

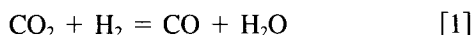
On the Relative Rates of CO₂—CO and H₂O—H₂ Reactions with Liquid Silver at 1283 K and a Liquid Silicate at 1373 K

Y. SASAKI and G. R. BELTON

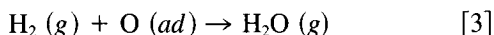
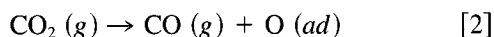
Measurements have been made of the steady-state oxygen activity in liquid silver at 1283 K in flowing CO₂—H₂ and H₂O—CO gas mixtures. It is shown that the results are consistent with the consecutive reactions CO₂ (g) → O (ad) + CO (g) and H₂ (g) + O (ad) → H₂O (g) as the rate determining steps under the limiting conditions of low coverage by adsorbed oxygen. Measurements of the steady-state oxygen activity in two iron oxide-containing lithium silicates under flowing CO₂—H₂ gas mixtures at 1373 K are in agreement with a similar mechanism. The study indicates that the rate of dissociation of H₂O is about 4.6 times higher than the rate of dissociation of CO₂ on the liquid silver surface at 1283 K and about 2.1 times higher on the lithium silicate surface at 1373 K. From the present and previous work, it appears that the ratio of the rates of dissociation of H₂O and CO₂ at high temperatures is not strongly influenced by the nature of the reaction surface, despite significant differences in absolute reaction rates.

I. INTRODUCTION

In an earlier paper,¹ the authors reported on measurements of the steady-state oxygen activity in liquid copper when exposed to flowing CO₂—H₂ gas mixtures at 1423 K. For impinging gas flowrates above about 10⁻⁴ mol s⁻¹ cm⁻² and for CO₂/H₂ ratios varying between 0.25 and 6, it was shown that the oxygen activity expressed as pO_2 , was one to two orders of magnitude below that consistent with equilibrium in the water-gas reaction:



Following Wagner,² the results were interpreted in terms of the two consecutive steps:



It was shown that the results were consistent with the above steps and ideal adsorption of oxygen on liquid copper for CO₂/H₂ ratios below about 3 (steady-state value of $p^{1/2}O_2 \leq 7 \times 10^{-7}$ atm^{1/2}). Above this value, a deviation from this simple behavior occurred and it was noted that this was at about the same oxygen activity that Gallois and Lupis³ found the initial depression of the surface tension of liquid copper by oxygen.

The results were analyzed to show that the rate of dissociation of H₂O was about 2.5 times the rate of dissociation of CO₂ on the surface of liquid copper at 1423 K. The present work was undertaken to establish the relationship between the rates of the H₂O—H₂ and CO₂—CO reactions on a liquid metal (silver) with a lower affinity for oxygen than copper and also to extend the technique to liquid slags. Originally, it was intended that iron blast furnace type slags

would be studied in view of their practical importance. However, initial experiments with these slags and flowing CO₂—H₂ gas mixtures showed that the degree of conversion to H₂O and CO was too high to permit the necessary conditions of the steady-state technique to be met, *i.e.*, either negligible contribution from the reverse reaction or approximately constant gas composition. Accordingly, the work with slags has been confined to the reaction of CO₂—H₂ mixtures with a liquid lithium silicate containing iron oxide at 1373 K. Results have been obtained by floating the slag on liquid silver and determining steady-state oxygen activities by means of a solid electrolyte cell in the liquid metal.

The work with liquid silver has been confined to the single temperature of 1283 K, but measurements of the steady-state oxygen activity have been made under both CO₂—H₂ and H₂O—CO mixtures.

II. EXPERIMENTAL DETAILS

The experimental arrangement was basically similar to that described previously¹ with only a few modifications to accommodate available refractory shapes and sizes. Liquid silver (approximately 40 g) was contained in a vertical round-bottom alumina tube of 25 mm I. D. For the experiments with slags, the liquid silver with the slag layer was held in a fused silica tube of similar dimensions. A solid electrolyte cell, consisting of a 7 mm O. D. lime-stabilized zirconia tube containing a roughly equimolar Ni/NiO reference electrode, was dipped into the liquid metal. Contact to the reference electrode was by platinum wire and the zirconia tube was sheathed by a 10 mm O. D. alumina tube to just below the surface of the liquid silver. Electrical contact to the silver was by means of a stainless steel wire similarly sheathed by a 4 mm O. D. alumina tube. Gas mixtures were delivered through a 3 mm I. D. alumina tube held approximately 5 mm above the surface of the liquid silver or slag. The whole assembly was held in a vertical resistance furnace by an appropriate system of end caps and seals. Temperature measurement was by means of a noble metal thermocouple held to within 5 mm of the base of the tube containing the liquid silver.

