Kinetics of Evolution of SO_2 From Hot Metallurgical Slags

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The kinetics of the evolution of SO_2 gas from a liquid synthetic blast furnace-type slag $(CaO-Al_2O_3-SiO_2)$ in an atmosphere of $O_2 + Ar$ gas at a total pressure of 1 atm for $0.003 \leq P_{O_2} \leq 1.00$ atm has been studied in the range 1360 to 1460°C. The process has been followed by collecting and analyzing the SO_2 as it forms, and also by observing the change in weight of the slag sample with time. The effect of slag composition has also been studied. For partial pressures of oxygen less than about 0.1 atm, the rate is very rapid and is controlled by transport in the gas phase. At greater values of P_{O_2}, the rate is much slower and is controlled by a chemical process. In the high P_{O_2} region, the process is half-order with respect to the concentration of sulfur in the slag. This half-order dependence on sulfur concentration in the slag may be explained by an initial fast irreversible reaction to form two intermediate species which then decompose at equal rates to give the final products. Additions to the slag of iron or manganese oxides greatly accelerate the rate of evolution of SO_2 at $P_{O_2} = 1.00$ atm. This is interpreted to mean that a charge transfer process, possibly involving S^{2-} and O^{2-} ions, is rate-controlling at $P_{O_2} = 1$ atm. It is also apparent that Fe^{2+} and Fe^{3+} (or Mn^{2+} and Mn^{3+}) ions can act as charge carriers. Some measurements with actual industrial blast furnace slags are also reported.

THE growing concern for the environment necessitates investigation of means to minimize the contamination of the atmosphere by sulfur-bearing gases. In a steel plant, gases containing sulfur may be evolved when hot blast furnace slags, which may contain in excess of 2 wt pct sulfur, and waste products of external desulfurization processes are exposed to air or water vapor. The present paper reports the results of a study of the rate at which sulfur dioxide is released by a synthetic liquid blast furnace slag when it is exposed to an atmosphere of oxygen and argon at 1 atm total pressure. The temperature and composition of the slag, partial pressure of oxygen, and velocity of gas over the slag are the primary experimental variables.

The only previous kinetic investigation of this type is that of Turkdogan and Pearce[1] who used $CO + CO_2$ gas mixtures to study the rate of desulfurization of $CaO-SiO_2$ and $CaO-Al_2O_3$ melts at 1550°C. For shallow melts with depths between 1 to 4 mm the experimental data could not be explained on the basis of a single rate-controlling step that would be valid at all partial pressures of oxygen. The rate data were analyzed using theoretical equations for a process controlled either by diffusion in the slag or by an interfacial reaction at the slag-gas interface. Equally good agreement was obtained between the experimental results and theoretical predictions for either rate process.

EXPERIMENTAL

A horizontal platinum resistance tube furnace was used for the study. The slag sample of approximately 1.5 g was held in a 99.8+ pct pure high density alumina boat inside a 7/8 in. ID alumina reaction tube which in turn was placed within the furnace tube. The depth of the melt was approximately 0.4 cm. In a few experiments, a larger boat with a capacity of about 3.0 g of slag was used. The boat was held in a larger ceramic carrier boat which was attached to a ceramic rod so that the entire assembly could be inserted quickly into or withdrawn from the furnace. After more than three hours at temperature, the alumina boats were not attacked by the slag.

The flow rates of oxygen and argon were measured using capillary flow meters. A long semi-cylindrical ceramic insert was placed in the lower half of the reaction tube upstream from the reaction zone to give well-defined flow conditions over the sample. The reaction temperature was measured with a Pt-Pt/10 pct Rh thermocouple embedded in the ceramic insert with its hot junction about 1 cm from the sample. Slag temperatures were varied over the range 1360 to 1460°C, and measurement of the temperature is estimated to be accurate to within ±2°C.

The exit gases were analyzed for SO_2 by a Leco automatic titrator using iodometric titration with a starch indicator. Calibration runs with NBS standard Fe samples showed that quantitative stoichiometric titrations could be achieved with an uncertainty of ±2 pct.

To begin a typical run, the tube was flushed with argon for several minutes. Then the sample was inserted quickly into the furnace tube from the downstream end with the flow of argon maintained through the furnace. A tubular connection was made between the furnace tube and the titrator, and the titrator was immediately turned on. The slag sample was allowed to come to temperature in the argon stream for a period of about 10 min. During this time, about 1 to 2 pct of the total sulfur in the sample was lost to the gas stream, apparently by reaction with the small amount of oxygen in the air admitted during insertion of the sample. The argon flow was then replaced by a stream of an O_2/Ar gas mixture having the desired partial pressure of

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oxygen and at the desired total flow rate. The exiting gas passed into the titrator which continuously titrated the SO_2 contained in the gas.

A synthetic slag was made by mixing high purity CaS powder (99.9 pct CaS) with a powdered oxide mixture with the composition: SiO_2 38.8 pct, Al_2O_3 17.8 pct, CaO 42.7 pct and MgO 0.7 pct (by wt). The mixture was melted in a covered graphite crucible, then poured out, cooled and ground to approximately −20 mesh. The slag was analyzed for total sulfur by two different methods using the Leco titrator. In one method, a sample of pure slag was placed in the platinum resistance furnace used for the kinetic experiments, and in the other, a mixture of slag and Fe, Sn and Cu "accelerators" was heated in a standard Leco combustion furnace. The total sulfur content of the slag was 1.59 ± 0.03 wt pct, which is typical of that found in an actual industrial blast furnace slag. The amount of slag charged was weighed carefully, but the actual quantity varied slightly from run to run. A typical sample of a total weight of 1.5 g thus contained about 0.024 g of sulfur.

In some experiments additions of Fe_2O_3, Fe_3O_4 and MnO were made to the powdered slag. The Fe_2O_3 was reagent grade while the Fe_3O_4 was Fisher purified grade. The MnO was prepared by calcination of reagent grade $MnCO_3$.

A few experiments were also performed with actual blast furnace slags. The three slags used had the following composition (wt pct): SiO_2 36 ±1 pct, Al_2O_3 9.5 ±1 pct, CaO 35 ±1 pct, Mgo 16 ±1.5 pct, MnO 0.4 ±0.1 pct, S 2 ±0.2 pct, total Fe 0.83 to 1.43 pct (by wt). A few experiments were performed with these actual slags, and, unless otherwise stated, all results refer to measurements made using the synthetic slag.

