

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

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### 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 ( $\text{CO-CO}_2$  or  $\text{CO}_2\text{-H}_2$ ) to within  $\pm 0.02 \log_{10}$  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-manometer fugacity control systems. Figure 1 is a schematic of a system using  $\text{CO-CO}_2$  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  $\pm 2$  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 ( $\text{CO}$  and  $\text{CO}_2$  with two-stage regulators and  $\text{O}_2$  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  $\text{CO}$  while

the  $\text{CO}_2$  flow rate is controlled by a mass-flow controller. The  $\text{CO}$  flow rate is controlled by a rotameter because of the tendency of the  $\text{CO}$  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 7632R 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  $\log_{10}$  units below fayalite-magnetite-quartz. The  $\text{CO}$  consumption at that setting is approximately one 5-m<sup>3</sup> tank per 3000 h of continuous operation. Larger furnace tubes or lower oxygen fugacities will require higher  $\text{CO}$  flow rates.

The  $\text{CO}_2$  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  $\pm 1$  SCCM of  $\text{CO}_2$  flow, which gives better than 1% precision in the  $\text{CO}_2$  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  $\pm 0.2\%$  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  $\text{CO}_2$  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  $\times$  600 mm  $\text{SiO}_2$  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

electrolyte pellet is located in the furnace hot zone. The cell requires two electrical contacts. I use 0.25-mm diameter Pt wire for both contacts. The external contact is passed through a 99.8% alumina tube of 0.30-mm inside diameter that is sealed at the hot end with resistor cement to protect the Pt wire from graphite precipitation in the colder parts of the furnace. (Pt wires have a very short life when exposed to graphite at temperatures near 1000 °C.) One end of that wire is simply wrapped around the exposed electrolyte, which is grooved and platinized to facilitate electrical contact. The other end of the wire passes through the bottom closure of the furnace, where it is connected to a subminiature type-U (Cu) thermocouple connector plug. The internal electrical contact can be a bit of a problem because thermal expansion of the alumina portion of the cell can cause the contact to break during heating. Consequently, I pass the contact wire through one bore of a four-bore alumina tube of 1.5-mm outside diameter. The tube fits through a modified 1/4-in. (0.635-cm) tube fitting and is spring loaded (with a ball-point pen spring) to ensure positive contact with the electrolyte. To further assure electrical contact, I also form the contact end of the wire into a spiral coil, which compresses against the electrolyte. The free end of the sensor wire is connected to the same connector as the outside sensor wire. The four-bore alumina tube also acts as a conduit for the sensing thermocouple (I use a Pt<sub>90</sub>Rh<sub>10</sub>-Pt thermocouple). The four-bore tube is ground at the end to provide a recess to prevent electrical contact between the sensing electrode and the thermocouple. This arrangement ensures that the temperature at the electrolyte is measured as required for accurate fugacity measurements. The thermocouple wires are terminated at a compensated subminiature thermocouple plug. The only other parts of this system are an alumina tube (single bore of 1.5-mm outside diameter) for introducing the reference gas into the fugacity sensor and a vent to allow gas to escape from the sensor. Both tubes are passed through the same 1/4-in. (0.635-cm) tube fitting as the four-bore tube containing the sensor wire and the thermocouple and are held in place with silicon rubber cement. The gas vent tube need not extend into the sensor more than 2–3 cm.

An Apple IIe computer with a Metrabyte APM-08 (A/D, D/A) interface board is used to monitor both the electrochemical cell EMF and the furnace temperature and to control the mass-flow controller. IBM-compatible hardware would work equally well. The EMF output of the electrochemical cell is connected to a digital voltmeter with an isolated 1V/V output (OMEGA DP2000A2). The output from the digital voltmeter is connected to one of the A/D converters on the computer interface board. The thermocouple in the electrochemical cell is connected to a digital thermometer with an isolated 1 mV/°C output, which is also connected to one of the A/D converter inputs for the computer. The computer also provides a 0- to 5-V signal to control the setting of the mass-flow controller via the D/A output of the interface board.

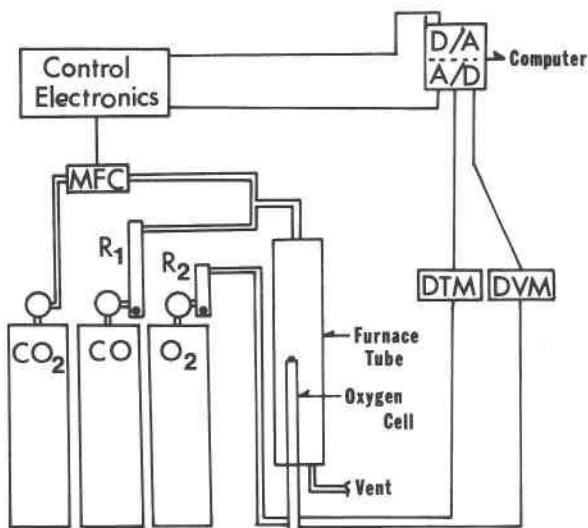


Fig. 1. Schematic of the automated oxygen-fugacity control system showing gas tanks, rotameters for CO (R1) and O<sub>2</sub> (R2) flow control, the mass-flow controller (MFC) for CO<sub>2</sub> flow control, the control box for the MFC, the D/A and A/D converter in the computer, the electrochemical cell, the digital thermometer (DTM), and the digital voltmeter (DVM). Gas connections are shown as double lines and electrical connections are shown as single lines.

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 rotameter 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

$$E = -(RT/4F)\ln[f_{\text{O}_2}(\text{ref})/f_{\text{O}_2}(\text{furnace})],$$

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  $f_{\text{O}_2}(\text{ref})$  is the oxygen fugacity of the reference gas (1 for pure oxygen). The CO flow rate is then set using the rotameter, and the CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> flow rate) and the associated set-point offsets (in log<sub>10</sub> units of fugacity) are (10%, 2), (5%, 1), (1%, 0.4), and (0.2%, 0.1); the CO<sub>2</sub> 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 *T*), 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  $\pm 0.1 \log_{10}$  units of oxygen fugacity, and after 30 min the control is generally within  $\pm 0.02 \log$  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 (Fe<sub>2</sub>O<sub>3</sub>) 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 log<sub>10</sub> 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 log<sub>10</sub> 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