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AN APPARATUS FOR SIMULTANEOUSLY MEASURING ELECTRICAL CONDUCTIVITY AND OXYGEN FUGACITY

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January 31, 1978

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AN APPARATUS FOR SIMULTANEOUSLY MEASURING ELECTRICAL CONDUCTIVITY AND OXYGEN FUGACITY

ABSTRACT

Electrical conductivity studies of silicates are useful in determining temperature vs depth in the earth. Realistic laboratory measurements of conduction mechanisms require that exact determinations of oxygen fugacity (f_{O_2}) be made in the experimental environment. An apparatus is described that monitors system f_{O_2} with a calcia-doped zirconia-oxygen cell while measuring electrical conductivity of iron-bearing silicates at high temperature (>1000 K). The f_{O_2} calculated thermodynamically from CO/CO₂ mixing ratios agreed well with measurements made with the zirconia cell at 1473 K, except for $f_{O_2} > 10^{-4}$ Pa, where, on a log₁₀ scale, mixing-ratio errors were as large as ± 0.2 . These errors are attributed to oxygen contamination in the CO₂ and to mobile carbon deposits that formed in the apparatus.

INTRODUCTION

Electrical conductivity (σ) of silicates has been studied extensively as a means to determine temperature vs depth in the earth. The control of oxidation

state has been shown to be essential during high-temperature measurements of the electrical conductivity of iron-bearing silicates such as olivine¹ and pyroxene.² Oxidation-state control is also necessary when measuring other material properties like optical absorption³ and high-temperature creep,⁴ which are sensitive to trace impurities. However, control of oxidation state alone is not always sufficient when measuring high-temperature conductivity; the oxygen fugacity (f_{O_2}) of the experimental environment must also be known before precise interpretation of conductivity mechanisms is possible.

The oxygen fugacity with which a silicate is in equilibrium is temperature dependent. This is shown in Fig. 1, which illustrates the oxidation-reduction boundaries for olivine⁵ containing about 9 wt% iron ($Mg_{1.8}Fe_{0.2}SiO_4$). The iron-wüstite (I-W, Fe-FeO) and the wüstite-magnetite (W-M, FeO-Fe₃O₄) boundaries⁶ are shown in this figure as

Fig. 1. The stability field of olivine containing ~10% fayalite as a function of temperature and f_{O_2} . OPM line is the boundary above which olivine oxidizes to form pyroxene and magnetite. OPI-OSPI line is boundary below which olivine reduces to form either olivine (forsterite), pyroxene, and iron or olivine (forsterite), silica, pyroxene, and iron, depending on temperature. The I-W and W-M lines are the iron-wüstite and wüstite-magnetite boundaries, respectively.

references to the low oxygen fugacity in equilibrium with olivine. Within this broad olivine stability field, conductivity may vary up to one-half an order of magnitude as a function of oxygen fugacity.⁷ Controlled studies of conductivity as a function of oxygen fugacity should help us to understand the

defect structure and complex conduction mechanisms in olivine and pyroxene. Such studies can also be used to interpret electromagnetic induction data from the earth⁸ and moon.⁹ In this report, we describe the design and operation of an apparatus for simultaneously measuring σ and f_{O_2} .

BACKGROUND

Gas mixers have long been used to control the f_{O_2} of experimental atmospheres.¹⁰ The gases are assumed to be in equilibrium, and f_{O_2} is calculated from their free energies of formation¹¹ as described below.

We use CO_2 and CO for controlling f_{O_2} . To calculate f_{O_2} , we consider the reaction

with an equilibrium constant,¹² K_p of

$$K_p = \frac{[P_{CO}][P_{O_2}]^{1/2}}{[P_{CO_2}]} \quad (2)$$

where P_i is the partial pressure of the i^{th} component ($i = CO, CO_2$, etc.) in the gas phase. Solving for P_{O_2} , we find that

$$P_{O_2} = K_p^2 \frac{[P_{CO_2}]^2}{[P_{CO}]^2} \quad (3)$$

Because

$$\Delta G^\circ = -RT \ln K_p \quad (4)$$

and

$$\Delta G^\circ = \Delta G_f^\circ(\text{products}) - \Delta G_f^\circ(\text{reactants}), \quad (5)$$

then

$$K_p = \exp(-\Delta G^\circ/RT), \quad (6)$$

where ΔG_f° is the free energy of formation, R is the gas constant, and temperature T is in kelvins.