RESULTS

In Fig. 1 are shown rate curves obtained for several partial pressures of oxygen, P_{O_2}. All curves shown were obtained at about the same temperature (1405 to 1416°C), and the same total gas flow rate of 1250 to 1350 ml/min measured at 25°C and 1 atm. To illustrate the nature of the results, actual experimental points are shown on the curve for P_{O_2} = 0.54 atm. The

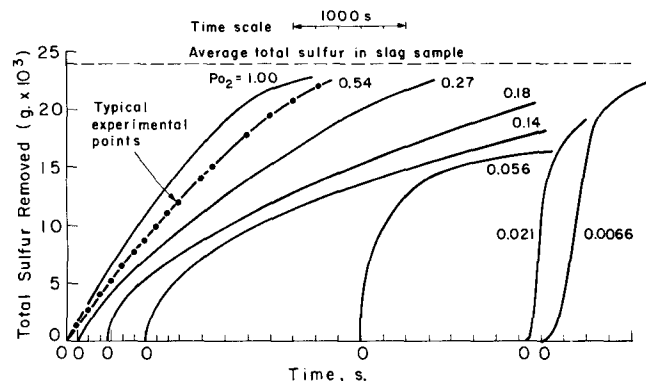time coordinate is displaced for each curve with each curve originating at zero time to avoid confusion between the results at different oxygen partial pressures. For each curve, a very small correction has been made for the sulfur which was lost before the oxygen was admitted. All the experiments shown in Fig. 1 were continued for much longer times than shown so that virtually all of the sulfur in the slag was removed. The nominal surface area of the slag as calculated from the dimensions of the boat with no account taken of meniscus effects was 1.85 cm^2, but since the actual surface area is not accurately known, the results are presented simply as total grams of sulfur removed.

Fig. 1 shows that the rate of sulfur removal is relatively slow at the higher partial pressures of oxygen, and that this rate increases as the oxygen partial pressure increases. However, below approximately P_{O_2} = 0.3 atm, a rate curve has two parts: an initial period when the rate is quite high, and a later period when the rate is much lower. For instance, at P_{O_2} = 0.14 atm, the rate during the first 20 to 300 s is faster than is the rate during the equivalent period with P_{O_2} = 1.00 atm. However, after this initial period, the rate with P_{O_2} = 0.14 atm slows to become less than it is with P_{O_2} = 1.00 atm. This observation of the initial rates is consistent with that of Turkdogan and Pearce[1] who noted that the rates of desulfurization of CaO-SiO_2 melts in pure oxygen were noticeably slower than in a 1 pct O_2+N_2 mixture. However, no actual rate data were presented by these investigators. In Fig. 2 the rate curve for P_{O_2} = 0.021 atm is shown expanded so that details are more evident. Points shown are actual experimental points. The very early induction period apparently arises because the initial flow of oxidizing gas forward-mixes with the inert gas stream in the reaction tube just after the gas flow is changed to start the experiment. This induction period becomes negligible for values of P_{O_2} greater than 0.1 atm. From the curve, which is typical of all rate curves for P_{O_2} < 0.1 atm, it can be seen that the early fast period obeys a linear rate law. The onset of the slower process, point B, occurs quite abruptly. As the partial pressure of oxygen is decreased, point B occurs at higher and higher fractions of total sulfur removed (Fig. 1). However, the rate of the slower process after point B is reached decreases as the partial pressure of oxygen in the incoming gas is reduced.

The Initial Fast Process

The linearity of the initial fast portion of the rate curves when P_{O_2} < 0.1 atm suggests that in this range of oxygen partial pressures, the reaction is gas transport-controlled. In Fig. 3 the rate of evolution of sulfur during the initial period (*i.e.*, the slope of the line AB in Fig. 2) is plotted versus P_{O_2} for experiments at several oxygen partial pressures with three different total gas flow rates and for a nominal surface area of the slag of 2.90 cm^2. The dashed lines are calculated rates which would be observed if the total supply of oxygen gas were consumed by the reaction:

$$(S^{2-}) + 3/2\ O_2\ (g) = SO_2\ (g) + (O^{2-}) \qquad [1]$$
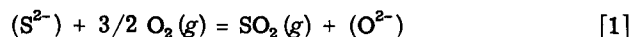
The species in parentheses are in the slag. Evidence that this is the overall process will be given later. It

Fig. 1—Sulfur removal at different P_{O_2} (in atm). Curve for P_{O_2} = 0.18 atm obtained at 1406°C. All other curves in the temperature range 1411 to 1417°C. Total gas flow rate in the range 1250 to 1350 ml/cm. Nominal surface area 1.85 cm^2. Origin of abscissa scale displaced for each curve to avoid overlap.

can be seen that the experimental rates vary directly with oxygen pressure at constant total flow rate and that approximately 60 pct of the total amount of oxygen supplied is consumed by the reaction. When smaller boats with a nominal surface area of 1.85 cm^2 were used, linear plots of the desulfurization rate vs P_{O_2} again were obtained. In this case, only about 40 pct of the total oxygen supply was consumed. It was also found that temperature in the range of 1360 to 1460°C had very little effect upon the rate for the initial linear period of the curves. Furthermore, the same curve for the rate of sulfur removal versus P_{O_2} was obtained when the actual industrial slags rather than the synthetic slag were studied. These observations indicate that the reaction is controlled by transport in the gas phase for the fast linear period of the rate curves obtained at lower values of P_{O_2}.