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Flowrates and compositions of the gas mixtures were controlled by means of calibrated capillary flowmeters. Carbon monoxide, initial purity 99.6 pct, and carbon dioxide, initial purity 99.9 pct, were purified by standard techniques.⁴ High purity hydrogen was dried over magnesium perchlorate. H₂O—CO mixtures were prepared by passing purified CO through a water saturator of the design described by Belton and Richardson.⁵

Facilities were provided to estimate roughly the amount of H₂O produced during reactions with CO₂—H₂ mixtures by incorporating an ice-water cooled U-tube in the gas exit line from the apparatus.

High purity silver was first inductively melted in an alumina crucible in air, quenched, and surface ground to remove oxidizable impurities. Li₂O—SiO₂ slags were prepared by melting reagent grade SiO₂ and Li₂CO₃ in a silica crucible, cooling, and crushing to granules.

Procedure

The apparatus was charged with about 40 g of silver and melt-down was carried out under flowing argon. The solid electrolyte cell and stainless steel contact wire were then inserted into the liquid metal. Either a CO₂—CO, CO₂—H₂, or H₂O—CO mixture was then introduced and the cell potential recorded as a function of time. After a steady potential was reached, changes in gas mixture or flowrate were made and the cell potential again recorded.

Experiments with the Li₂O—SiO₂ slags were carried out by adding about 5 g of the granulated slag to the surface of the liquid silver after insertion of the solid electrolyte cell and contact wire. Potentials were then recorded under CO₂—H₂ mixtures only. The surface of the melt was occasionally observed through an optical flat at the top of the apparatus to ensure that the surface was fully covered by the slag. Samples for subsequent analysis were obtained by briefly inserting a stainless steel rod into the liquid slag. Thermoelectric potentials between the stainless steel contact wire and platinum were determined by briefly inserting a platinum wire into the liquid silver.

III. RESULTS

A. Liquid Silver at 1283 K

Measurements of the steady-state cell potentials under CO₂—H₂ and H₂O—CO mixtures were generally followed by measurements under CO₂—CO mixtures to serve as a check on the reliability of the solid electrolyte cell. A typical sequence of results is shown in Figure 1, where it will be noted that steady values were reached within about one hour of a change in gas composition. The potentials were generally measured at gas flowrates in the range of 300 to 400 ml min⁻¹, and independence was usually demonstrated by changing the flowrate after the potential reached a steady value. A wider variation in flowrate was examined for a CO₂/H₂ ratio of 2. Results from these experiments are shown in Figure 2. Values of the steady-state cell potentials for both CO₂—H₂ and H₂O—CO gas mixtures are summarized in Table I.

Derived values of the steady-state activity of oxygen^{6,7} in the liquid silver, expressed as pO_2 (atm), are presented in

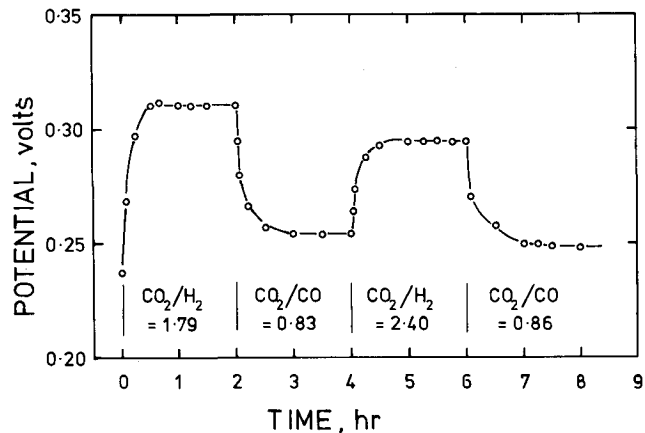


Fig. 1—Typical results for the cell potential as a function of time and changes in gas composition for liquid silver at 1283 K.

