In situ Determination of the Viscosity of Gas Mixtures Containing Trace Quantities of Oxygen

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An electrochemical cell was used to add trace quantities of oxygen to a gas stream. The viscosity of these gas mixtures was determined using an established method that measures the rate of change of viscosity with oxygen concentration. Viscosity data are reported for nitrogen/oxygen and helium/oxygen mixtures at very low oxygen concentrations. The data are compared with values for the viscosity of these gas mixtures, interpolated from results reported in the literature.

Introduction

In this article we describe a novel apparatus for the *in situ* addition of oxygen to other gases. The ultimate aim is to carry out controlled oxidation reactions, but here, as a test, this technique is applied to the determination of the viscosity of dilute mixtures of oxygen in helium and oxygen in nitrogen.

Oxygen addition

The controlled addition of oxygen is based on the fact that oxygen may be quantitatively transported (pumped) as oxygen ions through dense solid electrolyte membranes (such as yttrium stabilized zirconia, YSZ or calcium stabilized zirconia, CaSZ) if an electrical potential gradient is applied (Vayenas and Bebelis, 1999). Unfortunately, significant oxygen conductivity of the electrolyte material is only observed at elevated temperatures (Shriver et al., 1994); so, the oxygen addition has to be carried out in a furnace.

Based on Faraday's law, the oxygen flux across the electrolyte (in form of O^{2-} ions) may be calculated by

$$n_{O_2} = \frac{I}{z \cdot F} \cdot E \qquad (1)$$

where

n_{O_2} = molar oxygen flux (mol/s)
I = measured current (A)
z = number of electrons transferred (4 electrons to produce O_2)
F = Faraday's constant (96,489 C/mol), and
E = ionic efficiency of electrolyte (a measure of ionic vs. electronic conductivity of the electrolyte).

A particular current therefore adds oxygen to a stream of diluent gas at a precise rate. This rate is known when the ionic conductivity of the electrolyte is known.

The combination of a solid-electrolyte gas mixing device with a flow and viscosity measuring device yields our combined instrument. The flow and viscosity of the gas mixture are measured with a capillary tube meter. Because there is a delay line (a length of empty tube) in the system, the capillary tube meter acts as both a flowmeter and a viscometer.

Viscosity measurement

To see how this is done, consider the notional system in Figure 1, which contains all the important elements. A constant carrier flow is established through the system which comprises the solid electrolyte cell, a pressure transducer, and a capillary tube. A back pressure regulator sets the pressure at p_{BPR} at the outlet of the capillary tube. The capillary tube

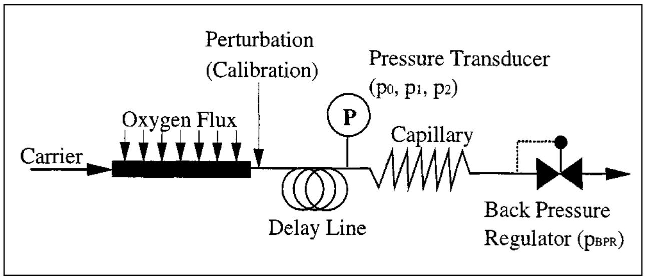

Figure 1. Notional system.

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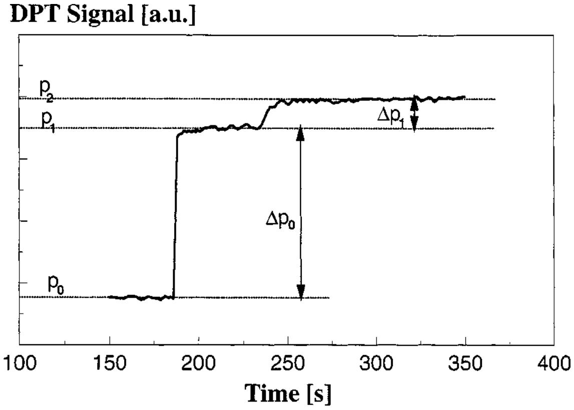

Figure 2. Example of system response.

at the end of the system restricts the flow and, hence, causes the upstream pressure (p_0) in the system to be higher than p_{BPR}. This system pressure is detected by the pressure transducer. Figure 2 shows the signal trace (pressure changes) observed with our technique. For calibration purposes, a small but constant perturbation stream can be introduced into the carrier gas stream. When this is done, the pressure transducer will record an increased pressure (p_1). A perturbation can also be introduced by applying a voltage across the solid-electrolyte membrane, in which case oxygen will be added to the system. The introduction of the perturbation gas changes the composition of the combined flow. This mixed flow moves through the delay line at the superficial velocity of the carrier flow plus perturbation flow. It eventually reaches the capillary at the end of the system. A capillary tube meter is sensitive to flow rate and viscosity; so, if the viscosity of the gas is changed by the perturbation (addition of a different gas), the pressure indicated by the transducer will change to a new pressure p_2. The change in pressure from p_1 to p_2 will be an indication of the change in viscosity of the gas.