Weight Loss Experiments

Additional information on the nature of the reaction was obtained by withdrawing samples rapidly from the furnace after various exposure times, quenching them in air, and recording the loss in weight. For these experiments, large Al_2O_3 boats holding about 3.0 g slag were used. The results are shown in Fig. 4. In this figure, $t = 0$ is the time at which the oxygen flow was started with $P_{O_2} = 0.0039$ atm. For this low value of P_{O_2}, Fig. 1 shows that the initial linear fast portion of the rate curve persists until nearly all the sulfur
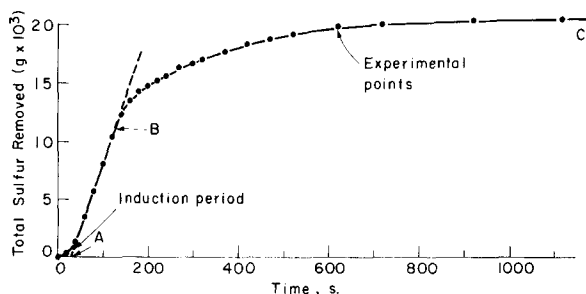

Fig. 2—Typical removal curve for low oxygen levels (P_{O_2} = 0.021 atm) indicating two rate processes. A-B initial linear rate, B-C chemical control. T = 1414°C. Total gas flow rate 1300 N ml/min. Nominal surface area 1.85 cm^2.
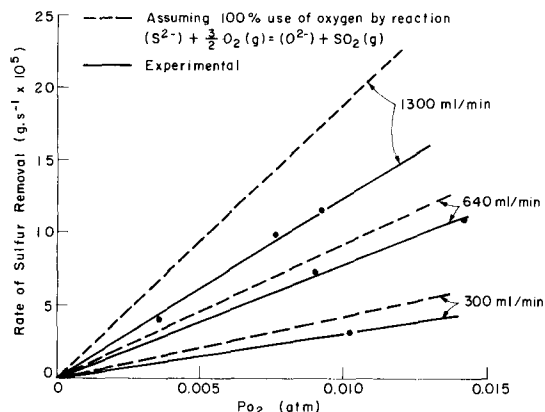

Fig. 3—Rate of sulfur removal for initial linear portion of curves at low P_{O_2}. T = 1410 to 1420°C. Nominal surface area 2.90 cm^2. Flow rate measured at 25°C, 1 atm total pressure.
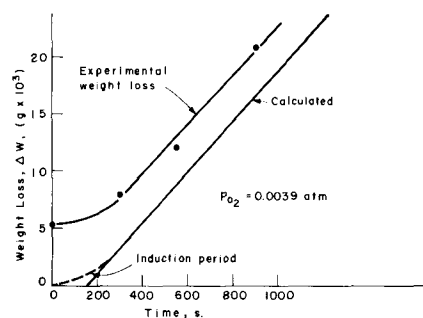

Fig. 4—Weight loss measurements at low P_{O_2}. P_{O_2} = 0.0039 atm, T = 1398 to 1412°C. Total gas flow rate 1250 to 1350 ml/min. Nominal surface area 2.90 cm^2. Calculated curve-weight loss calculated from weight of sulfur removed and stoichiometric addition of oxygen to melt by reaction. $(S^{2-}) + 3/2\ O_2(g) = (O^{2-}) + SO_2(g)$.

has been removed before the transition occurs to the slower process. The point at $t = 0$ was obtained from a sample which was melted under argon and then quenched in air. It can be seen that a weight loss of about 0.005 g occurs in quenching. If the overall reaction is that given by Eq. [1], then every S^{2-} ion removed from the melt is replaced by an O^{2-} ion, and so the observed weight loss, Δw, at any time would be one half of the weight change due simply to the removal of sulfur, *i.e.*:

$$\Delta w = \frac{M_S - M_O}{M_S} \cdot (w_S^o - w_S) = \frac{16.06}{32.06}\ (w_S^o - w_S)$$

$$= 0.50\ (w_S^o - w_S) \qquad [2]$$

where M_S and M_O are the molecular weights of sulfur and oxygen, w_S is the weight of sulfur in the sample at any time, and w_S^o is the initial sulfur content. A plot of $0.50\ (w_S^o - w_S)$ calculated from the results of the titration experiments described earlier is also shown in Fig. 4. The slope of this line is obtained by multiplying the rate corresponding to $P_{O_2} = 0.0039$ atm and a total flow rate of 1300 ml/min, as read off Fig. 3, by the factor of 0.50. An initial induction time of 250 s has been estimated for this curve. This is approximately the start-up time actually observed in titration experiments at this oxygen partial pressure. Fig. 5 shows results similar to those of Fig. 4, except that the experiments were performed at $P_{O_2} = 1.00$ atm where no initial fast portion is observed in the rate curves.

Although the weight loss is not determined precisely because of the nature of the experiment, it appears that Eq. [1] describes the overall reaction occurring at any time both during the initial fast process at low values of P_{O_2} and for the slower process at $P_{O_2} = 1.00$ atm. That is, no appreciable amounts of sulfate ions or other oxy-sulfide species are formed within the slag at any time during the process even though SO_4^{2-} is probably the thermodynamically stable form of sulfur in these slags at these oxygen pressures and temperatures.[2,3] It is to be noted that P_{SO_2} is kept essentially at zero by the nature of the experiment. However, these results do not rule out the possibility that species such as sulfates and pyro-sulfates form on the surface of the melt.

For every experiment, the total weight loss was measured after the sulfur had been completely removed
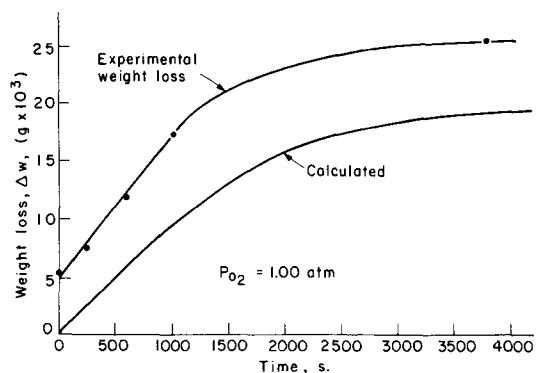
Fig. 5—Weight loss measurements at P_{O_2} = 1.00 atm. T = 1395 to 1405°C. Total gas flow rate 1300 ml/min. Nominal surface area 2.90 cm². Calculated curve-weight loss calculated from weight of sulfur removed and stoichiometric addition of oxygen to melt by reaction. $(S^{2-}) + 3/2\ O_2(g) = (O^{2-}) + SO_2(g)$.

from the samples. For the overall process represented by Eq. [1], the weight loss should be $(0.50) \cdot w_S^O$ (Eq. [2]). In all cases, the total weight loss was $(0.63 \pm 0.1) \cdot w_S^O$. This discrepancy can be explained if about 6 pct of the sulfur in the sample was initially present as sulfate rather than sulfide ions. Some of the weight loss could also result from the oxidation of carbon dissolved or entrained in the slag during melting of the slag in graphite crucibles. Some loss in weight might result from volatilization of other species. However, no deposits were observed in the cooler portions of the system downstream from the slag sample.

