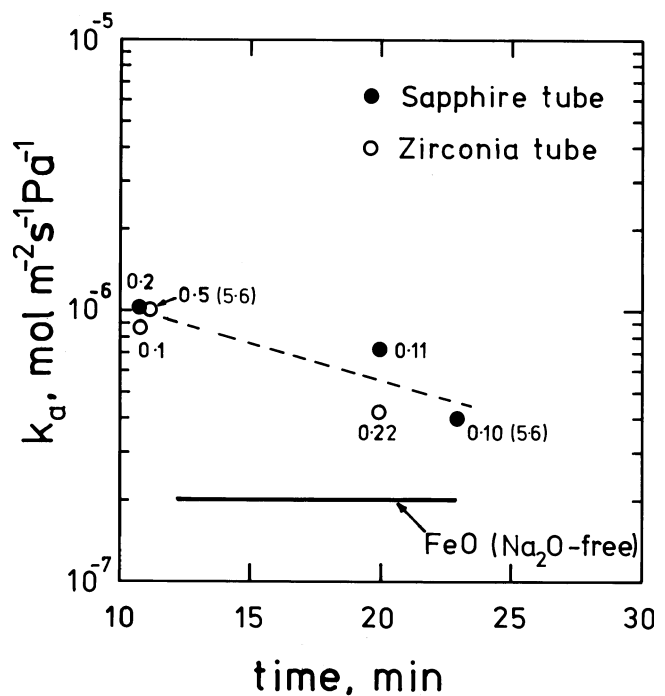

Fig. 7—Apparent first-order rate constants at 1673 K and $pCO_2/pCO = 5$ for melts with initial Na_2O contents of 1.6 and 5.6 wt pct as a function of total reaction time. The numbers next to each datum point are the final concentrations of Na_2O, and the two experiments which began with 5.6 wt pct Na_2O are indicated by the values in parentheses.

calculated[8] from the reduction rate constant due to Nagasaka and co-workers.[4–7] There is satisfactory agreement among the studies, and the present data indicate a significant depression of the apparent rate constant at small concentrations of P_2O_5. Broadly, 2 mol pct P_2O_5 leads to a reduction by a factor of about 3. This is a factor of about 2 greater than the effect reported by Nagasaka et al.[7] for the reduction kinetics at 1673 K, as shown in Figure 2(b).

A second series of experiments was conducted at 1673 K and $pCO_2/pCO = 1$ using narrow-bore (7-mm i.d.) recrystallized alumina containment tubes rather than the wider bore sapphire (11-mm i.d.) and zirconia (10-mm i.d.) tubes. The results of these measurements are presented in Figure 6. The trend closely follows that in Figure 5, but the derived values of the rate constants, based on the nominal surface area, are a factor of about 2 higher. This difference is consistent with the exposed surface area of the melt being approximately that of a hemisphere in the narrow-bore tubes and approximately that of a disc in the wider bore tubes. Unfortunately, it was not possible to determine the shapes of the surfaces during the experiments.

