An automated oxygen-fugacity control system for 0.1-MPa high-temperature furnaces

TODD DUNN
Department of Geology, University of New Brunswick, P.O. Box 4400, Fredericton, New Brunswick E3B 5A3, Canada

INTRODUCTION
The combination of a mass-flow controller, a solid-state electrochemical cell for monitoring furnace oxygen fugacity, and a microcomputer for controlling the mass-flow controller as a function of the measured oxygen fugacity provides a very flexible oxygen-fugacity control system. The following is a description of the system I have set up in my laboratory and includes enough practical information to fabricate a similar system.

The system described here is designed to control oxygen fugacity using a binary gas mixture (CO-CO₂ or CO₂-H₂) to within ±0.02 log₁₀ units over long periods of time and during furnace temperature changes. The system can also be used to change the oxygen fugacity as a function of time and has many additional advantages over conventional systems. One of the major advantages is that the flow controllers (rotameter and mass-flow controller) do not need to be calibrated because the control settings are based on direct measurements of oxygen fugacity. The system is also very conservative of gas, since all of the gas passes through the furnace, unlike in capillary-manganometer fugacity control systems. Figure 1 is a schematic of a system using CO-CO₂ gas mixtures. The major components are (1) an electronic mass-flow controller that can accept an external set point signal; (2) a rotameter to control the flow of carbon monoxide; (3) an electrochemical yttria-doped zirconia oxygen-fugacity cell; (4) a 0 to ±2 V dc digital voltmeter with an isolated analog output; (5) a digital thermometer with an isolated analog output; (6) a microcomputer equipped with an interface card with at least two analog to digital (A/D) conversion channels and one digital to analog (D/A) conversion channel; and (7) three gas bottles with regulators (CO and CO₂ with two-stage regulators and O₂ with a two-stage regulator and an integral rotameter).

Detailed descriptions of the individual components and their functions follow. The inclusion of names of manufacturers and specific part numbers is not meant as an endorsement of those products, but rather as an indication of the specific components used in my system and as a guideline to suitable components and suppliers.

PHYSICAL DESCRIPTION OF THE SYSTEM
The system design is based on the fact that a binary-gas mixing ratio can be controlled by controlling the flow rate of one of the gas components while that of the other component is fixed. Consequently, the system uses a high precision rotameter to set the flow rate of the CO while the CO₂ flow rate is controlled by a mass-flow controller. The CO flow rate is controlled by a rotameter because of the tendency of the CO to break down to graphite, which plugs the sensor capillary of a mass-flow controller at the low flow rates used during fugacity control. The rotameter used in my system is a Matheson model 762T with a 610 tube and a high-precision valve (any rotameter with a low total flow range and a precision valve can be substituted). I generally use a ball-float height of 25 mm, corresponding to approximately 25 standard cubic centimeters per minute (SCCM). Such a setting maintains a sufficient total gas flow through my 3.0-cm internal-diameter furnace tube at oxygen fugacities as low as 2 log₁₀ units below fayalite-magnetite-quartz. The CO consumption at that setting is approximately one 5-m³ tank per 3000 h of continuous operation. Larger furnace tubes or lower oxygen fugacities will require higher CO flow rates.

The CO₂ flow rate is controlled with a mass-flow controller (Matheson modular dynablender model 8210 with a 10–500 SCCM flow range). The mass-flow controller can be set by a front-panel potentiometer (for stand-alone operation) or by an external 0- to 5-V dc signal and has a digital read-out of the set point or the measured flow rate. The controller can be manually set to ±1 SCCM of CO₂ flow, which gives better than 1% precision in the CO₂ percentage at typical mixing ratios. Automatic set-point generation (e.g., via a D/A board in a computer) can give considerably more precise mixing-ratio control (approximately ±0.2% for a 12 bit D/A converter generating a 0- to 5-V signal). The mass-flow controller is extremely sensitive to ground loops that cause the system to periodically lose control, opening the servo valve all the way (resulting in a CO₂ flow rate in excess of 1300 SCCM), which causes the oxygen fugacity in the furnace to oscillate. This problem can be eliminated by using plastic tubing for all the plumbing connections to and from the mass-flow controller and taking care not to ground the body of the instrument.

One of the most important system components is the oxygen-fugacity sensor. Sensors are available from several suppliers, but I have found the 8 mm × 600 mm sro2 cell manufactured by Ceramic Oxide Fabricators Pty. Ltd. (83 Wood Street, Eaglehawk, Victoria 3556, Australia) to be extremely reliable and durable. The cell consists of an yttria-doped zirconia electrolyte pellet fused onto the end of an alumina tube and is consequently much more resistant to thermal shock than full-length electrolyte cells. I introduce the oxygen sensor into the furnace from the bottom at an off-center location such that the
The final components for the system are the three gas bottles equipped with two-stage regulators. I use oxygen of either 99.98% or 99.8% as the reference gas for the electrochemical cell and set its flow rate with a rotometer that is attached to the regulator.