The Slow Process

For the latter portions of the rate curves at the lower values of P_{O_2}, and for virtually the whole of the rate curves at the higher values of P_{O_2} (>0.3 atm), the relatively slow process that is observed is no longer gas transport-controlled. For example, the rate of removal of sulfur is quite insensitive to the total gas flow for flow rates greater than about 500 ml/min measured at 25°C, 1 atm. Increasing the total rate from 1300 to 2300 ml/min only increases the rate of evolution of SO_2 by about 3 pct. For flow rates less than 500 ml/min, the reaction rate drops off slowly. At a flow rate of 160 ml/min, the rate of SO_2 evolution has decreased by about 20 pct from its value at 1300 ml/min. All experiments discussed subsequently in this section were performed in the high P_{O_2} range at a total gas flow rate of 1300 ml/min.

Attempts were made to fit these rate curves with a wide variety of mathematical relationships, and it was found that the curves for the slow process can be fitted very well by a rate equation of order one-half with respect to sulfur concentration. That is:

$$dw_S/dt = -kc_S^{1/2} \qquad [3]$$

where k is the overall rate constant and w_S is the weight fraction of sulfur in the slag at any time t. The sulfur concentration, c_S, is defined in terms of the weight of sulfur in the slag at time t and the total weight of the slag, w_T:

$$c_S = w_S/w_T \qquad [4]$$

Thus, the initial sulfur concentration in the synthetic

slag, c_S^O, is 0.0159 ± 0.0003. However, c_S^O may vary slightly from run to run because of the small amount of sulfur lost during equilibration of temperature under an argon atmosphere before oxygen is admitted.

The value of c_S^O is not known precisely for any given run, and a method of analyzing the data has been devised which does not depend on it. A calculated value of the initial sulfur content, w_S^O, is obtained which then gives a self-consistent value of c_S^O. Inserting Eq. [4] into Eq. [3] and integrating the resulting equation between the limits of w_S^O at t_0 and w_S at t gives:

$$\frac{(w_S^O - w_S)}{(t - t_0)} = k \cdot \left(\frac{w_S^O}{w_T}\right)^{1/2} - \left(\frac{k}{w_T^{1/2}}\right)^2 \cdot \frac{(t - t_0)}{4} \qquad [5]$$

The integrated equation has been manipulated and squared to obtain this form. In Eq. [5], $(w_S^O - w_S)$ is simply the amount of sulfur removed from time t_0 until time t. A plot of $(w_S^O - w_S)/(t - t_0)$ vs $(t - t_0)$ has $k \cdot (w_S^O/w_T)^{1/2}$ as the intercept, and $(k^2/4w_T)$ as the slope. w_T is known, and so k and w_S^O can be obtained for each experiment. For all rate curves analyzed in this way, the value of w_S^O obtained was within 7 pct of the total initial sulfur content of the slag which was found by chemical analysis to be 1.59 pct by weight.

Several plots of $(w_S^O - w_S)/(t - t_0)$ vs $(t - t_0)$ are shown in Fig. 6 for various temperatures when P_{O_2} = 1.00 atm, and also for various oxygen partial pressures with temperatures within 5° of 1412°C. For all the curves with P_{O_2} = 1.00 atm, and for the curve with P_{O_2} = 0.54 atm, t_0 was taken as the time at which the oxygen was first admitted. The linear plots obtained indicate that the process is described satisfactorily by Eq. [3], and that this rate law is obeyed even during the initial period of the experiments when $P_{O_2} \geq 0.54$ atm.

With $P_{O_2} \leq 0.27$ atm, linear plots are not obtained in Fig. 6 during the initial portions of the curves because of the rapid initial rate. However, these curves do become linear after some time has elapsed and thus the slower process encountered during the latter parts of these experiments also complies with Eq. [3]. In the analysis of the curves for $P_{O_2} \leq 0.27$ atm, it was not possible to take t_0 as the time at which the oxygen was
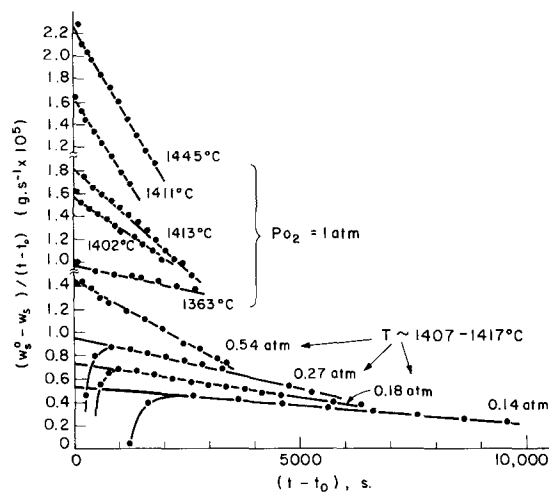

Fig. 6—Test of half-order rate law (Eq. [5]) at different temperatures and P_{O_2}. Total gas flow rate 1250 to 1350 ml/min. Nominal surface area 1.85 cm².

first admitted. Rather, a calculated value of t_0 in each case was obtained by solving Eq. [5] for t_0 using three widely spaced experimental points taken from the later portion of the rate curve, and by eliminating w_S^0 and k from the three resultant simultaneous equations. Alternatively, these curves could be analyzed by arbitrarily choosing t_0 as some large value (say 3000 s), and then plotting $(w_S^0 - w_S)/(t - t_0)$ vs $(t - t_0)$ as before. In this case, w_S^0 is the value of w_S at $t = t_0$, and $(w_S^0 - w_S)$, as well as $(t - t_0)$, can have positive or negative values. Rate constants were also calculated in this way, and were found to be in excellent agreement with those obtained by the first method.

The rate constant k for the slow process increases with increasing P_{O_2} and the most satisfactory correlation found is shown in Fig. 7, where $\log k$ varies directly with $1/P_{O_2}$ over the range $0.14 \leq P_{O_2} \leq 1.00$ atm. No simple correlation of the form $k \propto P_{O_2}^n$ was found.