For laminar flow through a capillary, the pressure gradient is proportional to the product of the fluid velocity and viscosity. For a gas (assumed ideal), the velocity is inversely proportional to the pressure, which depends on axial position. Nevertheless, the mass (or molar) velocity is independent of position. Consequently, $-p(dp/dz)$ (where dz is a differential distance along the capillary) is proportional to $(\mu \cdot M)$. Integration over the whole length of the capillary shows that

$$p^2 - p_{BPR}^2 = 2K\mu MRT \tag{2}$$

where
p = system pressure (bar),
p_{BPR} = pressure set by back pressure regulator (bar),
K = capillary constant,
μ = viscosity of gas (μP),
M = molar flow of gas (mol/s),
R = universal gas constant (J/(mol·K)
T = temperature

The addition of the perturbation gas gives rise to an increase in flow ΔM which is related to p_0 and p_1 by

$$p_1^2 - p_0^2 = 2K\mu_0 RT\Delta M \tag{3}$$

At this moment, only the flow rate in the system changes and ΔM denotes the molar flow of the added perturbation (the viscosity in the capillary stays constant because the perturbation gas and, hence, the change in composition has not yet reached the capillary).

Consider now the second step (the perturbation reaches the capillary). The flow is $M + \Delta M$ and the viscosity changes by $\Delta\mu$

$$p_2^2 - p_1^2 = 2KRT[M + \Delta M]\Delta\mu \tag{4}$$

If the step sizes are Δp_0 and Δp_1, then

$$\Delta p_1 = p_2 - p_1 \tag{5}$$

and

$$\Delta p_0 = p_1 - p_0 \tag{6}$$

Substituting and dividing Eq. 4 by Eq. 3, we get

$$\frac{2p_1\left(\Delta p_1 + \dfrac{\Delta p_1^2}{2p_1}\right)}{2p_0\left(\Delta p_0 + \dfrac{\Delta p_0^2}{2p_0}\right)} = \frac{(M + \Delta M)\Delta\mu}{\mu_0 \Delta M} \tag{7}$$

Now, if all the pressure changes are small relative to the absolute pressure, then $p_0 \approx p_1$ and $p_0,\ p_1 \rangle\rangle \Delta p_1,\ \Delta p_2$ and Eq. 7 reduces to

$$\frac{\Delta p_1}{\Delta p_0} = \frac{(M + \Delta M)\Delta\mu}{\mu_0 \Delta M} = R_{\mathrm{add}} \tag{8}$$

Note that $\Delta p_1/\Delta p_0$ is a measurable quantity (Figure 2).

If the perturbation is the addition of pure oxygen, flow rate ΔM is to a carrier which contains no oxygen, then the final mol fraction of oxygen is given by

$$X_{\mathrm{O}_2} = \frac{\Delta M}{\Delta M + M} \tag{9}$$

Now,

$$\Delta\mu = \mu_1 - \mu_0 \tag{10}$$

So, from Eq. 8 and 9

$$\mu_1 = \mu_0\left[1 + \frac{R_{\mathrm{add}}\Delta M}{M + \Delta M}\right] = \mu_0\left[1 + R_{\mathrm{add}} X_{\mathrm{O}_2}\right] \tag{11}$$

where
X_{O_2} = mol fraction of oxygen in the total gas flow,
μ = viscosity of gas mixture (μP),
p_0 = system pressure prior to perturbation introduction (bar),
p_1 = system pressure after addition of perturbation flow (bar),
p_2 = system pressure when perturbation has reached the sensing capillary (bar)

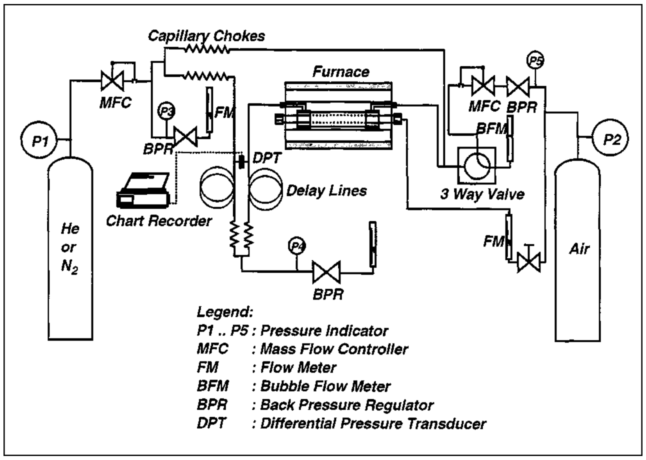

Figure 3. Experimental setup.