**Operation of the System**

The control system can be operated either in manual or automated mode. Manual operation is very simple. After the desired temperature and oxygen fugacity have been determined, the expected EMF output of the electrochemical cell is calculated from

\[ E = -(RT/4F)\ln(f_{O_2}(\text{ref})/f_{O_2}(\text{furnace})) \]

where \( R \) is the gas constant [8.3143 J/(mol·K)], \( T \) is the absolute temperature, \( F \) is the Faraday constant (96487 J/mol), and \( f_{O_2}(\text{ref}) \) is the oxygen fugacity of the reference gas (1 for pure oxygen). The CO flow rate is then set using the rotometer, and the CO₂ flow rate is adjusted (using the front-panel control on the mass-flow controller) until the calculated EMF is achieved.

The details of automated operation depend on the software used to operate the system. My program allows a choice of operating modes that include (1) control at a fixed oxygen fugacity, (2) control of oxygen fugacity relative to a specific buffer with or without an offset (the choices are iron-wüstite, wüstite-magnetite, fayalite-magnetite-quartz, magnetite-hematite, and nickel-nickel oxide), (3) control of oxygen fugacity as a function of time (using the timer on the A/D, D/A interface board in the
computer), and (4) control of oxygen fugacity based on a user-defined function of temperature. The control algorithm periodically reads the electrochemical cell EMF and the temperature, calculates the furnace oxygen fugacity and the set-point oxygen fugacity, and either increases the CO₂ flow rate (if the measured oxygen fugacity is too low) or decreases it (if the measured oxygen fugacity is too high). Recall that the CO flow rate is fixed.

The critical aspects of the control algorithm are the timing between successive control-setting changes and the magnitude of the changes. My program uses an increment that decreases as the offset from the set point decreases. The increments (in percent of the total CO₂ flow rate) and the associated set-point offsets (in log₁₀ units of fugacity) are (100/0, 2), (50/0, 1), (10/0, 0.4), and (0.2/0, 0.1); the CO₂ flow is not changed if the system is within 0.02 units of the set point. The time between changes depends on the flow rate of the gas. In my system the linear gas-flow rate through the furnace is approximately 1 cm/s, and the system takes about 20–25 s to fully respond to a change in the control settings. Thus, I use a 50-s delay between readings of the system conditions (EMF and 7), but the response time must be determined experimentally for each system. Starting from an initial air atmosphere, my system takes from 6 to 10 min to achieve control within ±0.1 log₁₀ units of oxygen fugacity, and after 30 min the control is generally within ±0.02 log units. The use of the microcomputer also provides a convenient method of recording the temperature and oxygen fugacity during an experiment.

**Calibration of the system**

The only part of the system that must be calibrated is the oxygen fugacity sensor. I calibrate my sensor at the magnetite-hematite and wüstite-magnetite transitions. However, other workers might prefer to use the fayalite-magnetite-quartz or iron-wüstite buffers. I chose the iron oxide buffers because they span my normal operating range, the required reagent (Fe₂O₃) is readily available, and the reaction kinetics are reasonably fast at 1200 °C.

My normal calibration procedure is as follows: (1) Introduce 1 g of hematite into the cold zone of the furnace and set the furnace to 1200 °C. (2) Set the furnace to an oxygen fugacity 0.1 log₁₀ units above the magnetite-hematite buffer. (3) Lower the hematite sample into the hot zone and allow the system to stabilize for 1 h. (4) Remove the hematite from the furnace and weigh it to determine if the system oxygen fugacity is above the magnetite-hematite buffer (no weight change) or below it (weight loss). (5) Repeat steps 1–4 using progressively lower oxygen fugacities (0.05 log₁₀ unit steps) until the magnetite-hematite transition has been bracketed.

I use the same procedure to bracket the wüstite-magnetite buffer using magnetite (produced by reducing hematite) as the starting material. I do not normally reverse my calibration because the reversals I have done indicated that it was not necessary. I have found that the oxygen-fugacity cells I use retain their calibration for several months of continuous high-temperature operation. The only real risk to the calibration is that a wire-loop sample might fall off the loop and land on the fugacity sensor. I guard against that possibility by placing a small Pt umbrella over the electrolyte.

**Summary**

The combination of an electrochemical oxygen-fugacity cell, a microcomputer, and a mass-flow control valve can be used to provide automated, high-precision oxygen-fugacity control in 0.1-MPa high-temperature furnaces. The system is easily calibrated and more conservative of gas (i.e., cheaper to operate) than flow-control systems of the capillary-manometer type. The cost (approximately U.S. $3500 for my system) is somewhat higher than a capillary-manometer-based or rotameter-based system, but the expanded control and data-logging capabilities make the extra cost worthwhile.

**Manuscript received August 10, 1989**

**Manuscript accepted November 16, 1989**