Temperature has a large effect upon the rate of the reaction when $P_{O_2} = 1.00$ atm. Values of the rate constant k calculated using Eq. [5] are shown in Fig. 8 for experiments at 1445, 1413, 1411, 1402 and 1363°C. An apparent experimental activation energy of 65 kcal is obtained for the process at $P_{O_2} = 1.00$ atm.

The use of Eq. [5] to obtain k depends upon the total sample weight w_T. To examine the effect of changes in w_T, an experiment was conducted with $w_T = 0.8216$ g which is about one-half the usual amount of slag. The results are shown in Fig. 6 as the curve at 1411°C and $P_{O_2} = 1.00$ atm. The value of k so calculated is plotted in Fig. 8, and is in good agreement with the values obtained for $w_T \approx 1.5$ g.

Because the slow process obeys a rate equation which is half-order with respect to the concentration of sulfur in the slag, (Eq. [3]), it would appear that the reaction is controlled by a chemical process. The reaction is much faster than would be expected if bulk diffusion in the slag were the rate-determining step with the diffusion coefficients for oxygen and sulfur being of the order 10^{-5} to 10^{-6} cm^2/s, which is the probable range for species in liquid slags at these temperatures.[4] This indicates that there is some bulk mixing of the melt; however, the mixing appears not to be rapid over the several minutes required for a typical experiment. The broad shallow configuration of the sample combined with such stirring should ensure that diffusion in the slag is not rate-limiting for this experimental arrangement. Examination of the surfaces of quenched specimens indicated that a slight bubbling action occurs at the slag surface. However, no bubbles were found within the bulk of the melt or along the walls of the alumina boats. The bubbling is audible as a slight
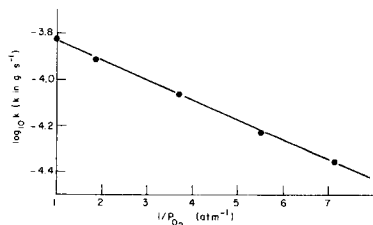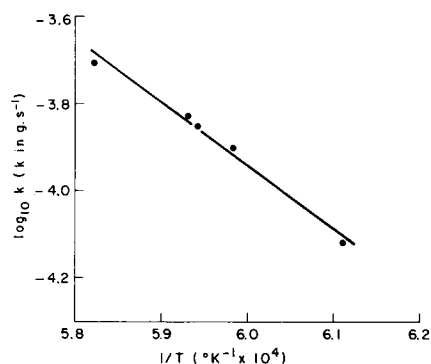

Fig. 8—Effect of temperature on rate constant for $P_{O_2} = 1.00$ atm. Nominal surface area 1.85 cm^2. Flow rate 1300 N ml/min.

crackling sound when oxygen is admitted and ceases immediately when the reaction tube is flushed with argon. To demonstrate that the surface bubbling was caused by the evolution of SO$_2$ alone and not by the oxidation of carbon dissolved or entrained in the synthetic slag during premelting in a graphite crucible, a sample of slag was prepared in situ by mixing the powdered oxides (CaO + Al$_2$O$_3$ + SiO$_2$) with CaS and melting the mixture in the alumina boat in the reaction furnace under argon. Bubbling occurred as soon as oxygen was admitted. Turkdogan and Pearce[1] also observed gas bubbles in quenched samples of CaO-SiO$_2$ slags which had been desulfurized in pure carbon dioxide. However, these bubbles were attributed to the presence of CO$_2$ in the liquid slag.

Transition from Fast to Slow Process

The transition from a fast to a slow process, approximately point B in Fig. 2, was also studied by the experiment shown in Fig. 9. A sample of slag was exposed to a gas stream with a relatively high oxygen partial pressure of 0.22 atm for 1000 s. The partial pressure of oxygen in the stream was then quickly decreased to 0.045 atm where it was held for 410 s, and then it was decreased to 0.0032 atm. In each case, the rate of sulfur evolution immediately increased following the decrease in oxygen partial pressure. Thus, the transition from the fast to the slow process is reversible, and may also occur in the opposite direction.
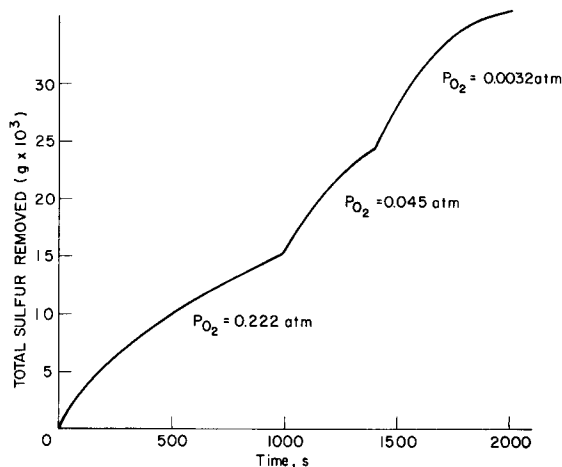

Fig. 7—Effect of oxygen pressure on rate constant for half-order process. Nominal surface area 1.85 cm^2. Temperatures in the range of 1407 to 1417°C.

Fig. 9—Effect of suddenly changing oxygen pressure on sulfur removal. $T = 1411$°C. Total gas flow rate 700 ± 50 ml/min. Nominal surface area 2.90 cm^2.

The results shown in Fig. 9 are consistent with the observations in the rest of this investigation in that a sudden decrease in the oxygen partial pressure to zero during an experiment by flushing with argon resulted in an immediate cessation of SO_2 evolution.

The point B in Fig. 2 can be determined accurately, and this point may be taken as a semi-quantitative measure of the position of the transition from the fast to the slow process. As P_{O_2} is decreased, the point occurs at continually lower concentrations of sulfur remaining in the slag. Fig. 10 is a plot of the concentration of sulfur remaining in the slag at point B (expressed as the fraction of the initial sulfur) vs P_{O_2} for several experiments with different surface areas and at different total flow rates of gas. The line drawn on the logarithmic plot in Fig. 10 has a slope of $\frac{1}{2}$, and thus defines a locus of constant $c_S/P_{O_2}^{1/2}$.

The position of the line in Fig. 10 is not affected significantly by temperature. Rate curves obtained with actual blast furnace slags also exhibited "break points." These points, when plotted in Fig. 10, lay slightly above the points for the synthetic slags. More significantly, the addition of 2.02 wt pct MnO has no apparent effect on the position of the break point, although the addition of this much MnO has a large accelerating effect upon the rate of the slow process which occurs after point B as discussed in the following section.