Experiments were attempted at 1673 ± 5 K and $pCO_2/pCO \approx 5$ (4.5 to 5.6) on melts with initial Na_2O concentrations of 1.6 and 5.6 wt pct, using both sapphire and zirconia containment tubes. The derived values of the apparent rate constants are shown in Figure 7 as a function of the time each melt was held at temperature under the flowing gas mixture. The numbers next to each datum point are the analyzed Na_2O concentrations of the solidified films in wt pct, and the two experiments that began with the highest Na_2O content are indicated. Collection of the samples of reacted gas took about 7 minutes. Accordingly, the periods before actual rate measurements were begun for the
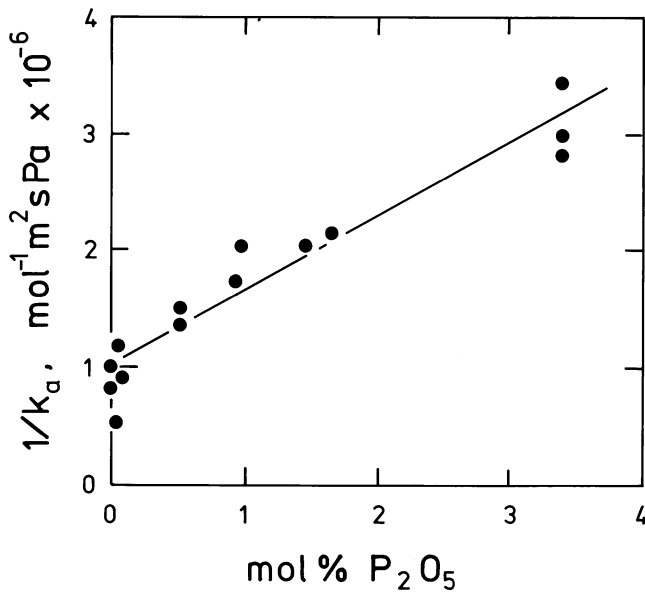
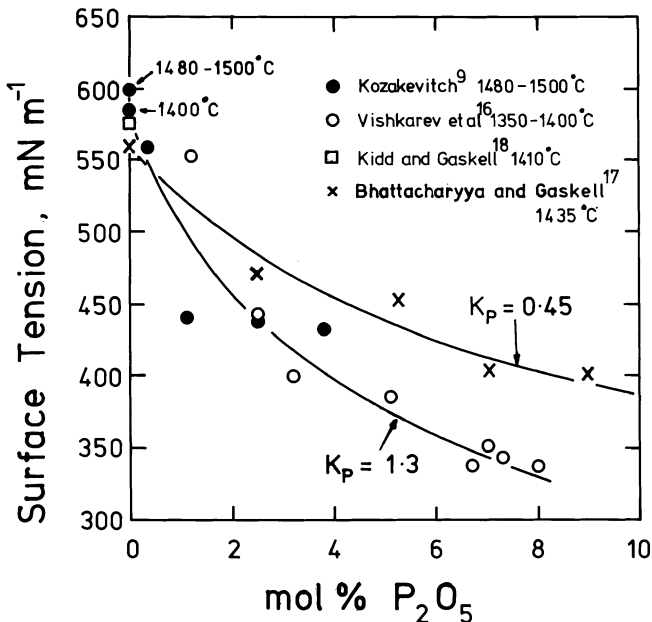Fig. 8—Dependence of the rate constants on P_2O_5 concentration, plotted in accordance with Eq. [11].

Fig. 9—Available surface tension data for "FeO"-P_2O_5 melts at about 1400 °C in comparison with values from Eq. [12] for $K_P = 0.45$ and 1.3.

data shown at 11 to 12, 20, and 23 minutes were roughly 4, 13, and 16 minutes.

The analytical results show that about 90 pct of the Na_2O was lost from the melt by the end of the shortest time experiments, and it is not possible to attribute the approximately fivefold increase in the apparent rate constant (with respect to Na_2O-free iron oxide) to a well-defined average Na_2O concentration. The longer experiments probably represent steady-state studies more closely, with the bulk of the Na_2O having been lost before the determination of the rate began. Qualitatively, all the experiments show that there is a marked effect of Na_2O in increasing the rate of reaction of CO_2 with liquid iron oxide. Quantitative deductions are more difficult to reach, but it would appear that a

concentration of about 0.2 wt pct leads to at least a doubling of the apparent rate constant. A fivefold increase in the apparent rate constant can be reasonably attributed to a concentration somewhere between 0.5 wt pct, the highest residual concentration, and 1.6 wt pct, the lowest starting concentration.

IV. DISCUSSION

As noted previously, P_2O_5 is surface active. There is little change in the Fe^{3+}/Fe^{2+} ratio at a given oxygen activity with the addition of a small amount of P_2O_5.[13] Similar behavior is expected for Na_2O in liquid iron oxide.[14] Thus, there is good reason to attribute the marked changes in the rate constant to changes in the surface constitution of the melt. If ideal Langmuir adsorption of the thermodynamic component P_2O_5 is assumed, we may write

$$\frac{\theta_P}{1 - \theta_P} = K_P a_P \qquad [7]$$

where K_P is the Langmuir equilibrium constant or adsorption coefficient, a_P is the activity of P_2O_5, and θ_P is the fraction of the surface occupied by the component P_2O_5. The quantity θ_P is defined by the equation

$$\theta_P = \Gamma_P / \Gamma_P^\circ \qquad [8]$$

where Γ_P is the surface concentration of P_2O_5, and Γ_P° is the value at surface saturation. Kambayashi et al.[15] have shown that the activity of P_2O_5 closely follows Henry's law below 8 mol pct at 1370 °C to 1390 °C. Accordingly, we may write

$$1 - \theta_P = 1/\left[1 + K_P \left(\text{mol pct } P_2O_5\right)\right] \qquad [9]$$

for a standard state of 1 mol pct.