Table 1. Experimental Conditions for Pumping Experiments

Carrier Gas	He	N_2
Temperature (K)	773	773
Carrier Flow Rate (mL/min)	8.9	9.7
Air Flow Rate (mL/min)	20	20
Max. Voltage Applied (V)	14	12

This means that by simply measuring the ratio of the two pressure changes (caused by the addition of the perturbation) and knowing the viscosity of the pure carrier gas, the final viscosity of the gas mixture can be determined. The mol fraction of oxygen in the gas stream is derived from the calibrated first pressure change (see Eq. 3) using Eq. 9.

An error in calculation shows that the simplification of Eq. 7 to yield Eq. 8 is valid within our range of measurement: Our system operates at just above atmospheric pressure (1.315 bar). At an electrochemical cell voltage of 8 V (one of the highest voltages applied-resulting in one of the highest oxygen flow rates induced), the pressure transducer gave values of $\Delta p_0 = 4.74 \times 10^{-4}$ bar and $\Delta p_1 = 3.68 \times 10^{-4}$ bar. The error introduced by the approximation mentioned above amounts in this case to 0.032%, which can be neglected. The application of voltages in excess of 2.5 V to the electrochemical cell is not recommended (leads to electrolysis of the electrolyte).

Experimental Studies

A working experimental setup is much more complicated than the basic system shown in Figure 1. The full system is given in Figure 3. The electrochemical cell employed consisted of a tube of CaSZ (6 mm od, 280 mm long, 1 mm wall thickness), which was coated with silver on both sides (acting as electrode/catalyst material). The assembled electrochemical cell was of the form Air, Ag//CaSZ//Ag, Carrier Gas (N_2 or He),

The experimental setup represented in Figure 3 has two sides, one being the measurement side and the other the reference side. This enables a differential pressure transducer to be used as shown by Mason et al. (1998). The carrier gas is fed to both sides at a constant pressure upstream of the two matched upstream capillary chokes. The upstream capillary chokes were 150 cm long, 0.25 mm id stainless steel tubes. Both streams pass through the downstream capillary tubes before joining just before a second back pressure regulator, which is set slightly above atmospheric pressure (about 1.3 bar). Both sides of the apparatus have matched delay lines to balance their volumes. The difference in pressure between the two sides is measured before the downstream sensing capillaries by a sensitive differential pressure transducer (DPT), FCO 40, supplied by Furness Controls Ltd. (range ± 10 mm H_2O gauge). The pressure transducer and the sensing capillaries are enclosed and operate at a constant temperature of 298 K.

The flow of calibration gas was set with a mass-flow controller. During the calibration procedure, calibration gas is allowed to pass through a three-way valve into an external bubble flow meter, where the perturbation flow rate is measured accurately. Then, the three-way valve is switched to allow the perturbation flow to join the carrier on the measurement side of the apparatus. The response of the DPT is recorded on a chart recorder (see also Figure 2). A calibration of the response of the DPT to various flows of both carrier gases was produced. During oxygen ion pumping experiments, air passes through the inside of the CaSZ cell and the carrier gas flows through the annulus between the electrolyte and the stainless steel wall. The conditions for the pumping (electrochemically forced oxygen ion transfer) of the oxygen are given in Table 1.

Constant voltages were applied using a Thurlby 30 V-1A power supply (RS Components Ltd. UK) configured as a potentiostat. The cell was heated inside a furnace supplied by Severn Science Ltd. (U.K.). The furnace temperature (500°C) was controlled using an Eurotherm 94 PID Furnace Controller.

All gases were supplied by BOC, and their specifications are listed in Table 2. Since the oxygen is supplied via an electrochemical device, that is, through a dense ceramic electrolyte, the purity of the oxygen is 100%.