Addition of Oxidizable Species

The overall reaction of oxidizing sulfur from the slag to form SO_2, Eq. [1], involves a charge transfer step. A possible reaction is:

$$(S^{2-}) + O\,(ad) = (O^{2-}) + S\,(ad) \qquad [6]$$
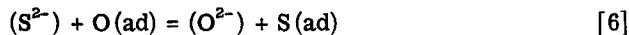
where O (ad) and S (ad) represent oxygen and sulfur adsorbed on the surface of the melt and the charged species are dissolved in the slag. In the present discussion, it is postulated that this charge transfer is the rate-determining step in the slow process occurring at the higher values of P_{O_2}. The addition of an oxidizable species such as iron to the melt could accelerate the process by providing a charge carrier as, for example, in the paired reactions:

$$(S^{2-}) + 2Fe^{3+} = S\,(ad) + 2Fe^{2+} \qquad [7]$$

$$O\,(ad) + 2Fe^{2+} = (O^{2-}) + 2Fe^{3+} \qquad [8]$$
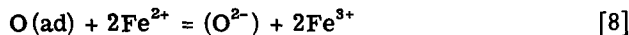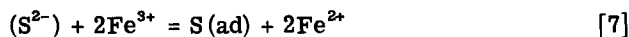
where Eq. [7] and Eq. [8] sum to give Eq. [6]. The same general effect would also be obtained if the adsorbed species were for example S^- (ad) and O^- (ad).

To test the possible effects of the presence of an oxidizable species on the rate of evolution of SO_2, small quantities of several oxides were mixed in with the powdered slag when it was charged into the reaction boat. The effect of each oxide was tested separately, and additions were made up to 0.28 pct Fe_2O_3, 0.26 pct Fe_3O_4 and 6.93 pct MnO. As was the case with the synthetic slags without these special additions, no SO_2 is evolved unless the gas passing over the system contains oxygen.

The results showed at $P_{O_2} = 1$ atm that additions of iron and manganese oxides greatly accelerate the rate of evolution of SO_2 and that the rate is no longer half-order with respect to c_S (Eq. [3]). An addition of 0.28
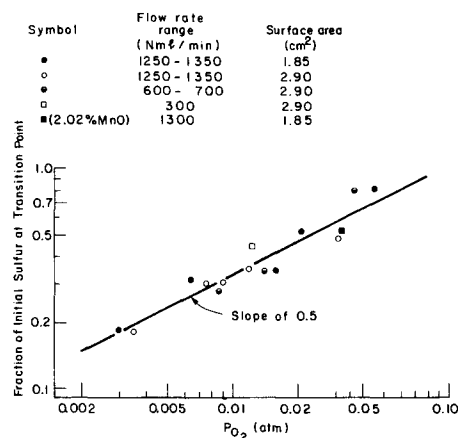

Fig. 10—Effect of oxygen pressure on sulfur content of slag at transition point (point B, Fig. 2) in sulfur removal curve $(c_S/P_{O_2}^{1/2} \simeq 3)$. Nominal temperature, 1412°C. Error limit is ±0.06 on all points.

pct Fe_2O_3 was found to be ten times more effective than was a like addition of MnO in increasing the rate of removal of sulfur. On the basis of the model described by Eqs. [6], [7] and [8], it is to be expected that the effect of manganese would not be as great as that of iron. This is because the trivalent state of Mn is less stable relative to the divalent state than is the case for Fe and also the difference between the second and third ionization potentials of manganese is approximately 30 pct greater than that for iron.

Kinetic analysis of the data indicates that above a critical concentration of MnO and for the particular amounts of Fe_2O_3 considered, the initial rate is approximately first order with respect to the concentration of sulfur in the slag. As the reaction proceeds, apparently the rate process changes back to being half-order in slag sulfur concentration. This apparent change in the order of the reaction depends on the concentration of the metal ion added and the time over which the reaction takes place and requires further investigation.

When actual industrial blast furnace slags were exposed to oxygen gas at high partial pressures ($P_{O_2} \geq 0.1$ atm), SO_2 was evolved so rapidly that the slags foamed out of the alumina boats. This rapid evolution is believed to result from the relatively large amounts of iron and manganese in these slags. When additions of more than 1.0 wt pct Fe_2O_3 were made to the synthetic slag, it also foamed out of the boat, and the rate of evolution of SO_2 was too rapid to be measured.

Effect of Changes in Slag Basicity

Additions of calcium oxide and magnesium oxide modestly increased the rate of evolution of SO_2. Typical curves for the two oxides are shown in Fig. 11 where it is seen that an addition of MgO has almost the same effect as does one of CaO. The addition of 4 pct CaO increased the initial rate over that of the untreated slag by approximately 30 pct; this is equivalent to increasing the lime-silica ratio (wt pct) to 1.2 from 1.1. The addition of 4.6 pct MgO increased the initial rate over that of the untreated slag by approximately 20 pct; this is equivalent to increasing the basicity ratio (pct CaO + pct MgO)/(pct SiO_2 + pct Al_2O_3), from 0.77 to 0.85. Because neither calcium nor magnesium are oxidizable
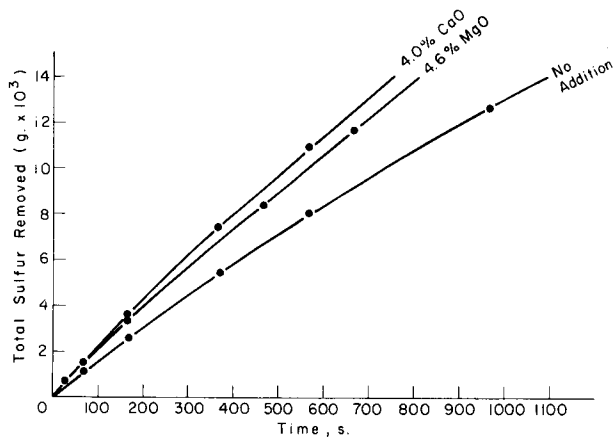
Fig. 11—Increase in the rate of sulfur removal by MgO and CaO additions at P_{O_2} = 1 atm for temperatures in the range 1400 to 1407°C. Flow rate 1340 N ml/min.

in the slag, it is believed that the effect is to be associated with their influence on slag basicity. It is to be noted that these oxides had approximately 1/15th the effect of MnO and 1/150th the effect of iron oxides for a given weight of addition on the rate of evolution of SO_2 from the liquid slag. It was also found that small additions of SiO_2 slightly decreased the rate of SO_2 evolution from the slag (P_{O_2} = 1 atm). The influence of slag basicity on the kinetics of evolution of SO_2 does not appear to be large, but more work on the matter is needed.