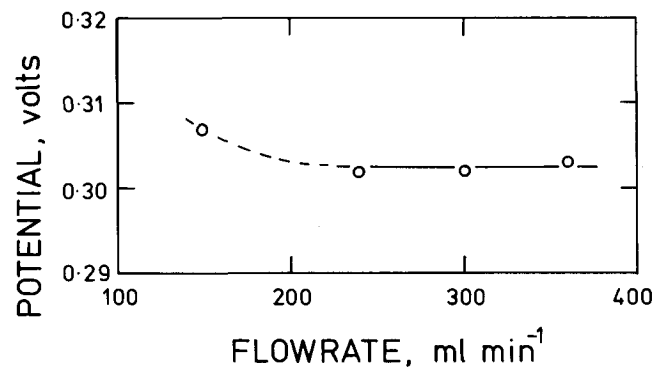


Fig. 2—Effect of flowrate on the steady-state cell potential for liquid silver at $pCO_2/pH_2 = 2$.

Table I. Steady-State Cell Potentials for Silver at 1283 K, Ni/NiO Reference Electrode Positive

| pCO_2/pH_2 | Potential, V | pH_2O/pCO | Potential, V |
|--------------|--------------|-------------|--------------|
| 1.79 | 0.313 | 0.086 | 0.294 |
| 2.00 | 0.302 | 0.104 | 0.282 |
| 2.40 | 0.295 | 0.139 | 0.270 |
| 3.00 | 0.284 | 0.174 | 0.264 |
| 4.80 | 0.259 | 0.245 | 0.246 |
| 5.33 | 0.252 | | |

logarithmic form in Figures 3(a) and 3(b) as functions of the gas composition. The calculated⁷ oxygen activities for complete water-gas equilibrium are shown as dashed curves in the same figures. Steady-state activities are about 1.5 orders of magnitude lower than those for full equilibrium in the case of CO₂—H₂ mixtures and about 1 order of magnitude higher in the case of H₂O—CO mixtures.

One experiment was carried out with a small bundle of platinum and platinum-rhodium wire inserted into the bottom of the gas delivery tube. The steady-state oxygen activity in this experiment, as shown in Figure 3(a), approaches that for full water-gas equilibrium in the particular gas mixture. This is consistent with the known⁸ catalytic activity of Pt and Rh in the water-gas shift reaction. Steady cell potentials in the experiments with CO₂—CO mixtures were all

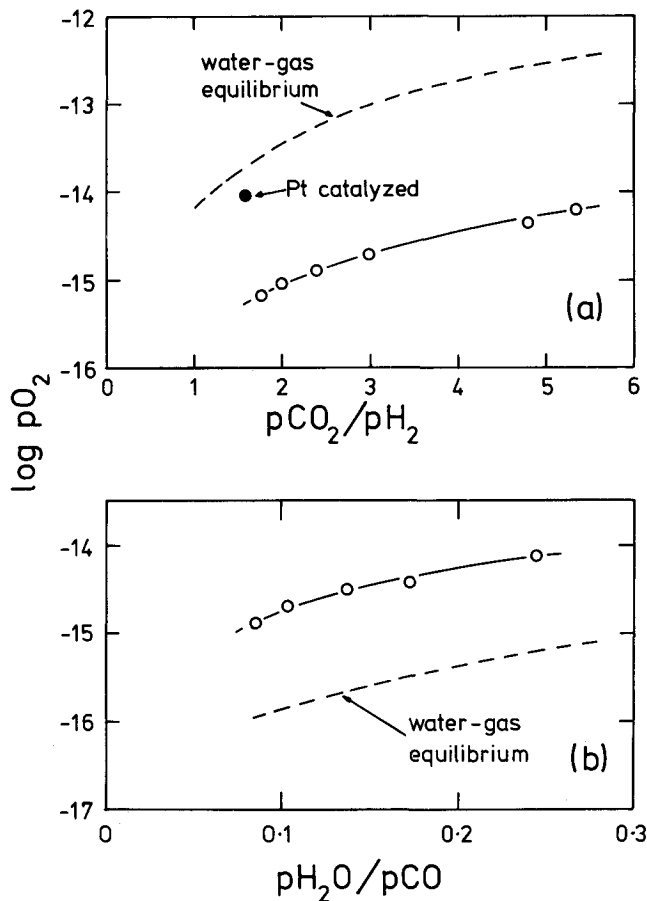


Fig. 3—Comparison of measured steady-state oxygen activities, expressed as pO_2 (atm), with calculated values for complete water-gas equilibrium. Liquid silver at 1283 K and (a) CO_2 — H_2 mixtures and (b) H_2O — CO mixtures.

