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REACTION KINETICS OF SOME LIQUID SLAGS AT LOW IRON OXIDE CONTENT

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SYNOPSIS

Results are presented from several previously unpublished studies by the author's research group. They form part of a larger program aimed at understanding interfacial rate phenomena in reactions of slags typical of proposed iron bath smelting processes. Slag compositions are restricted to calcium aluminium silicates with $CaO/SiO_2 \approx 1$ and about 20 wt% Al_2O_3 with additions of up to 10 wt% "FeO", and results are reported only for 1350°C. Redox equilibria are presented for oxygen potentials ranging from $CO_2/CO = 0.01$ to air. Rotating iron disc studies are used to derive the interdiffusivity of iron in the melts as a function of the total iron concentration. Determinations of steady-state oxygen activities under high flowrates of H_2O-CO gas mixtures are used to provide information on the relative interfacial rates of H_2O-H_2 and CO_2-CO reactions. The results of isotope exchange rate studies involving deuterium and ^{14}C are used to derive rates of dissociation of H_2O and CO_2 on melts containing up to 1 wt% "FeO".

Key words: bath-smelting slags, redox equilibria, interdiffusivity, relative reaction rates, isotope exchange, iron dissolution, rotating disc.

INTRODUCTION

Interfacial rates of reaction of CO_2 and CO with liquid iron oxide and many simple molten slags containing more than about 30 mol% "FeO" are now reasonably well-established. First order rate constants for reduction by CO at iron-saturation have been shown [1,2] to increase with basicity, varying at 1400°C from about 3×10^{-6} mol cm^{-2} s^{-1} atm^{-1} for silica-saturated iron oxide to about 1×10^{-5} for iron oxide and about 1×10^{-4} for lime-saturated iron oxide.

Rates of dissociation of CO_2 on iron oxide-containing melts have been determined from measurements [3-5] of the rates of the isotope exchange reaction

$$^{14}CO_2 + CO \rightarrow CO_2 + ^{14}CO \qquad (1)$$

for melts in chemical equilibrium with various values of the CO_2/CO ratio. Where studies have been carried out on the same systems, it has been found that rate constants deduced from the isotope exchange studies are in very close agreement with those obtained from the available chemical reduction studies [1,2,6]. This agreement has been discussed in detail in two previous symposia [7,8].

Less information is available on interfacial rates of reaction of H_2O and H_2 with iron oxide-containing melts. Ban-ya et al [9] have shown that the rate of reduction of liquid iron oxide by hydrogen is very high. They concluded that the apparent first order rate constant at 1400°C was of the order of 1×10^{-3} mol cm^{-2} s^{-1} atm^{-1}, ie., about two orders of magnitude greater than that for CO. Relative rates of H_2O-H_2 and CO_2-CO reactions with silica-saturated liquid iron silicates have been studied [10] by measurement of the steady-state oxygen activity (obtained from the Fe^{+3}/Fe^{2+} ratio) of the melt under flowing H_2O-CO mixtures. It was deduced from these studies that the apparent first order rate constant for H_2 exceeded that for CO by a factor of about 50 at 1250°C and that for H_2O exceeded that for CO_2 by a factor of about 20, over the range of conditions of the study.

Rates of dissociation of H_2O on silica-saturated iron silicates have been measured [11] by the deuterium exchange reaction

$$HDO + H_2 \rightarrow HD + H_2O \qquad (2)$$

The results were shown to be consistent with an apparent first order rate constant for reduction by H_2 being about 1 order of magnitude higher than that for reduction by CO at 1400°C. This is consistent with work by Nagasaka [12] who showed that the H_2 reaction was at least six times faster than the CO reaction for an "FeO"-36 mol% SiO_2 melt at 1400°C.

In contrast to the foregoing, very little is known about interfacial reaction rates for slags of low iron oxide content and, in particular, those relevant to proposed iron bath smelting processes, ie., slags containing about 2-10 wt% FeO. It has been shown [13] that the mechanism of reduction of such slags by suspended iron-carbon droplets involves CO-CO_2 reactions across a gas halo and a knowledge of the kinetics at the gas-slag interface is needed for a full analysis. In the post-combustion region of such smelting processes, the gaseous atmosphere will contain significant amounts of H_2O and H_2 in addition to the carbon-oxygen gases, dependent on the rank of the coal used in the process. Accordingly, a knowledge of the interfacial rates of oxidation of the slags by both H_2O and CO_2 will be needed for detailed modelling of oxygen transfer processes in this region.