DISCUSSION

Transition from Fast to Slow Process, Pure Oxide Melts

The transition from the initial fast process to the slow process as oxygen partial pressure is increased may result from the "poisoning" of the surface at higher oxygen partial pressures. Let it be assumed that oxygen and sulfur may be adsorbed on the surface as S(ad) and O(ad) atoms, and that an active surface site may be occupied by either oxygen or sulfur or it may be vacant. If the assumptions used in the derivation of the Langmuir isotherm[5] are valid in the present case, then:

$$P_{O_2}^{1/2} = K_O \cdot \frac{\Gamma_O}{\Gamma_\square}$$ [9]

$$c_S = K_S \cdot \frac{\Gamma_S}{\Gamma_\square}$$ [10]

where Γ_O, Γ_S and $\Gamma_\square$ are the numbers of active surface sites that are occupied by oxygen, O(ad); sulfur, S(ad); and are vacant, respectively. It is to be recognized that the adsorbed oxygen and sulfur may be charged. K_O and K_S are constants, and c_S is the bulk concentration of sulfur in the slag. It is assumed here that the rates of adsorption and desorption of species to and from the gas phase and the rate of diffusion of species in the liquid slag are sufficiently rapid relative to the rate of reaction of the adsorbed species to form SO_2 so that equilibrium between S(ad) and the sulfur in the bulk of the melt, and between O(ad) and O_2(g), can be assumed. From Eqs. [9] and [10]:

$$\frac{\Gamma_S}{\Gamma_O} \propto \frac{c_S}{P_{O_2}^{1/2}}$$ [11]

If the surface is nearly covered with O(ad) atoms, then $\Gamma_O/(\Gamma_S + \Gamma_O + \Gamma_\square) \approx 1$, and

$$\Gamma_S \propto c_S / P_{O_2}^{1/2}$$ [12]

As the oxygen partial pressure increases and the sulfur concentration decreases, Γ_S continually decreases. Assuming that the fast process occurring during the initial stages of the rate curves depends strongly upon there being a sufficient concentration of adsorbed sulfur on the surface, there may come a critical value of Γ_S, and hence $(c_S / P_{O_2}^{1/2})$, below which a transition to another reaction mechanism may occur. The abrupt nature of the observed transition may be the result of a transition from a disturbed to a more quiescent surface as Γ_S reaches a critical value and the rate of SO_2 evolution abruptly decreases. Thus, the observation of a "critical" value of $c_S / P_{O_2}^{1/2}$ as shown in Fig. 10 can be explained by "poisoning" of the surface by adsorbed oxygen.

Another possible explanation of the observations is that "poisoning" of the surface by adsorbed oxy-sulfide species such as SO_4^{2-}(ad) or SO_2(ad) occurs at the higher oxygen partial pressures.

Order One-Half Reaction, $CaO-Al_2O_3-SiO_2$ Melts

For a $CaO-Al_2O_3-SiO_2$ slag containing sulfur only, the rate of evolution of SO_2 at higher oxygen partial pressures has been shown to be half-order with respect to c_S, Eq. [3]. Furthermore, the overall process is described by Reaction [1], and the results of the studies with iron and manganese oxide additions indicate that a charge transfer process is rate-controlling even though the reaction no longer obeys Eq. [3] with appreciable additions of these oxides.

For the pure oxide melts (no iron or manganese additions), the results may be explained as follows: A reaction obeying an order one-half rate law will occur in the following general case. Suppose that a number of reactants, $R_1, R_2, \ldots, R_n$ react to form two intermediate species I_1 and I_2:

$$R_1 + R_2 + \ldots\ldots + R_n = I_1 + I_2$$ [13]
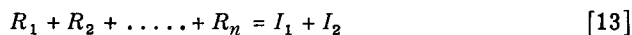
Reaction [13] is assumed to be fast in both directions and the equilibrium is described by

$$K_{13} = \frac{c_{I_1} \cdot c_{I_2}}{c_{R_1} \cdot c_{R_2} \cdot \ldots \cdot c_{R_n}}$$ [14]

where K_{13} is the equilibrium constant, and c_i is the concentration of species i. The two intermediates I_1 and I_2 now form products P_1 and P_2 according to:

$$I_1 \rightarrow P_1$$ [15]

$$I_2 \rightarrow P_2$$ [16]

Reactions [15] and [16] are assumed to be slow relative to reaction [13], and it is assumed that no significant back-reaction occurs in either case.

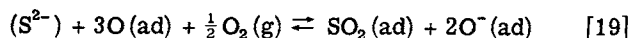At steady-state, stoichiometric restrictions require that the rates of formation of P_1 and P_2 be equal.

Hence, the overall rate, dw/dt, is given by

$$dw/dt = k_{15} \cdot c_{I_1} = k_{16} \cdot c_{I_2} \qquad [17]$$
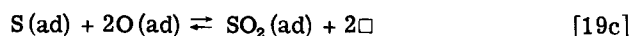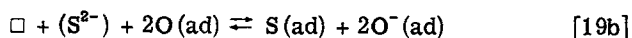
where k_{15} and k_{16} are the rate constants for reactions [15] and [16] in the forward direction. Combining Eqs. [14] and [17] results in the expression:

$$dw/dt \propto (K_{13}k_{15}k_{16})^{1/2} \cdot c_{R_1}^{1/2} \cdot \ldots \cdot c_{R_n}^{1/2} \qquad [18]$$

For the desulfurization process, then, it is required that two intermediate species be formed during the course of the overall reaction (Eq. [1]), and that these two intermediates then decompose by two slow parallel steps. Assume, for example, that adsorbed oxygen and sulfur in the slag react with O_2 (g) to form SO_2 (ad). The existence of the species O^- (ad) is also postulated, and the following equilibrium equation may be written:

$$(S^{2-}) + 3O\,(ad) + \tfrac{1}{2}O_2\,(g) \rightleftarrows SO_2\,(ad) + 2O^-\,(ad) \qquad [19]$$

it being the sum of the following:

$$\square + \tfrac{1}{2}O_2\,(g) \rightleftarrows O\,(ad) \qquad [19a]$$

$$\square + (S^{2-}) + 2O\,(ad) \rightleftarrows S\,(ad) + 2O^-\,(ad) \qquad [19b]$$

$$S\,(ad) + 2O\,(ad) \rightleftarrows SO_2\,(ad) + 2\square \qquad [19c]$$

where $\square$ represents a vacant active surface site. The equilibrium constant for Eq. [19] is:

$$K_{19} = \frac{\Gamma_{O^-}^2 \cdot \Gamma_{SO_2}}{\Gamma_O^3 \cdot P_{O_2}^{1/2} \cdot c_S} \qquad [20]$$

where Γ_i is the surface concentration of species i (ad).