in very close accord (± 3 mV) with the calculated equilibrium values.^{6,7}

The water vapor content of the exit gas for the CO_2 — H_2 experiments was found to be very low with only a slight misting of the inside surface of the U-tube for the lowest CO_2/H_2 ratios in a period of about two hours. Presuming saturation of the gas with water vapor at 0 °C, this would give a maximum conversion of H_2 to H_2O of about 1 pct.

B. Liquid Lithium Silicates at 1373 K

Experiments were attempted with silica-saturated lithium silicates containing no added iron oxide, an addition of approximately 0.25 wt pct FeO, and an addition of approximately 2 wt pct FeO. Subsequent analyses of the iron oxide-containing melts gave an identical Li_2O/SiO_2 weight ratio of 0.14, an Al_2O_3 content of approximately 7 wt pct, and FeO contents of 0.27 and 1.71 wt pct. Traces of Cr (<0.06 wt pct Cr_2O_3) and Ni (<0.10 wt pct NiO) were found.

The experiments with iron oxide-free melts under CO_2/H_2 mixtures gave only slowly drifting cell potentials and were abandoned. Steady cell potentials could be achieved, however, with iron oxide-containing melts after periods of 100 to 150 hours following changes in gas composition. An example of this slow approach to steady-state is shown in Figure 4 for an experiment with the melt containing 1.71 wt pct FeO and a change in CO_2/H_2 ratio from 1.95 to 1.01.

Steady-state cell potentials were obtained for four CO_2/H_2 ratios with the low iron oxide content melt and for two ratios with the higher iron oxide content melt, all at gas flowrates of 300 to 400 ml min^{-1} . The values are listed in Table II and are presented as oxygen activities in Figure 5. The values are approximately 1 order of magnitude lower than those calculated for water-gas equilibrium,

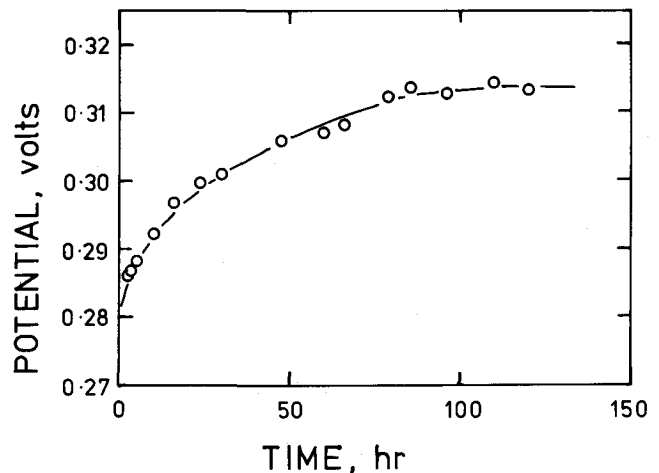


Fig. 4—Cell potential as a function of time for the lithium silicate containing 1.71 wt pct FeO at 1373 K and for a step change in CO_2/H_2 ratio from 1.95 to 1.01.

Table II. Steady-State Cell Potentials for Liquid Lithium Silicate at 1373 K, Ni/NiO Reference Electrode Positive

| pCO_2/pH_2 | Potential, V | pCO_2/pH_2 | Potential, V |
|--------------|--------------|--------------|--------------|
| 1.01* | 0.325 | 1.95* | 0.281 |
| 1.02 | 0.313 | 2.30 | 0.270 |
| 1.77 | 0.295 | 3.80 | 0.235 |

*1.71 wt pct FeO, others 0.27 wt pct FeO.