The present paper presents some of the results from several investigations which form parts of a broad study of kinetic phenomena in appropriate low iron oxide content slags. These investigations include studies of redox equilibria, interdiffusion phenomena, rates of isotope exchange with gases, steady-state oxygen activities in flowing gases, and rates of reduction at the gas-slag interface. Reported work will be for the idealized slag 40 CaO - 40 SiO_2 - 20 Al_2O_3 (mol%) with additions of iron oxide and, in general, the temperature will be restricted to 1350°C.

REDOX EQUILIBRIA

Redox equilibria have been studied by Xie [14]. In this work, a sample of about 50g of slag was held in an alumina crucible, 36 mm ID x 90 mm, within an alumina reaction tube in a resistance furnace. Dried air or purified CO_2-CO mixtures, prepared by calibrated capillary flowmeters, were bubbled into the molten slag at a total flowrate of 600 ml min^{-1} through a 4 mm ID recrystallized alumina tube inserted to within 5-10 mm above the the bottom of the crucible.

Slag samples were taken by quickly inserting and withdrawing a 4 mm ID alumina suction tube through a sealable hole in the water-cooled brass end cap of the reaction tube. Samples were broken from the tube, ground in a tungsten carbide mill, dissolved in 50% HCl, and analysed by the potassium dichromate method in accordance with the procedures described by Jeffrey and Hutchison [15]. Grinding was carried out with and without petroleum spirit to demonstrate the absence of oxidation during this process. Dissolution and titrations were carried out under flowing CO_2.

The results of measurements on a slag containing 3.3 wt% Fe as a function of time are shown in Figure 1, where the closed symbols for the data for $CO_2/CO = 1$ are for samples prereduced at $CO_2/CO = 0.01$. All other data are for samples which were initially produced by simply dissolving Fe_2O_3 in the master slag.

The data for $CO_2/CO = 0.01$ possibly indicate a slowly decreasing value of the Fe^{3+}/Fe^{2+} ratio with time but no time dependence is obvious at the other conditions. Accordingly, a fixed time of 60 min was taken for the remainder of the experiments. Results for slags with 0.65, 3.3, and 6.3 wt% total Fe and for oxygen potentials ranging from $CO_2/CO = 0.01$ to air are presented in the form of log Fe^{3+}/Fe^{2+} versus log CO_2/CO in Figure 2. Within the experimental scatter, the results are independent of the iron concentration and are represented by the expression:

$$(Fe^{3+} / Fe^{2+}) = 0.14\,(CO_2 / CO)^{0.45} \qquad (3)$$

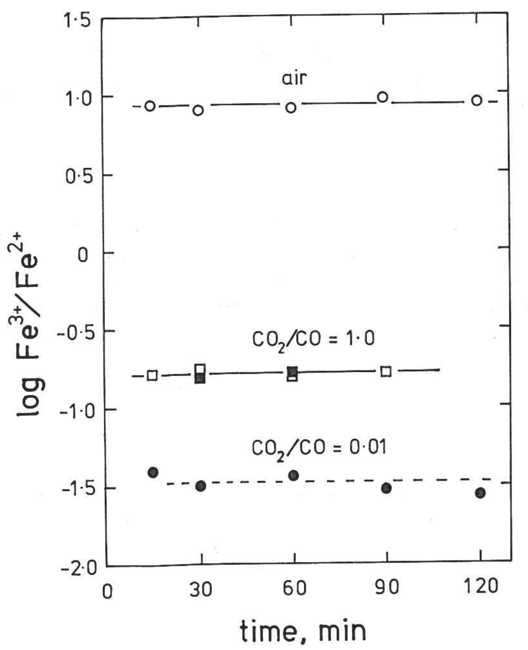


Fig. 1. Dependence of the Fe^{3+}/Fe^{2+} ratio on time for three sets of experiments with a melt containing 3.3 wt% total iron. The closed squares are for measurements with initially reduced melts (~ 1 hr at $CO_2/CO = 0.01$.)