Table 1 lists ΔG° for CO and CO_2 from 1000-2000 K as compiled by Coughlin.¹¹ As required in Eq. (6), ΔG° is included in this table, and because the ΔG_f° of O_2 is zero, ΔG° is simply calculated by:

$$\Delta G^\circ = \Delta G_f^\circ(CO) - \Delta G_f^\circ(CO_2). \quad (7)$$

Table 1. Free energies (cal mole⁻¹) of formation for CO , CO_2 , $\Delta G^\circ(CO-CO_2)$, and K_p as a function of temperature.

Temperature, K	$-\Delta G_f^\circ CO$	$-\Delta G_f^\circ CO_2$	$\Delta G^\circ(CO-CO_2)$	$K_p = \exp \left[\frac{-\Delta G^\circ(CO-CO_2)}{RT} \right]$
1000	47 940 (± 20)	94 610 (± 30)	46 670	6.30×10^{-11}
1100	50 050	94 640	44 590	1.38×10^{-9}
1200	52 150	94 660	42 510	1.81×10^{-8}
1300	54 240	94 680	40 440	1.59×10^{-7}
1400	56 310	94 690	38 380	1.02×10^{-6}
1500	58 370	94 710	36 340	5.07×10^{-6}
1600	60 430	94 730	34 300	2.06×10^{-5}
1700	62 460	94 720	32 260	7.12×10^{-5}
1800	64 480	94 720	30 240	2.13×10^{-4}
1900	66 500	94 720	28 220	5.67×10^{-4}
2000	68 510	94 720	26 210	1.37×10^{-3}

Table 1 also includes values of K_p calculated from Eq. (6). This value of K_p can then be substituted in-

to Eq. (2) to calculate f_{O_2} for a given gas mixture at any temperature.

EXPERIMENTAL

The gas mixer shown in Fig. 2 was constructed to control the CO_2/CO ratio in our apparatus. Carbon monoxide and carbon dioxide are supplied at approximately 65 kPa through a line filter (also serving as a surge tank) to precision regulators that supply gas at about 40 kPa to filter-protected micro-meter valves. The valves are used to regulate flow indicated by floating-ball flowmeters. The gases are then mixed and supplied to the experimental assembly, which is inside a furnace capable of reaching 2000 K.

Figure 3 is a calibration curve for the flowmeters of the gas mixer. Calibration was made by transit-time measurements of soap bubbles in either 10- or 50-ml burettes connected to the furnace outlet. A smaller-capacity flowmeter is used for CO because our applications generally require less CO than CO_2 .

The dashed lines of Fig. 4 illustrate the f_{O_2} limits achieved by the mixer in Fig. 2. These calculations were made using Eq. (6) and Table 1. For reference,

the oxidation-reduction reactions of Fig. 1 are also reproduced in Fig. 4.

The f_{O_2} of pure CO_2 shown in Fig. 4 is calculated as follows. For CO_2 only, $P_{CO_2} = 1$, and

$$[P_{CO}] = [P_{O_2}]^{1/2}. \quad (8)$$

Combining Eqs. (2) and (8), we obtain

$$P_{O_2} = K_p^{3/2}. \quad (9)$$

The calculated value of f_{O_2} described above may not be the true f_{O_2} in the assembly for several reasons. Contamination of the experimental atmosphere by outgassing of ceramics, carbon deposition at low f_{O_2} , impure gases, failure to achieve equilibrium between the gases, and inaccurate flow measurement are possible error sources. Because of these and other sources of uncertainty as discussed by

Fig. 2. Schematic diagram of the gas-mixing system.

Fig. 3. Flow of (a) CO_2 and (b) CO as a function of flowmeter setting for the gas mixer.