If an ideal site blockage model is assumed, i.e., the rate on that fraction of the surface which is covered by P_2O_5 is negligible, we obtain

$$k_a = k_{a,o} \left(1 - \theta_P\right) \qquad [10]$$

where $k_{a,o}$ refers to the apparent rate constant for the P_2O_5-free iron oxide. Combination of Eqs. [9] and [10] gives

$$\frac{1}{k_a} = \frac{1}{k_{a,o}} + \frac{K_P}{k_{a,o}} \left(\text{mol pct } P_2O_5\right) \qquad [11]$$

The experimental data from Figure 5 are shown plotted in the appropriate form in Figure 8. There is reasonable agreement with the form of Eq. [11], and the consistent value of the adsorption coefficient, K_P, is 0.63.

The depression of the surface tension of iron-saturated liquid iron oxide by P_2O_5 has been studied by Kozakevitch[9] at 1480 °C to 1500 °C and by Vishkarev et al.[16] at 1350 °C to 1400 °C. Most recently, Bhattacharyya and Gaskell[17] have carried out measurements at 1435 °C on melts which were unsaturated with respect to iron. They found that the values were essentially independent of equilibrium CO_2/CO ratios of 3.15 to 14. Data for P_2O_5 contents of the melts up to 9 mol pct are plotted in Figure 9. This figure also includes a point for pure liquid iron oxide at 1410 °C from the work of Kidd and Gaskell.[18] Assuming ideal ad-
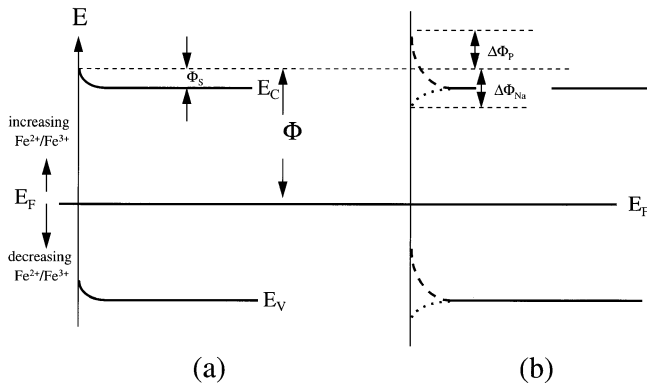
Fig. 10—Simplified energy band diagram assumed for liquid ''FeO'': (*a*) for the pure liquid and (*b*) in the presence of surface segregation of Na_2O or P_2O_5. The meanings of the symbols are given in the text.

sorption, the data may be analyzed by the following form of the Szyszkowski equation:[19]

$$\sigma = \sigma° - RT\Gamma°_P \ln \left(1 + K_P a_P\right) \qquad [12]$$

where σ and σ^O are the surface tensions of the melt and of the P_2O_5-free iron oxide, respectively.

The partial molar volume of the component P_2O_5, $\overline{V}_P$, in CaO-FeO-P_2O_5 melts at 1500 °C has been shown by Keene and Mills[20] to be about 65.7 cm³ mol⁻¹. Accordingly, an estimate may be made of the virtual surface coverage at saturation by assuming the spreading of one mole of P_2O_5, occupying a similar molar volume, through the expression.

$$\Gamma°_P = N^{-1/3} \overline{V}_P^{-2/3} \qquad [13]$$

where N is Avogadro's number. This gives a value for $\Gamma°_P$ of about 7.3×10^{-10} mol cm⁻², or $RT\Gamma°_P = 102$ mN m⁻¹ at about 1400 °C. Consistent values for K_P, through Eq. [12], are about 0.45 for the data of Bhattacharyya and Gaskell and about 1.3 for the data of Vishkarev *et al.* This is illustrated by the curves in Figure 9. Thus, the available information on the depression of the surface tension is broadly in accord with the magnitude of K_P required for the ideal surface blockage model.