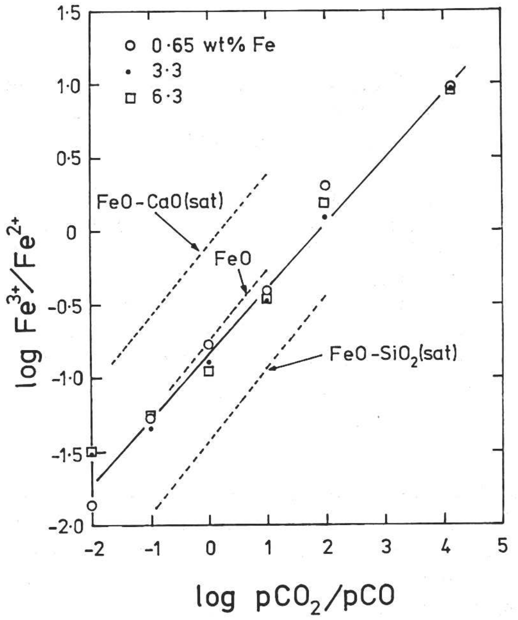


Fig. 2 Redox equilibria for melts of three iron concentrations at 1350°C.

As indicated in the figure, the behavior is close to that of liquid iron oxide at 1400-1600°C from the work of Darken and Gurry [16]. The results are also essentially coincident with the 1450°C data of Timucin and Morris [17] for a calcium iron silicate with $CaO/SiO_2 \approx 1$. For a 40 wt% "FeO" melt their data are closely described by

$$(Fe^{3+} / Fe^{2+}) = 0.15\,(CO_2 / CO)^{0.43} \qquad (4)$$

Also shown on the same figure are lines indicating the behavior of CaO-saturated iron oxide at 1300-1550°C [18], [19], and SiO_2-saturated iron oxide at 1250-1350°C [20].

ROTATING IRON DISC STUDIES

The experimental arrangement which was developed by Xie [14] for the rotating disc assembly within the hot zone of a vertical tube furnace is illustrated in Figure 3. Details on the preparation of the alumina-sheathed electrolytic iron cylinder to produce 20-22.5mm dia discs will be fully described elsewhere, as will details of the bearing assembly for holding the alumina rotating shaft within the furnace tube, maintaining an effective seal at the top of the furnace, and coupling of the shaft to a variable speed motor, etc.

The steps in the experimental procedure consisted of melting 1 03-110 g of premixed and pressed xides in the 36 mm ID crucible, bubbling air through the melt for a period of up to 1 hr, allowing the melt to remain stagnant for about 1/2 hr, introducing argon from the bottom of the furnace tube (600 ml min^{-1}), introducing the iron disc to about 14 mm above the bottom of the crucible, waiting 15 min, then stirring at 300 rpm for about 3 min. After taking an initial slag sample, kinetic experiments were then started at controlled rotation speeds with interceptions for slag sampling at appropriate intervals (≤15 min). Slag analysis was as described for the equilibrium studies.

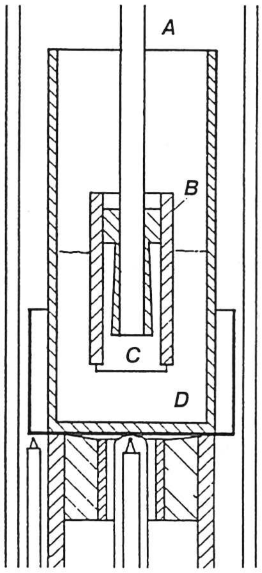
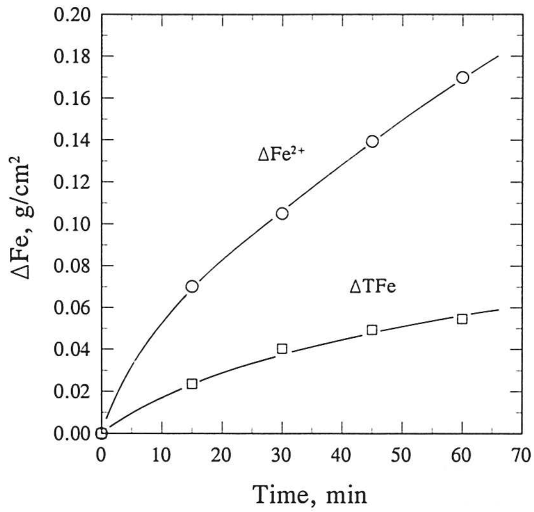


Fig. 3. Arrangement of the reaction zone for rotating disc experiments. A, rotating alumina shaft; B, alumina sheath; C, iron sample; D, slag.