Huebner,¹³ we have constructed the apparatus shown in Fig. 5 to monitor f_{O_2} while measuring σ . The basic σ -measuring assembly is adapted from Duba and Nicholls,¹ while the f_{O_2} -measuring assembly is adapted from Williams and Mullins.¹⁴ Except for the calcia-doped zirconia tube, all ceramic parts are high-purity alumina (99.95% Al_2O_3).

Platinum-rhodium thermocouples (Pt-Pt 10% Rh) welded to 0.25-mm platinum foil are used to measure sample conductance. Having the thermocouples exiting from opposite ends of the furnace decreases the leakage conductance between electrode leads, which can affect measurements in systems where electrode leads emerge from the same end.¹⁵ The sample, painted with platinum paint, is sandwiched between 0.25-mm platinum foils to prevent electrode evaporation and iron contamination of the thermocouple at temperatures >1400 K.

Fig. 4. The calculated limits (dashed lines) of the gas mixer in Fig. 2 compared to oxidation-reduction reactions in Fig. 1.

Thermocouple wires and the platinum lead to measure electromotive force (emf) of the f_{O_2} cell exit to the atmosphere by hose barbs. The platinum wire of the thermocouple inside the zirconia (ZrO_2) cell serves as the lead to the inner electrode of the f_{O_2} cell. Soft rubber tubes over the hose barbs are clamped around the wire to provide an airtight seal. The O-ring seals, lubricated with vacuum grease and cooled by water jackets, form a seal against gas contamination. A small compression spring from a ballpoint pen holds the sample between the thermocouples and foil electrodes.

The outer alumina tube inside the furnace area is wrapped in 0.025-mm platinum foil, and is therefore electrically shielded. The foil overlaps a layer of silver paint that is the shield on the portion of the tube not inside the furnace. The wires are also shielded, and all shields are connected to a ground in common with the instruments used to measure σ and the emf generated by the f_{O_2} cell. This shielding assures measurement stability with little or no detectable interference from the furnace. As calibrated against the melting point of gold (1337 K), temperature is measured with an accuracy of 1 K.

Fig. 5. Schematic of the assembly used to measure σ and f_{O_2} . Dashed lines inside ceramic tubes indicate Pt or Pt-Rh wires.

RESULTS AND DISCUSSION

The emf generated by the zirconia-calcia $[(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}]$ ceramic is a function of oxygen fugacity ¹⁴:

$$\log f_{\text{O}_2} = - \frac{20.159}{T} E \quad (10)$$

where E is the emf in mV. Using Eq. (10), the emf measurement system was checked against the air/ O_2 cell as a function of temperature from ~ 1075 to 1725 K. Figure 6 shows the results for two separate measurements.

The comparison of f_{O_2} for air, calculated vs measured, is affected by prior adjustments of the assembly. Measurements of f_{O_2} for air were initiated at about 1700 K in an assembly that previously had pure CO flowing at about 1600 K, to check that the cell would generate more than 1 V with O_2 as the reference gas. This caused some carbon to deposit in the cooler portion of the furnace (see Fig. 1 of Ref. 6). Air was then purged through the system and the temperature increased to bake out the deposited carbon. Because the maximum temperature of 1707 K was maintained for slightly more than one hour before the emf was measured, we assumed that the carbon deposit was not completely removed. This was confirmed by the initial high emf reading of the cell at 1707 K and the good agreement between calculated and measured emf at lower temperatures where carbon contamination is small because of the previous high-temperature event that outgassed deposited carbon.

Carbon deposition is a problem for all low- f_{O_2} mixtures, as indicated by the following example. After an f_{O_2} of 10^{-12} was maintained in the assembly for several hours at 1473 K, the air/ O_2 cell emf was measured both on heating to 1725 K and cooling. These data, plotted as squares in Fig. 6, indicate that all emf values generated upon initial heating are high by as much as 1.3 mV. However, at the highest temperature maintained for only 20 min prior to measurement, and upon cooling, measured and calculated emf values agreed. We conclude that the f_{O_2} (and presumably the composition) of a gas circulated in an experimental assembly, is affected by that assembly. Before accepting the thermodynamically calculated f_{O_2} as the true f_{O_2} , the assembly must be equilibrated with the gas mixture at a temperature greater than that at which the f_{O_2} is to be calculated. If we use only data from the cooling

cycles in Fig. 6, the measured emf is within 0.5 mV of the calculated emf at temperatures between 1250 and 1700 K. However, below 1250 K, the measured emf is too low, which is consistent with the observations of Huebner ¹³ who found that achieving equilibrium is difficult between the gases at low temperatures. The equilibrium problem is compounded because, in our furnace, we use large temperature gradients to reduce conductance-measurement errors caused by conduction in the alumina tubes.