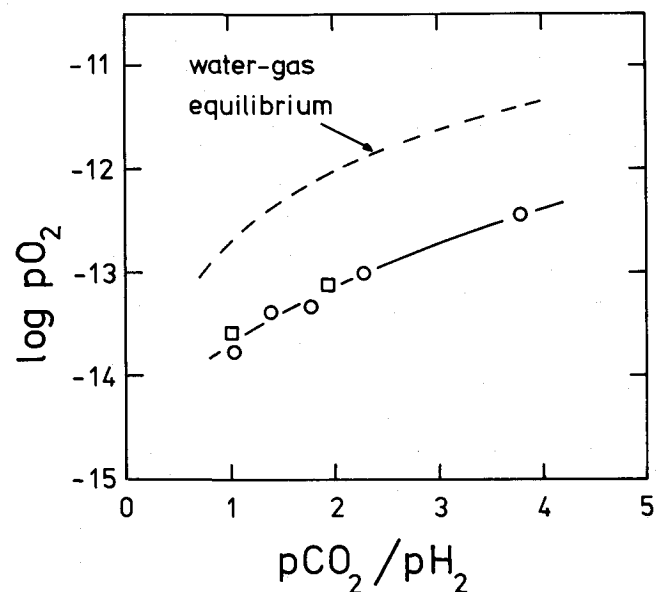


Fig. 5—Comparison of measured steady-state oxygen activities with calculated values for complete water-gas equilibrium for the lithium silicates at 1373 K under CO_2 — H_2 mixtures.

and no significant difference is apparent for the two iron oxide contents.

Conversion of H_2 to H_2O was again found to be small, but measurable amounts of water were deposited in the cooled U-tube. Maximum conversion was estimated to be 3.1 pct for the 1.71 wt pct FeO melt.

IV. DISCUSSION

A. Reaction on Liquid Silver

As discussed previously,¹ if the rate determining steps are taken to be given by Eqs. [2] and [3], adsorption and reaction sites are identical, and the only significant adsorbed species is atomic oxygen with a reactivity independent of coverage, we may express the reaction velocities as:

$$V_2 = k_2 p_{CO_2}(1 - \theta) - k'_2 p_{CO}\theta \quad [4]$$

$$V_3 = k_3 p_{H_2}\theta - k'_3 p_{H_2O}(1 - \theta) \quad [5]$$

where θ is the fractional coverage by oxygen, and k_i and k'_i represent forward and reverse rate constants, respectively. At steady-state we may assume equilibrium between chemisorbed oxygen and dissolved oxygen and write a general adsorption isotherm of the form:

$$\frac{\theta\gamma^s}{1 - \theta} = K(p^{1/2}O_2)_{Ag} \quad [6]$$

where K is the adsorption coefficient for oxygen, γ^s is a coverage-dependent surface activity coefficient, and $(p^{1/2}O_2)_{Ag}$ is the oxygen activity in the liquid silver.

Total production of H_2O was found to be very small. Accordingly, the contribution to the reaction velocities from the reverse reactions on the surface can be reasonably neglected and Eqs. [4] and [5] may be equated and combined with Eq. [6] to give:

$$(p^{1/2}O_2)_{Ag} = \frac{\gamma^s k_2 p_{CO_2}}{K k_3 p_{H_2}} \quad [7]$$

Considering the reaction with H_2O —CO mixtures, the equivalent equation is:

$$(p^{1/2}O_2)_{Ag} = \frac{\gamma^s k'_3 p_{H_2O}}{K k'_2 p_{CO}} \quad [8]$$

The results of the experiments with CO_2 — H_2 mixtures are plotted in accordance with Eq. [7] in Figure 6. Over the full range of experimental conditions, the data are in close accord with the model for a constant value of γ^s . Results for H_2O —CO mixtures are similarly in accord with Eq. [8] as shown in Figure 7, although with a larger experimental scatter. Clearly, we may define $\gamma^s \rightarrow 1$ as $p^{1/2}O_2 \rightarrow 0$. Accordingly, the slopes in Figures 6 and 7 may be taken to give:

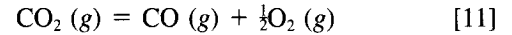
$$\frac{k_2}{Kk_3} = 1.5 \times 10^{-8} \text{ atm}^{1/2} \quad [9]$$

and

$$\frac{k'_3}{Kk'_2} = 4.0 \times 10^{-7} \text{ atm}^{1/2} \quad [10]$$

Provided that there were no significant differences in the impurity content of the liquid silver between the two types of experiment, the value of K should be common and expressions [9] and [10] should be related through the equilibrium constants for the dissociation of CO_2 and H_2O .