Figure 4 shows typical results for a slag which initially contained 3.2 wt% total Fe with a starting value for Fe^{3+}/Fe^{2+} of 5.56, stirred at 300 ppm. Within experimental error, the total amounts of iron and ferrous iron produced and ferric iron removed from the melt are consistent with the mass balance restrictions imposed by

$$Fe + 2Fe^{3+} = 3Fe^{2+} \qquad (5)$$



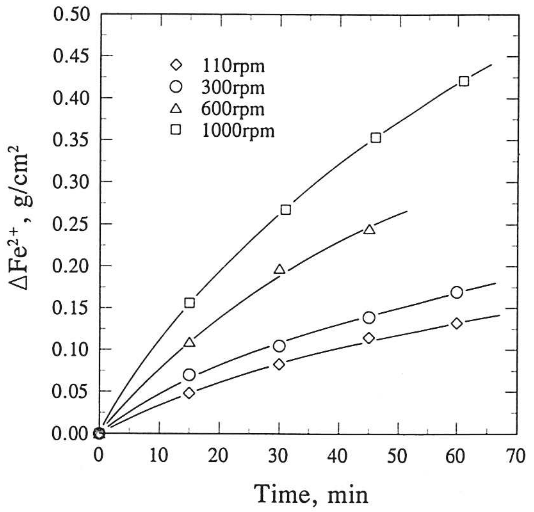


Fig. 4. Rates of iron dissolution and ferrous ion formation for a melt at a rotation speed of 300 rpm and with initial iron concentration and Fe^{3+}/Fe^{2+} ratio of 3.2 wt% and 5.6, respectively.

Fig. 5. Rate of iron dissolution for a melt initally containing 3.2 wt% total iron for different rotation speeds. Initial values for the Fe^{3+}/Fe^{2+} ratio were about 5.5.

This was found to be true for all experiments begun with Fe^{3+}/Fe^{2+} below about 5.6. Above this value a lack of mass balance indicated significant contributions from the simple dissociation of the slag ie., evolution of oxygen when the equilibrium oxygen pressure exceeded about 10^{-2} atm.

Results presented in Figure 5, again for melts initially containing 3.2 wt% total iron, show an increasing rate of dissolution of iron with increasing rotation speed. Xie [14] has demonstrated that the rate data are closely consistent with a first order dependence on the difference in bulk and interface concentrations of Fe^{2+} (or Fe^{3+}), assuming equilibrium (5) to be established at the interface. The resulting mass transfer coefficients were also found to be closely proportional to the square root of the rotation speed.

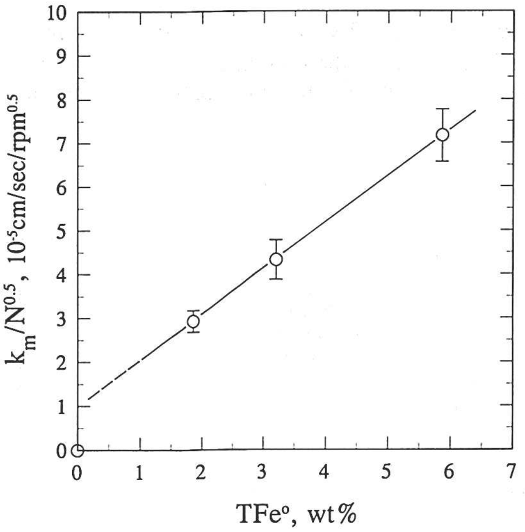
The results for 14 separate experiments covering three iron concentrations are summarized in Figure 6, the best line through the data being given by:

$$k_m = (1+1.05\%Fe)\, N^{1/2}\, x\ 10^{-5} cm\ s^{-1} \qquad (6)$$

where k_m is the mass transfer coefficient and N is the rotation speed in rpm. If the interdiffusivity is assumed to be a constant at each experimental condition, the well-established [21] solutions for diffusion to a rotating disc lead to:

$$D^{2/3}\ \nu^{-1/6} = 3.2\ x\ 10^{-5}\ (1+1.05\%Fe) \qquad (7)$$

where D is the interdiffusivity in cm^2s^{-1} and ν is the kinematic viscosity in $cm^2\ s^{-1}$. Two sets of experiments with initial Fe^{3+}/Fe^{2+} ratios differing by a factor of about two showed no significant differences in the values of the derived mass transfer coefficients (at given total iron contents).



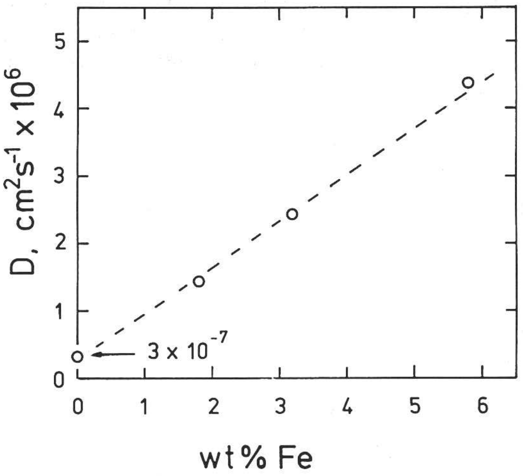


Fig. 6. Values of $k_m/N^{1/2}$ as a function of total iron concentration.

Fig. 7. Deduced values of the diffusivity of iron as a function of total iron concentration.

Viscosity and density data at 1350°C for this system are available from the work of Kato and Minowa [22]. Substitution in Eq. 7 gives the deduced values for the diffusivity at each of the iron concentrations shown in Figure 7. There is a marked dependence on the total iron concentration with a limiting value as $\%Fe \rightarrow 0$ of about $3 \times 10^{-7}\ cm^2\ s^{-1}$. This is in good accord with the self-diffusivities of the mobile cations for this melt at 1350°C; namely, $3.2 \pm 1 \times 10^{-7}\ cm^2\ s^{-1}$ for calcium from the work of Tower and Chipman [23] and about $1 \times 10^{-7}\ cm^2\ s^{-1}$ for aluminium from the work of Henderson and co-workers [24].

RELATIVE RATES OF H_2O-H_2 AND CO_2-CO REACTIONS

Following the success of the steady-state technique in establishing relative rate phenomena on SiO_2-saturated iron oxide[10], Yang [25] has carried out measurements of the steady-state Fe^{3+}/Fe^{2+} ratio in low iron oxide content slags under impinging flows of H_2O-CO gas mixtures The arrangement of the reaction zone, showing the positioning of the platinum crucible with respect to the 5 mm ID alumina gas delivery tube, is shown in Figure 8. Other experimental details were essentially the same as described elsewhere [10] and chemical analysis procedures were indentical to those used in the equilibrium studies.

The small slag samples, 0.2-0.25 g, were found to reach steady values for the Fe^{3+}/Fe^{2+} ratio after 30-40 min and the values were independent of total gas flowrate above 300 ml min^{-1}. Data were collected at times exceeding 60 min and with gas flowrates of about 500 ml min^{-1}. Figure 9 shows the resulting steady-state values for Fe^{3+}/Fe^{2+} as a function of the H_2O/CO ratio at 1350°C for slags with $CaO/SiO_2 \approx 1.08$, Al_2O_3 = 19-20 wt%, and "FeO" contents of 5 and 10 wt%. The higher iron oxide content melts tend to give lower values for the ratio but, within the experimental scatter, no significant separation of the results can be made. Also indicated on the figure is the expected behavior, assuming water-gas equilibrium and the redox equilibria shown earlier in this paper (and confirmed in more detail by Yang [25]).