This accordance cannot be taken as a demonstration that the rate of reaction on P_2O_5- or phosphate ion-covered surface sites can be considered to be negligibly small. The analysis would not be sensitive to an assumption that the rate on covered sites is, say, 5 to 10 pct of that on ''bare'' sites. Interpretation of the effect of Na_2O in increasing the value of the apparent rate constant in terms of a similar model would require a high, but obviously finite, value for the rate on Na_2O-covered sites. An alternative approach to modeling the effects of the surfactants is proposed, which avoids the introduction of the concept of covered and uncovered sites, and which includes the earlier proposal that charge transfer is involved in the rate-determining step for the dissociation of CO_2 on iron oxide-containing melts.

A Smoothed Surface Potential Model

It has been shown[1–3] that for high iron-oxide content melts, which include iron oxide, silica-saturated iron silicates, some calcium ferrites, and iron-calcium silicates, where kinetic and redox equilibrium data are available, the apparent rate constant, k_a, in Eq. [1] takes the form

$$k_a = k_f \left(\frac{Fe^{2+}}{Fe^{3+}}\right)^2 \qquad [14]$$

over the accessible range of experimental conditions. The rational rate constant, k_f, is a function of temperature and the basicity of the melt.

Assuming weak adsorption of CO_2, the rate-determining step which is consistent with Eq. [14] may be expressed as

$$CO_{2(ad)} + 2e^- \rightarrow O^{2-}_{(ad)} + CO_{(ad)} \qquad [15]$$
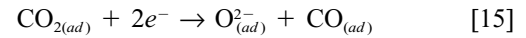
with the electrochemical potential of the electrons being established by the ferrous/ferric redox couple, *i.e.*,

$$Fe^{2+} = Fe^{3+} + e^- \qquad [16]$$

The overall rate-determining step may also be expressed in terms of the formation of a supposed unstable ionic species $CO^{2-}_{2(ad)}$ as a reaction intermediate, as done previously,[1–3] or in terms of the known[21] adsorbed ionic species $CO^-_{2(ad)}$ as an intermediate, *i.e.*,

$$CO_{2(ad)} + e^- = CO^-_{2(ad)} \qquad [17]$$

$$CO^-_{2(ad)} + e^- \rightarrow O^{2-}_{(ad)} + CO_{(ad)} \qquad [18]$$
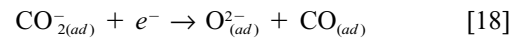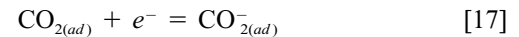
Irrespective of the details of the rate-determining step, the role of the electrochemical potential of the electrons in the virtual equilibria for the formation of the intermediates and/or the virtual equilibrium for the formation of the activated complex can be discussed in the language of the physics of semiconductors. Liquid iron oxide[22] and even the very basic iron-rich liquid calcium ferrites[23] are known to exhibit semiconductor properties. At room temperature, solid ''FeO'' has a band gap of about 2.4 eV, independent of stoichiometry,[24] but no detailed information is available on the magnitude of the band gap for the high-temperature liquid oxide. Following Vol'kenshtein,[25] we can assume that the energy change for the transfer of electrons to reactants is given by the difference between the energy of the electrons in the bottom of the conduction band *at the surface* and the Fermi energy (electrochemical potential of the electrons). This may be represented by the simplified energy-band diagram in Figure 10(a).

In this figure, the bottom of the conduction band in the bulk of the melt is represented by the level E_C, and the top of the valence band in the bulk is represented by the level E_V. In general, a space charge will exist due to excess negative or positive ions at the surface (donor or acceptor surface states). This results in bending of the conduction and valence bands over the ''screening'' distance of about 10^{-4} cm. The change in the energy by the surface potential Φ_S is shown to be toward higher electron energy on the assumption that surface ''lattice'' O^{2-} ions have less than the normal complement of cations. This assumption is not important to the discussion. The Fermi energy, or electrochemical potential of the electrons, is indicated by the level E_F, and the difference in energy between electrons at the bottom of the conduction band at the surface and the Fermi energy is indicated by $\Phi = E_C + \Phi_S - E_F$.