Considering the reaction



at equilibrium with the surface, it follows from Eqs. [4] and [6], under conditions where $\gamma^s = 1$, that

$$\frac{k_2}{Kk'_2} = K_C \quad [12]$$

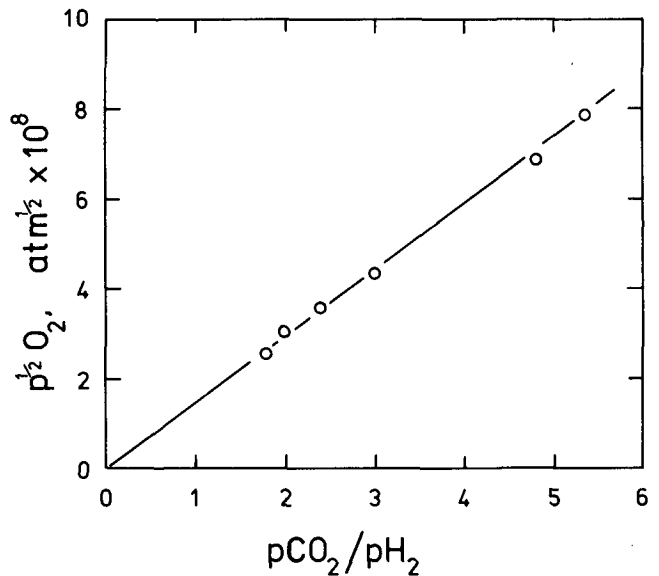


Fig. 6—Plot of steady-state values of $p^{1/2}O_2$ for liquid silver in accordance with Eq. [7].

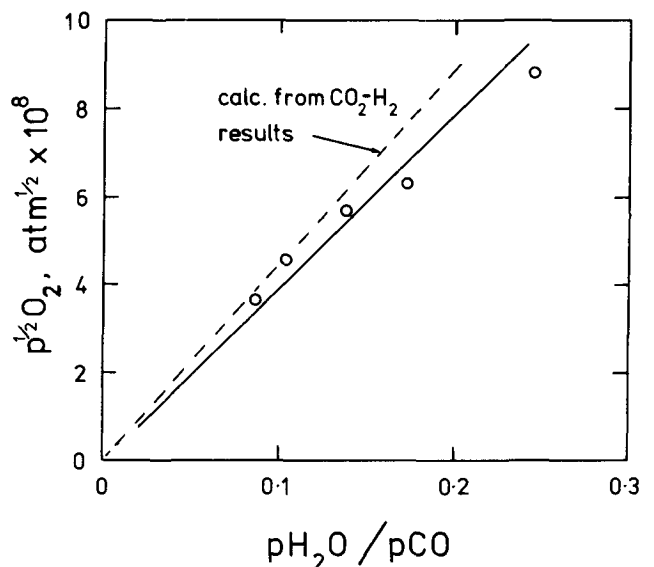
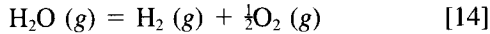


Fig. 7—Plot of steady-state values of $p^{1/2}O_2$ for liquid silver in accordance with Eq. [8].

where K_C is the equilibrium constant for reaction [11]. Similarly,

$$\frac{k'_3}{Kk_3} = K_H \quad [13]$$

where K_H is the equilibrium constant for the reaction:



Combining Eqs. [12] and [13] we obtain the expression

$$\frac{k'_3}{Kk'_2} \frac{k_2}{Kk_3} = K_H K_C \quad [15]$$

or

$$\frac{k'_3}{Kk'_2} \frac{k_2}{Kk_3} = \exp[(\Delta F_{\text{CO}_2}^\circ + \Delta F_{\text{H}_2\text{O}}^\circ - \Delta F_{\text{CO}}^\circ)/RT] \quad [16]$$

where ΔF_i° is the standard Gibbs energy of formation of the gaseous species i .

Evaluation of the exponential term at 1283 K using literature data⁷ for Gibbs energies of formation yields a value of 6.7×10^{-15} . This compares favorably with the product of the experimental values of the slopes, namely, 6×10^{-15} . This reasonable accord is further illustrated in Figure 7 where the calculated slope, based on the CO_2 - H_2 experiments, is compared with the experimental results for H_2 - CO mixtures.