We conclude that our system has an accuracy of at least 0.5 mV from 1250 to 1700 K. The error of calculating f_{O_2} will be greatest ($\leq 1.5\%$) for air where the emf generated by the cell is low, and will become insignificant ($\leq 0.2\%$) for the f_{O_2} routinely used that will generate greater than 300 mV.

To compare the f_{O_2} calculated from the CO_2/CO ratio using measured emf and Eq. (10), we first consider the special situation where only CO_2 is flowing in the gas mixer. Because large gas volumes are used for continuous operation of three furnaces, expensive, high-purity CO_2 is not used, and Fig. 7 shows that f_{O_2} measurements at 1473 K with the zirconia are higher than that calculated from Eq. (9), which assumes pure CO_2 . This difference in f_{O_2} should diminish as CO is added to the gas mixture because of the reaction, $\text{CO} + 1/2 \text{O}_2 \rightleftharpoons \text{CO}_2$. ¹² The carbon-contamination problem discussed above is evident in Fig. 7 also because f_{O_2} 's calculated from the data collected during the cooling cycle are higher than the f_{O_2} values calculated from the heating cycle. The previous gas mixtures flowing in the system were at f_{O_2} ranging from 10^{-5} to 10^{-8} Pa at 1473 K for several days.

In Fig. 8 is compared the f_{O_2} calculated from emf measured by the zirconia cell and that calculated from the CO_2/CO ratio. All measurements were made at 1473 K progressing from oxidizing to reducing atmospheres to introduce the minimum error from carbon contamination. However, the previous mixture in the system had been $\leq 10^{-6}$ Pa and no baking out at high temperature (1473 K) was attempted; therefore, the error is that expected in the worst situation. The data should be at the 1:1 line (Fig. 8) if the f_{O_2} values calculated from the zirconia cell agreed with those calculated from the gas mixture. Mixtures more oxidizing than 10^{-4} Pa at 1473 K fall above the 1:1 line, indicating the error introduced by the contamination of carbon produced by outgassing as indicated in Figs. 6 and 7. In more reducing f_{O_2} atmospheres, the 1:1 line is followed more closely.

Fig. 6. Voltage generated by the air/O₂ cell vs temperature. Solid line is the calculated emf for air using Eq. (10).

Fig. 7. The oxygen fugacity of CO_2 as a function of temperature. Line is calculated using Eq. (9), open circles are calculated from oxygen cell measurements made on temperature-increase cycle, closed circles are calculated from measurements made on temperature-decrease cycle on the same day.

Fig. 8. Oxygen fugacity (circles) calculated from the gas-mixing data using Eq. (2) compared to those calculated from the emf measured by the zirconia cell. Solid line indicates a slope of 1:1 in which the two calculations would agree.

CONCLUSIONS

From this study we conclude that the f_{O_2} calculated from gas mixing ratios are accurate to within ~ 0.2 of a $\log_{10}$ unit at f_{O_2} ranging from air to that of a mixture ($\text{CO}_2/\text{CO} = 9.75$) yielding $f_{\text{O}_2} \cong 10^{-3}$ Pa. Care should be taken, however, that carbon contamination is avoided. The best procedure is to bake out the system at higher temperatures before making measurements if accurate f_{O_2} control is

required. Because of these problems with contamination, if the f_{O_2} of the experimental atmosphere is to be determined precisely, it must be measured by an oxygen electrolyte cell and not calculated from gas-mixing ratios. However, for routine measurements where f_{O_2} accuracy of 0.2 of a $\log_{10}$ unit is suitable, the calculated f_{O_2} based on the gas mixing ratio is acceptable.

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