For the rate-controlling step (Eq. [15]), and the particular case of liquid iron oxide, we may express the rate as

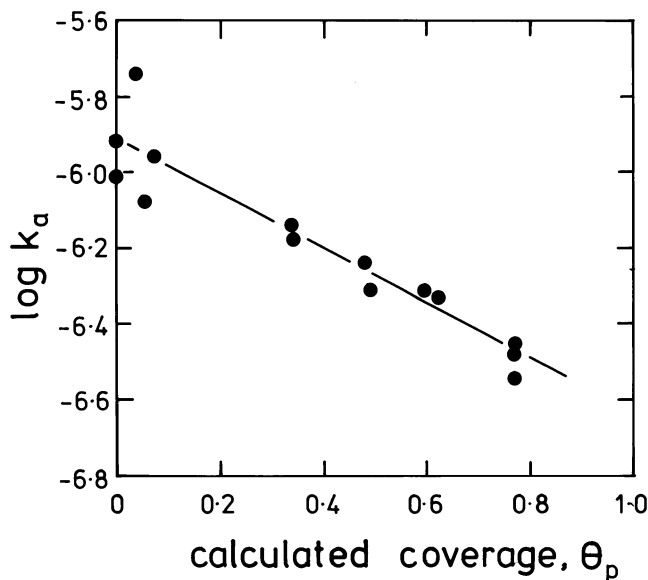$$v = k'pCO_2 \exp \frac{-2F\Phi}{RT} \qquad [19]$$

Fig. 11—Logarithms of the rate constants from Fig. 5 *vs* the calculated fractional surface coverage by P_2O_5.

where k' is a function of temperature (and density of surface reaction sites) and F is Faraday's constant. For an ideal redox couple, as discussed in detail by Reiss,[26] we may write

$$E_F = E^O + \frac{RT}{F} \ln \left(\frac{Fe^{2+}}{Fe^{3+}}\right) \qquad [20]$$

where E^O is a function of temperature only for a particular system. Substitution gives

$$v = pCO_2 \left[k' \exp \frac{-2F (E_C - E^O + \Phi_S)}{RT}\right]\left(\frac{Fe^{2+}}{Fe^{3+}}\right)^2 \qquad [21]$$

The studies of Gaskell and co-workers[17,18] have shown that there is a negligible change in the surface tension of liquid iron oxide with the Fe^{2+}/Fe^{3+} ratio over the complete liquid-phase field at about 1400 °C. Accordingly, there is a negligible change in the relative segregation of ionic species to the surface, and it is reasonable to expect that the surface potential Φ_S is approximately constant. Thus, the quantity in square brackets in Eq. [21] can be identified with the rational rate constant k_f in Eq. [14].

For semiconductor surfaces, a continuous space charge is considered to exist when the density of surface states exceeds about one for every thousand atoms at the surface.[27] If a surfactant has an adsorption coefficient of the order of unity with respect to a standard state of 1 mol pct, any effect on the space charge would therefore be expected to be continuous for bulk concentrations of the order of 0.1 mol pct and higher. Under these conditions, changes in the surface potential can be considered to be ''smoothed,'' *i.e.*, local structure can be ignored and the change in surface potential can be taken as the sum of the individual contributions of each adsorbed species. The compound P_2O_5 is the most acidic of the common components of slag systems, *i.e.*, it has the highest electron density (and lowest optical basicity).[28] Segregation of ''P_2O_5'' implies an excess in the

concentration of phosphate anions at the surface; hence, an increase in negative charge and an increase in the surface potential. It is reasonable to assume that segregation of ''Na_2O,'' one of the most basic oxides,[28] leads to an increase in the cationic (Na^+) concentration at the surface and, accordingly, to a decrease in the surface potential. An increase in the surface potential due to the segregation of phosphate ions is represented schematically in Figure 10(b) by the potential change $\Delta\Phi_P$. A decrease due to the segregation of Na_2O is represented by $\Delta\Phi_{Na}$.