Calibration/Verification

In order to verify that the electrolyte used (CaSZ) was a 100% ionic conducting at 773 K (our operating temperature), the molar flow produced via the pumping of oxygen was accurately measured. Using the capillary as a molar flow meter as described in the introduction, the correlation between applied current and the measured molar flow rate is shown in Figure 4. The ionic efficiency (transference number of O^{2-}) is given by the gradient of the line passing through the measured values. It is evident that there is a strictly linear relationship between the applied current and the induced molar

Table 2. Gas Specifications

Gas	Air	He	N_2
Purity %	–	99.995	99.998
Density, kg/m^3	1.29	0.17	1.18
Viscosity at 20°C, μP	18.12	19.61	17.54

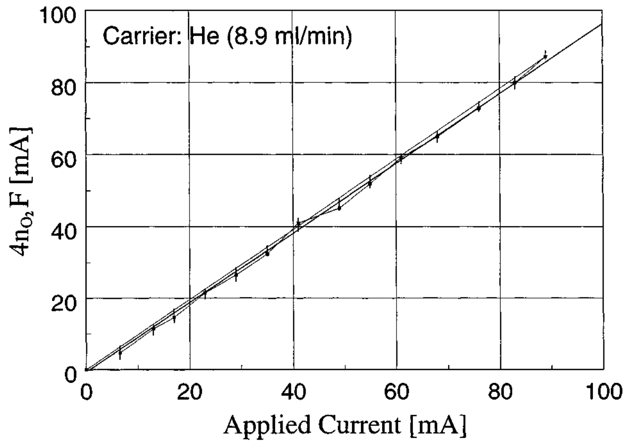

Figure 4. Evaluation of ionic efficiency of electrolyte using helium as carrier gas.

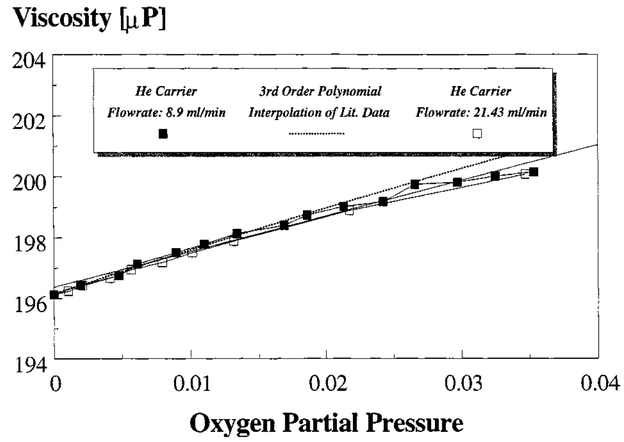

Figure 6. Viscosity of He/O_2 mixtures as function of oxygen partial pressure.

oxygen flow rate. The calculated slope in the case of the helium carrier is 0.97, which suggests that an ionic efficiency of the electrolyte of 97%.

Since the slope does not change with increasing current, it follows that the ionic conductivity is not affected by the current density in the range investigated. Degradation (reduction of the electrolyte) of the cell was only observed at higher current densities. Similar measurements were carried out using nitrogen as carrier gas (Figure 5). In this case it was found that the ionic efficiency was 100%. One reason for the somewhat lower ionic efficiency observed in the first case might be that the cell had been operated previously at higher current densities and, hence, might have developed some electronic conductivity.

These results show that binary gas mixtures with very low oxygen partial pressure can be readily and accurately produced by this method.

Composition/Viscosity Correlation

Because of the built-in delay line, the apparatus also allows the viscosity of the gas mixtures to be measured. According to Eq. 11, measurement of the two offsets Δp_0 and Δp_1 caused by the flow addition and the change in viscosity, respectively, directly yields the viscosity of the gas mixture (provided that the viscosity of the pure carrier is known and that the oxygen partial pressure can be calculated). The required oxygen partial pressure is determined from the carrier flow and the perturbation flow (added oxygen flow) according to Eq. 7. The oxygen flow in turn is obtained from either the first measured offset Δp_0 or by the application of Faraday's law (Eq. 1) (based on the measured current).

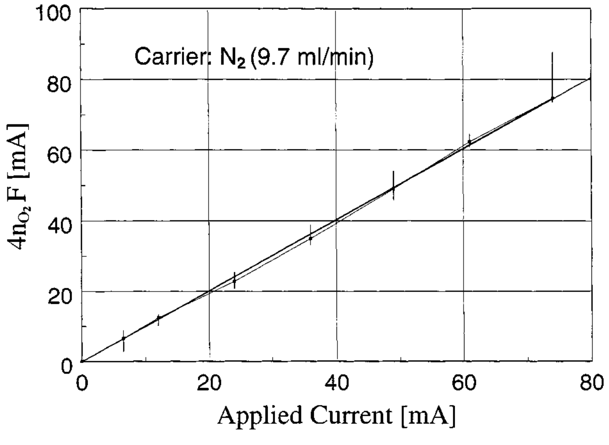

Figure 5. Evaluation of ionic efficiency of electrolyte using nitrogen as carrier gas.