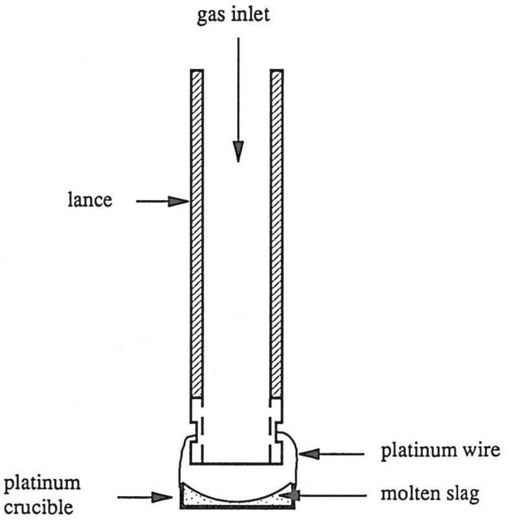


Fig. 8. Experimental arrangement used in the steady-state measurements.

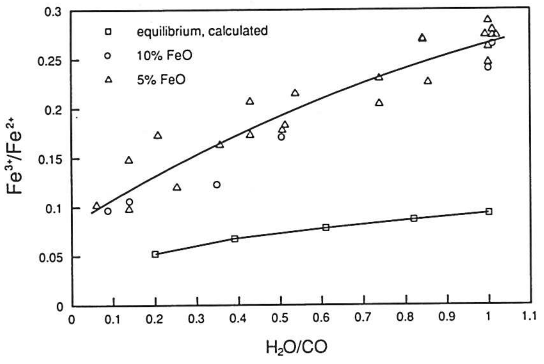


Fig. 9. Steady-state values for Fe^{3+}/Fe^{2+} as a function of the H_2O/CO ratio of the impinging gas stream.

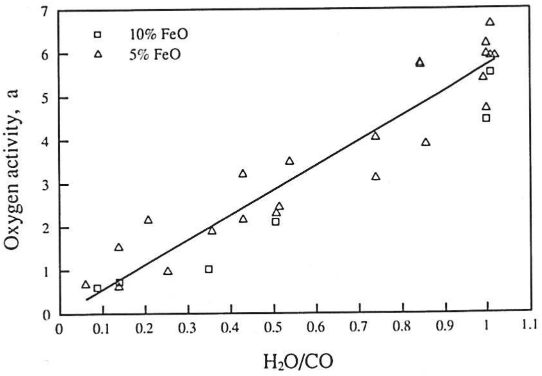


Fig. 10 Date of Figure 9 expressed as steady-state oxygen activities of the melts (standard state CO_2/CO = 1).

Assuming that the independence on flowrate indicates that the back reactions can be neglected, the data represent the values of Fe^{3+}/Fe^{2+} at which rates of oxidation by H_2O equal the rates of reduction by CO. Within the limits of the experimental scatter, additions of up to about 50% argon to the gas stream were found not to affect the results, indicating that the reaction orders with respect pH_2O and pCO are the same. If the reasonable assumption is made that the reactions are first order, the results indicate that the first order rate constant for oxidation by H_2O exceeds that for reduction by CO by a factor of 10 when $Fe+^3/Fe^{2+}$ is about 0.1. The rate constants are equal when Fe^{3+}/Fe^{2+} is about 0.25.

Formally, we may express the equality in rates as

$$k_1\ pCO\ a_o^{1-x} = k_2\ pH_2O\ a_o^{-y} \tag{8}$$

where k_1 and k_2 are apparent first order rate constants, a_o is the activity of oxygen in the melt and the reaction orders with respect to a_o are asumed to hold over the range of conditions of the experiments. If the standard state for a_o is taken as $pCO_2/pCO = 1$, it has been shown [10] that

$$a_o^{1-x+y} = \frac{k_1}{k_3}\frac{pH_2O}{pCO} \tag{9}$$

where k_3 is the apparent first order rate constant for the oxidation reaction by CO_2, defined by the consistent forward rate equation

$$v = k_3\ pCO_2\ a_o^{-x} \tag{10}$$

if microscopic reversibility is assumed.

The data of Figure 9 are shown again in Figure 10 as steady-state oxygen activities, calculated via Eq. 3, as a function of the H_2O/CO ratio. Within the experimental scatter there is a linear dependence, consistent with $x = y$, ie., the same dependences on the oxygen activity for H_2O-H_2 and CO_2-CO reactions. If this is correct, the rate constant for oxidation by H_2O exceeds that by CO_2 by a factor of about 6 over the range of oxidation states covered by the experiments. This conclusion must be regarded as tentative, however, since the linear dependence in Figure 10 has not been established with high precision.