For a potential change $\Delta\Phi$, Eq. [19] becomes

$$v = k'pCO_2 \exp \frac{-2F (\Phi + \Delta\Phi)}{RT} \qquad [22]$$

To a first approximation, it may be assumed that the value of E^O in Eq. [20] is unchanged by small *bulk* concentrations of a surfactant. Accordingly,

$$v = pCO_2 \left[k_f \exp \frac{-2F}{RT} \Delta\Phi\right]\left(\frac{Fe^{2+}}{Fe^{3+}}\right)^2 \qquad [23]$$

The expression in the square brackets is now the rational rate constant for the surfactant-containing melt, k_f'. It follows that

$$\frac{k_f'}{k_f} = \exp \frac{-2F}{RT} \Delta\Phi \qquad [24]$$

If the effect of the surfactant on the value of the bulk Fe^{2+}/Fe^{3+} ratio at constant oxygen potential is small, rate constants defined by Eq. [2] or [3] may be substituted in Eq. [24], *i.e.*,

$$\frac{k_f'}{k_f} \approx \frac{k_a}{k_{a,o}} \qquad [25]$$

where $k_{a,o}$ refers to the surfactant-free melt. If $\Delta\Phi°$ is defined as the total surface potential change at full coverage by the surfactant, we may therefore write

$$\ln \frac{k_a}{k_{a,o}} = \frac{-2F}{RT} \Delta\Phi° \theta \qquad [26]$$

where θ is the fractional coverage by the surfactant.

The rate constant data for P_2O_5-containing melts from Figure 5 are shown plotted in an appropriate form in Figure 11 with the values of the fractional coverage, θ_P, calculated for $K_P = 1$, approximately the average value for the adsorption coefficient from the earlier analysis of the surface tension data. The best straight line has a slope of −0.72, from which $\Delta\Phi_P° = 0.12$ V. If considered in terms of dipole moment changes at the surface, we may write

$$\Delta M_P° = \Delta\Phi_P°\varepsilon_O = N\Gamma_P° \Delta m_P \qquad [27]$$

where $\Delta M_P°$ is the total dipole moment change per unit area at saturation coverage, ε_o is the permittivity of free space (8.85×10^{-12} F m^{-1}), N is Avogadro's number, and Δm_P is the dipole moment per ''molecule'' of P_2O_5. The derived value of $\Delta M_P°$ is 1.1×10^{-12} C m^{-1}. For $\Gamma_P° = 7.3 \times 10^{-10}$ mol cm^{-2}, the value of Δm_P is 2.4×10^{-31} C m or 0.073 Debye per molecule.

No work function studies have been carried out on molten slag systems; hence, the derived magnitudes of $\Delta\Phi_P°$ or Δm_P cannot be directly tested against experiment. However,
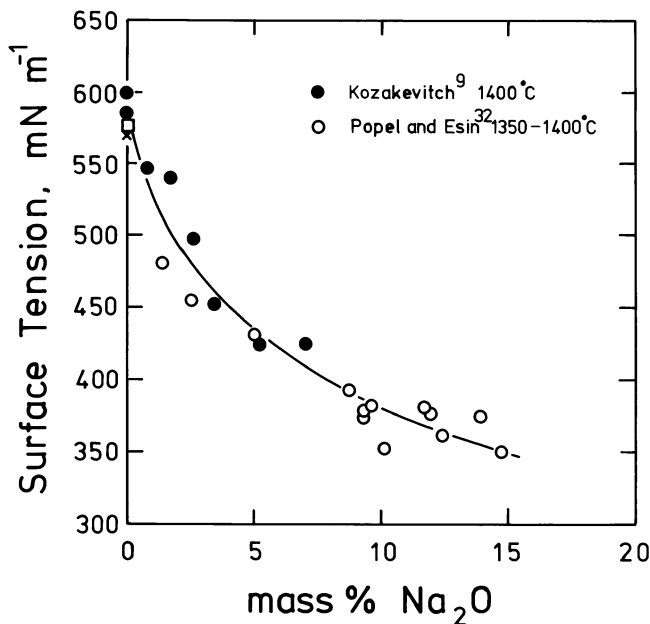
Fig. 12—Available surface tension data for ''FeO''-Na$_2$O melts at saturation with solid iron in comparison with Eq. [28].
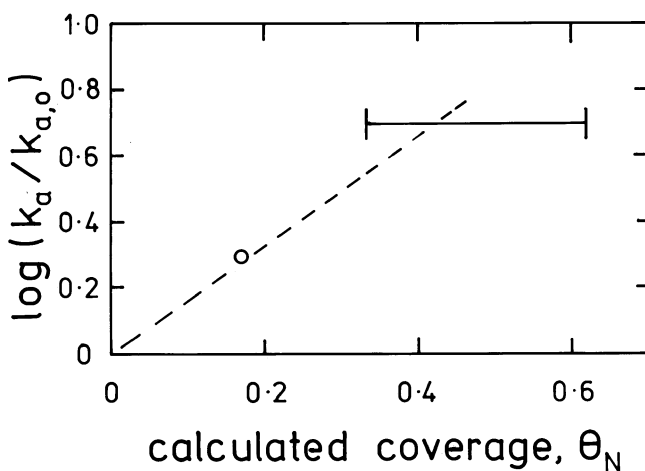