Thus, all the measurements appear to be internally consistent with the model and essentially ideal adsorption behavior for oxygen over the experimentally accessible range of oxygen activity ($p^{1/2}\text{O}_2 \leq 1 \times 10^{-7} \text{ atm}^{1/2}$). It should be noted, however, that this oxygen activity is some six orders of magnitude below that at which measurable depression of the surface tension of liquid silver occurs.⁹ Accordingly, the adsorption of oxygen might be better described as being in the limiting region where $\theta \propto p^{1/2}\text{O}_2$ and $(1 - \theta) \rightarrow 1$.

Substitution of Eq. [13] into Eq. [7] yields the following relationship for the ratio of the rate constants for the dissociation of CO_2 and H_2O on the surface of liquid silver:

$$\frac{k'_3}{k_2} = \frac{p\text{CO}_2}{p\text{H}_2} \frac{K_H \gamma^s}{(p^{1/2}\text{O}_2)_{\text{Ag}}} \quad [17]$$

Similarly, substitution of Eq. [12] into Eq. [7] gives the relationship for the ratio of the rate constants for the reaction of H_2 and CO with oxygen on the surface of liquid silver:

$$\frac{k_3}{k'_2} = \frac{p\text{CO}_2}{p\text{H}_2} \frac{K_C \gamma^s}{(p^{1/2}\text{O}_2)_{\text{Ag}}} \quad [18]$$

These equations may be readily evaluated at $\gamma^s = 1$ by using literature data⁷ for the equilibrium constants and the slope from Figure 6. The results indicate that the rate constant for the dissociation of H_2O is about 4.6 times higher than that for CO_2 at the surface of liquid silver at 1283 K. The rate constant for the reaction of H_2 with oxygen on the surface of liquid silver is about 6.9 times that of CO at this temperature.

These values will be discussed further after consideration of the results for the lithium silicates.

B. Reaction on the Lithium Silicate Melts

The work of Johnston¹⁰ on dilute solutions of iron oxide in liquid sodium disilicate would give a value for the

$\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of between 8 and 12 for the temperature and range of steady-state oxygen activities observed in the present study. Paul and Douglas¹¹ have shown that the ratio is higher in the lithium silicates and increases with SiO_2 content and additions of Al_2O_3 . Accordingly, it can be assumed that the results shown in Figure 5 are for the melt with iron predominantly in the ferrous state.

The steady-state oxygen activities are plotted as a function of the CO_2/H_2 ratio in Figure 8. The linear behavior is consistent with a similar mechanism to that considered for the liquid silver surface reaction. Taking Eq. [17], the value of K_H from the literature,⁷ and the slope from Figure 8, yields a value for the ratio of the rate constants for the dissociation of H_2O and CO_2 of about 2.1 on the silicate surface, independent of the approximately 7-fold change in iron oxide content. This independence is consistent with the adsorption isotherm constant for oxygen at the reaction sites being unchanged by the change of FeO concentration. The total number of reaction sites, and hence the individual rate constants, may be a function of the FeO concentration, but the results indicate that the ratio of the rate constants is essentially unchanged.

C. Relative Rates of Dissociation of H_2O and CO_2

Turkdogan and Vinters¹² have analyzed their own and previous experimental data¹³⁻²⁰ on the reaction of H_2O and CO_2 with solid iron and dense wustite, and have derived the apparent rate constants for the dissociation of these two species at what were considered to be equivalent oxygen coverages. The ratios of these rate constants on the two substances are shown in Figure 9 as functions of $1/T$ (K) and in comparison with the presently derived ratios for