ISOTOPE EXCHANGE STUDIES

Studies of the ^{14}C exchange reaction between CO_2 and CO, Eq. (1), have been carried out by Sun [16] on a number of slags in the CaO-SiO_2-Al_2O_3 system at low iron oxide content. The experimental technique was essentially identical to that described in detail elsewhere [3], [4], [5]. The studies were confined to concentrations of "FeO" below about 1.3 wt% where interactions with the platinum-rhodium susceptor did not significantly affect the iron oxide concentration of the thin slag films during the experiments.

No experimentally significant difference could be established for the apparent rate constant for the dissociation of CO_2 on given slag systems between pure melts (<0.1 wt% FeO) and those containing about 1 wt% "FeO".

Glaws [27] has extended his work on deuterium exchange, Eq. (2), to some calcium alumino silicates at low iron oxide content. Again, the experimental technique was identical to that previously described [11]. No difference in the apparent rate constants for the dissociation of H_2O could be found for melts containing 0.1 and 1.0 wt% "FeO", and substitution of about 1 wt% MnO or Cr_2O_3 resulted in no detectable change in the rate constants.

Results from both of these studies are presented in logathrimic form in Figure 11 as values of the apparent first order rate constant versus the imposed CO_2/CO or H_2O/H_2 ratio. The data are for the slag system with $CaO/SiO_2=1$ with 20 wt% Al_2O_3 at 1350°C. For convenience in comparing the data, the common oxygen potential of 10^{-9} atm is indicated for the two sets of data.

The independence on "FeO" concentration and the lack of effect of other solutes suggest that the measurements represent the rates at which oxygen can be exchanged with adsorbed oxygen on the surface under conditions where adsorption equilibria are not significantly affected by dissolved transition metal ions. Identification of the rates of dissociation with rates of chemical oxidation can only be expected when the chemisorption of oxygen is at virtual equilibrium with the dissolved oxidizable species. Accordingly, rate constants for oxidation of iron at low "FeO" contents would be expected to be lower than the values given in the figure.

Under steady-state conditions the Fe^{3+}/Fe^{2+} ratio in the melt will reach the value for equilibrium with the oxygen potential at the surface. Accordingly, the relative rates of dissociation of H_2O and CO_2 determined by either isotope exchange or the steady-state technique of the previous section should agree. The isotope exchange studies indicate a factor of about 10 for the ratio of rate constants at values of a_o (standard state $pCO_2/pCO=1$) varying between about 0.2 to about 3. The steady-state measurements gave a factor of about 6 at values of a_O varying between about 1 and 6 at concentrations of "FeO" of 5 and 10 wt%. Within the uncertainties of both studies, the agreement is satisfactory. It is reasonable to conclude that oxidation and reduction reactions involving H_2O-H_2 are roughly an order of magnitude faster than reactions involving CO_2-CO for these low iron oxide content melts.

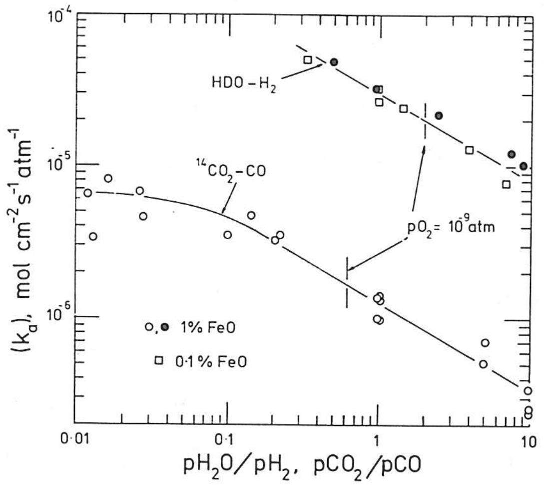


Fig. 11. Derived values of the apparent first order rate constants for the dissociation of H_2O and CO_2 on very low iron oxide content melts from isotope exchange measurements.

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