Fig. 13—Approximate data for the dependence of the rate constant on the calculated fractional surface coverage by Na$_2$O, plotted in accordance with Eq. [26].

indirect evidence suggests that the values are physically reasonable. Measurements[29,30] of the surface potential changes for solutions of aliphatic alcohols in water at about room temperature have generally found the dipole moment change per molecule adsorbed to be about 0.2 Debye. Taking the saturation coverage to be about 7.5×10^{-10} mol cm^{-2} gives a typical value for $\Delta M°$ of about 3×10^{-12} C m^{-1}. Studies by Derry and Ross[31] of work function changes caused by the adsorption of oxygen on the {111} and {100} faces of platinum have shown dipole moment changes of about 0.1 to 0.6 Debye per atom of oxygen adsorbed.

The limited observations on the effect of Na$_2$O on the kinetics allow only a rough analysis. The available surface tension data for ''FeO''-Na$_2$O melts at saturation with solid iron[9,32] are shown in Figure 12. The data are closely described by the Szyszkowski-form equation

$$\sigma = 584 - 86(\pm 12) \ln \quad [28]$$
$$\{1 + 0.95(\pm 0.4)[\text{mass pct Na}_2\text{O}]\}$$

where the uncertainties represent one standard deviation. No information is available on the activity coefficient of Na$_2$O in liquid iron oxide but, assuming that Henry's law is followed to a first approximation, it is reasonable to conclude that the adsorption coefficient of Na$_2$O, K_N, is of the order of 1.

It was deduced from the rate experiments that there was a twofold increase in the apparent rate constant at about 0.2 mass pct Na$_2$O and a fivefold increase at a concentration somewhere between 0.5 and 1.6 mass pct. Values of log $k_a/k_{a,o}$ vs the calculated fractional coverage by Na$_2$O are shown in Figure 13 and suggest a slope of the order of 1.5, which gives a value of $\Delta\Phi_N°$ of about -0.25 V. Taking the value of $RT\Gamma_N°$ to be 86 mN m^{-1} from Eq. [28] gives an effective dipole moment change per molecule of Na$_2$O, Δm_N, of about -0.18 Debye. Although this deduced value must be regarded as very approximate, the order of magnitude is again physically reasonable.

V. CONCLUSIONS

1. The apparent first-order rate constant for the dissociation of CO$_2$ on liquid iron oxide is decreased by small additions of the surfactant P$_2$O$_5$, up to a factor of about 4 at 3.5 mol pct P$_2$O$_5$ at 1673 K.
2. The apparent first-order rate constant at 1673 K is markedly increased by small additions of the surfactant Na$_2$O, probably by a factor of 2 at a concentration of 0.2 wt pct and by a factor of 5 at a concentration of between 0.5 and 1.6 wt pct.
3. The effects of P$_2$O$_5$ and Na$_2$O on the apparent first-order rate constant are significantly greater than would be expected from the small changes in the bulk basicity of liquid iron oxide, and must be attributed to the surface segregation of these components.
4. The present and previous studies are consistent with the transfer of two electrons being involved in the rate-determining step in the dissociation of CO$_2$ on liquid iron oxide.
5. A smoothed surface potential model, based on the Vol'kenshtein model for catalysis by semiconductors, may be used to relate changes in the value of the rate constant with changes in the surface potential due to the segregation of dilute surfactants.
6. Combination of the required surface potential changes with adsorption parameters deduced from available surface-tension measurements leads to physically reasonable values for the effective dipole moment changes per molecule of P$_2$O$_5$ or Na$_2$O.

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