He/O_2-mixtures

A graph of the viscosity of He/O_2 mixtures at low oxygen partial pressures is given in Figure 6. It is apparent that the viscosity of He/O_2 mixtures increases with increasing oxygen partial pressure. We carried out our experiments at two very different carrier flow rates (8.9 and 21.43 mL/min) to investigate a large range of oxygen fluxes through the solid electrolyte.

We have compared our data with published data (Kestin and Yata, 1968; Watson, 1972) to which we fitted a cubic polynomial (regression) in order to interpolate to very low oxygen partial pressures. It appears that our experimental data fit very well and compare favorably with interpolated data from literature.

A *linear* regression analysis of our data (oxygen partial pressure between 0 and 0.035) results in a gradient of **116.98 μP** with an R-square of 0.98. The gradient has the dimension of viscosity. Considering Eq. 11, the gradient corresponds to $(\mu_0 \cdot R_{add})$. A dimensionless gradient can be simply derived by division through μ_0.

It is important to point out that, as far as we know, *no* accurate viscosity measurements have been carried out at these very low oxygen partial pressures. This may be due to the lack of accurate mixing devices for the generation of these gas mixtures. At very low concentrations, there is negligible O_2-O_2 molecular interaction.

N_2/O_2-mixtures

A graph of the viscosity of N_2/O_2 mixtures is given in Figure 7 as a function of the oxygen partial pressure. It is clear

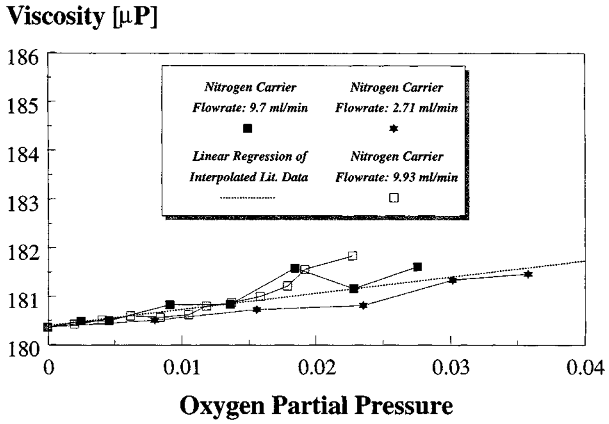

Figure 7. Viscosity of N_2/O_2 mixtures as function of the oxygen partial pressure.

from this figure that the viscosity gradient is rather shallow with respect to composition. There is a simple linear relationship between the viscosity of N_2/O_2 mixtures and the respective oxygen partial pressure (in the range investigated). Hence, the viscosity of any mixture may be calculated in this concentration range simply by the knowledge of the viscosity of nitrogen and the knowledge of the value of the gradient (33.46 μP). Again, our experimental data fit very well the interpolated data from literature (Watson, 1972; Johns et al., 1982; Cole and Wakeman, 1985).

As the difference in viscosity between pure nitrogen and pure oxygen is quite small, it was necessary to reduce the carrier flow to reduce the thermal noise that is picked up by the instrument. Hence, the data collected at the lower carrier flow rate of 2.71 mL/min are likely to be more accurate. The combination of the sensitive pressure transducer and capillary tube is a very sensitive flowmeter. Small random temperature changes in the furnace cause the gas in the electrochemical cell to expand and contract and this appears as random noise at the flow rate detector.

Conclusions

A novel system for the production of gas mixtures containing precise amounts of oxygen at very low levels has been demonstrated. The measurement of the viscosity of such mixtures has been made, and the viscosities of binary gas mixtures (He/O_2 and N_2/O_2) are reported. At low oxygen partial pressures, the viscosity of the gas mixtures (function of oxygen partial pressure) of both systems can be described by a simple linear correlation. The observed gradient in the case of the He/O_2 system was 116.98 μP and in the case of the N_2/O_2 system was 33.46 μP. The accuracy of the described system is of the order of 0.1 μP.

The solid electrolyte Ca-SZ is purely ionic conducting (100% ionic efficiency) at 500°C, which was readily determined with our technique.

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