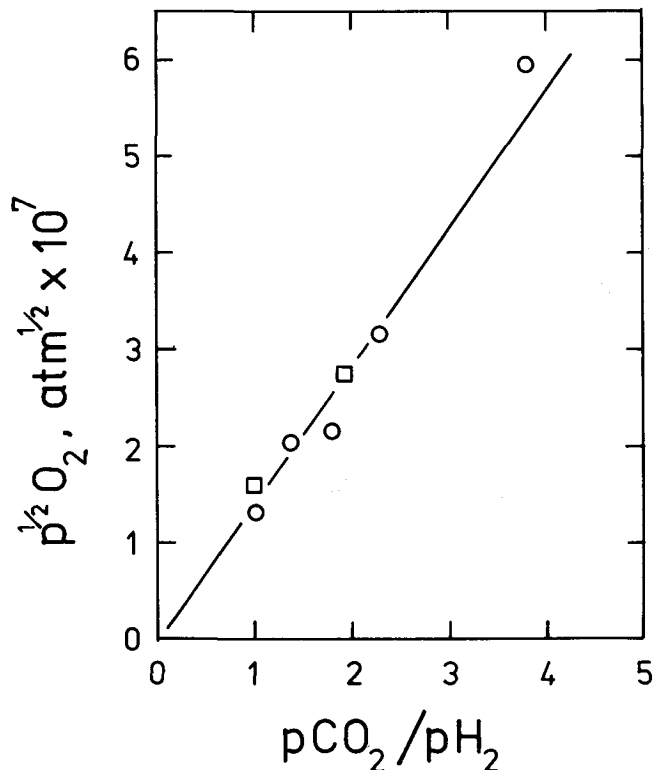


Fig. 8—Plot of steady-state values of $p^{1/2}\text{O}_2$ for the liquid lithium silicates in accordance with Eq. [7]. \square , 1.71 wt pct FeO; \circ , 0.27 wt pct FeO.

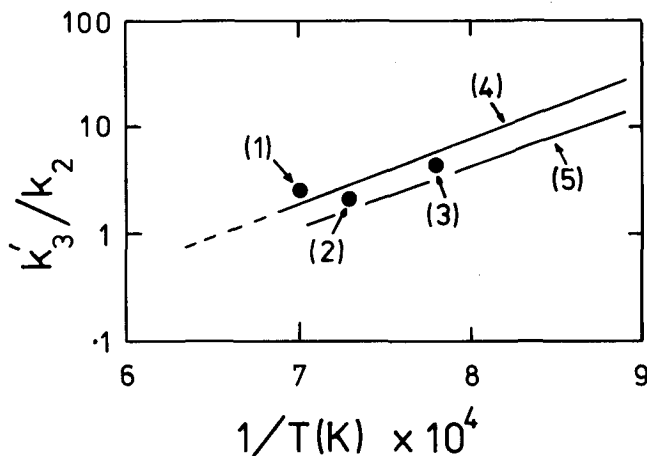


Fig. 9—The ratio of the rate constants for the dissociation of H₂O and CO₂ on different substances: (1) liquid copper,¹ (2) liquid lithium silicate, (3) liquid silver, (4) solid iron, after Turkdogan and Vinters,¹² and (5) dense wustite, after Turkdogan and Vinters.¹²

liquid silver and the lithium silicate, and the previously determined value for liquid copper.¹

The properties of the condensed substances vary widely. For example, the heats of formation of the first oxides of Ag, Cu, and Fe show a spread of about 230 kJ per mole of oxygen atoms. Also, the absolute values of the rate constants on these metals differ significantly. At about 1400 K, the rate constant for the dissociation of CO₂ on Ag is about 10⁻⁸ mol cm⁻² s⁻¹ atm⁻¹, if the data of Grabke¹⁵ are extrapolated from the solid to the liquid state, whereas the rate constant for Fe at this temperature is about 3 × 10⁻⁴ mol cm⁻² s⁻¹ atm⁻¹, even with a probable partial coverage by oxygen.¹² The work of Forster and Richardson²¹ suggests a value of about 10⁻⁷ mol cm⁻² s⁻¹ atm⁻¹ for liquid copper at this same temperature. No data are available for the lithium silicate, but the rate constant on wustite¹² is probably about 2 × 10⁻⁶ mol cm⁻² s⁻¹ atm⁻¹ at 1400 K.

Broadly, it appears that the ratio of the rate constants is principally a function of temperature only, despite marked differences in the physico-chemical properties of the condensed phases. It appears likely that this can be taken as a first approximation in the analysis of CO₂—CO and H₂O—H₂ reactions with substances of metallurgical interest. Experiments with several substances at higher temperatures, where the trend in Figure 9 indicates that the rate

of dissociation of CO₂ exceeds that of H₂O, would be particularly useful in establishing this behavior.

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