The first of the two slow parallel steps is the combination of the intermediate species O^- (ad) to form O^{2-} ions in the bulk of the melt. This may be the slowest step in the overall charge transfer process. The second slow parallel step is the desorption of SO_2 (ad) molecules. That is:

$$O^-\,(ad) + O^-\,(ad) \rightarrow (O^{2-}) + O\,(ad) + \square \qquad [21]$$

$$SO_2\,(ad) \rightarrow SO_2\,(g) + \square \qquad [22]$$
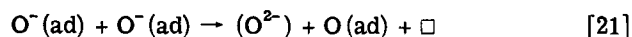
Setting

$$k_{21}\Gamma_{O^-}^2 = k_{22}\Gamma_{SO_2} \qquad [23]$$

and substituting this expression into Eq. [20], an expression is obtained for the overall rate of reaction 1 by Eq. [18]:

$$dw/dt \propto (K_{19} \cdot k_{21} \cdot k_{22})^{1/2} \cdot c_S^{1/2} \cdot P_{O_2}^{1/4} \cdot \Gamma_O^{3/2} \qquad [24]$$

Thus, $dw/dt \propto c_S^{1/2}$ as observed.

For nearly complete coverage by O (ad) atoms, Γ_O approaches a constant value and $dw/dt \propto P_{O_2}^{1/4}$. For very low coverage by O (ad) atoms, $\Gamma_O \propto P_{O_2}^{1/2}$ (Langmuir isotherm), and $dw/dt \propto P_{O_2}$. Near $P_{O_2} = 1.00$ atm, dw/dt is, in fact, observed to vary approximately as $P_{O_2}^{1/4}$.

This model is presented to illustrate the general sort of process which is occurring. Several different models, all with two parallel slow steps involving charge transfer and desorption, but differing in the details of the particular participating species, can be postulated, and will all result in an overall rate equation of the form of Eq. [3].

A possible explanation of the effects of additions of iron and manganese oxides is that reactions [7] and [8] could provide the means for partially, or wholly, by-passing reaction [21]. Then all steps necessary to

the formation of SO_2 (ad) would be fast and only Eq. [22] would be slow. As a result, the order of the process with respect to sulfur in the slag increases towards 1.

CONCLUSIONS

A liquid synthetic (CaO-Al_2O_3-SiO_2-S) blast furnace slag exposed to mixtures of oxygen and an inert gas will evolve SO_2 gas at a very rapid rate for $0.003 \leq P_{O_2} \leq 0.1$ atm. At about $P_{O_2} = 0.1$ atm, a transition in the rate occurs early in the process with the fast initial rate followed by a slower rate. With increasing oxygen pressures the fast initial process increases in rate, but decreases in duration and the slower second process increases in rate. The rate of the initial process is gas transport controlled and the second process is chemically controlled. The transition is reversible and this may be shown by suddenly decreasing P_{O_2} to a low value during an experiment to give an increased rate of SO_2 evolution and a transition back to the fast process. The transition may result from the "poisoning" of the surface at higher values of P_{O_2} by adsorbed oxygen or oxysulfide species.

Weight loss experiments indicate that the overall process at any time and at any P_{O_2} involves the replacement of S^{2-} ions by O^{2-} ions according to the reaction

$$(S^{2-}) + 3/2\,O_2\,(g) = SO_2\,(g) + (O^{2-}) \qquad [25]$$
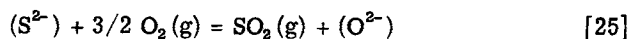
No appreciable amount of sulfate ions or other oxysulfide species is formed within the bulk slag at any time.

For the slower process occurring at oxygen partial pressures between 0.1 and 1 atm, the rate at which sulfur is removed from the CaO-Al_2O_3-SiO_2-S melts is proportional to the square root of the sulfur concentration in the slag, c_S, i.e., the process is half-order with respect to sulfur in the slag.

$$\frac{dw_S}{dt} = -k(c_S)^{1/2} \qquad [26]$$

This half-order dependence on sulfur concentration may be explained by an initial fast reversible reaction to form two intermediate species which then decompose at equal rates to give the final products. An activation energy of 65 kcal has been obtained for this process at $P_{O_2} = 1$ atm.

When the oxides of metals that can exist in two valence states, such as iron (Fe^{++}, Fe^{+++}) or manganese (Mn^{++}, Mn^{+++}) are added to the oxide melt, the rate of evolution of SO_2 at $P_{O_2} = 1$ atm is enhanced. It is found that iron is more effective than is manganese in increasing the rate. With more than 1 wt pct Fe_2O_3 in a synthetic slag, SO_2 is evolved so quickly that measurements cannot be made because violent bubbling occurs. The rate of evolution of SO_2 from a commercial slag is very rapid, apparently as a result of this slag containing some iron and manganese oxides. These observations indicate that a charge transfer process involving oxygen and/or sulfur ions is rate-controlling, and that ferrous and ferric ions (or Mn^{2+} and Mn^{3+}) ions can act as charge carriers. The order of the process with respect to sulfur in the slag appears to increase with the addition of iron and manganese oxides. This change to

a higher order process is dependent on the concentration of the metal ions added and the effect of such additions of metal ions requires further investigation.

Additions of MgO, CaO or SiO_2 to the slag have relatively little effect on the rate of evolution of SO_2 compared to additions of iron and manganese oxides. This indicates that there should be little effect of slag basicity on the process.

ACKNOWLEDGMENTS

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