AN EVALUATION OF AN ELECTROCHEMICAL CELL AS AN OXYGEN GAUGE OVER A WIDE RANGE OF OXYGEN PRESSURES*

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ABSTRACT

A galvanic cell using a commercially made calcium stabilized zirconia tube was used to measure the P_{O_2} of analyzed and premixed gas mixtures of Ar- O_2 and CO- CO_2 over a wide range of oxygen pressures near 1000°C. The accuracy of the cell was evaluated by comparing these results with the reported analyses of these mixtures. A model based on thermal diffusion was used to explain the variation of the emf with flow at low flow rates. Errors due to a temperature difference across the electrolyte were also evaluated. When properly employed this cell has been shown to be a sensitive research device for the accurate measurement of the P_{O_2} over a wide range of oxygen pressures.

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INTRODUCTION

A number of investigators¹⁻¹² have employed galvanic cells of the type

to measure the oxygen partial pressure in gases and vacuum. If the cell is reversible and electronic conduction is negligible, the theoretical open circuit emf, E , is given by the relation¹⁻⁴

$$E = \frac{RT}{nF} \ln \frac{P_2(\text{O}_2)}{P_1(\text{O}_2)} . \quad (1)$$

The value of n is taken as 4 based on the reversible reaction¹

Oxygen, air or a metal-metal oxide mixture is generally used as a reference electrode, $P_2(\text{O}_2)$, and the value of $P_1(\text{O}_2)$ is then calculated using Eq. (1). Weissbart and Ruka¹ using a ZrO_2 -CaO electrolyte have quantitatively verified Eq. (1) between 600° and 750°C in the oxygen pressure region 1 to 10^{-5} atm. Bates and Littlewood⁸ have suggested the industrial application of the oxygen gauge for measuring lower oxygen partial pressures (e.g. the value of P_{O_2} in hot furnace gases). They tested a cell similar to that used by Weissbart and Ruka¹ at 660°C using a few CO-CO_2 and $\text{H}_2\text{-H}_2\text{O}$ mixtures which correspond to values of P_{O_2} in the vicinity of 10^{-20} atm.

Schmalzried⁵ using ZrO_2 -CaO electrolytes has found that at higher temperatures and lower oxygen pressures the electronic transference number becomes significant and the use of Eq. (1) then becomes invalid for the accurate determination of $P(\text{O}_2)$. Baker and West¹⁰ have determined the critical oxygen pressure-temperature relationship corresponding to 2% electronic conductivity for commercially available line-stabilized zirconia.

Oxygen gauges using the above type of electrochemical cell are now commercially available for measuring the oxygen partial pressure above 10^{-6} atm. Weil et al.¹¹ while evaluating the use of a commercial oxygen gauge

for medical purposes observed that the emf was a function of the flow rate of the gases that flowed thru the cell. Sternbergh and Hickman¹³ have also reported a dependence of the cell emf on flow rate.

Similar problems were encountered during an investigation of a calcia-stabilized zirconia solid electrolyte oxygen gauge in this laboratory. These problems were 1) a dependence of the emf on gas flow rate, 2) asymmetric emfs when the electrode gases were reversed and 3) the presence of an emf that varied with gas composition, flow rate and temperature when identical gases were present at both electrodes.

Further study was undertaken to elucidate these problems and to evaluate the use of the oxygen gauge as a research tool for accurate measurement of the oxygen pressure over a wide range of oxygen pressures. The accuracy of the oxygen gauge was evaluated in the neighborhood of 1000°C by comparing the O_2 and CO concentrations determined from the cell measurements with the corresponding analyses of the premixed Ar- O_2 and CO-CO₂ gas mixtures.

EXPERIMENTAL

A schematic diagram of the oxygen gauge used in this investigation is shown in Fig. 1. A 0.5 in dia. 85 mole % ZrO_2 - 15 mole % CaO closed end tube obtained from Zircoa Corporation was used as the inner tube. The flat closed end served as a portion of the electrolyte. A 0.25 in dia. zirconia-calcia pellet of the same composition fabricated in this laboratory completed the electrolyte. The electrodes were made by applying Englehard 6082 platinum paste to the exterior of the bottom of the tube and the top surface of the pellet. The pellet was used because of the difficulty encountered in applying the platinum paste to the bottom of the closed zirconia-calcia tube. Two reference grade Pt, Pt + 13% Rh thermocouples were used to make electrical contact with the platinum electrodes. With this arrangement the platinum legs of the thermocouple located at each electrode served as the electrical leads for the emf measurements.

A 0.016 in dia. platinum wire wound around the alumina gas inlet tube located within the inner zirconia-calcia tube served as a small auxiliary

Fig. 1 Schematic of oxygen gauge.

resistance furnace for the thermoelectric measurements. Voltage measurements were made with a Sargent SR potentiometric recorder and a Leeds and Northrup K-3 potentiometer. The recorder was used to facilitate the determination of equilibrium. The time to purge the system and obtain equilibrium was a function of the type of gas mixture. For example, approximately 10 minutes was required to reach equilibrium with pure oxygen whereas 30 minutes was required when oxygen was replaced with a mixture of 10,000 ppm of oxygen in argon. As a precautionary measure the quartz outer tube was enclosed with nichrome screen which was grounded to shield against electric field effects produced by the furnace winding. An on-off proportioning type controller was used and no change in emf was observed between the on and off cycles.

RESULTS AND DISCUSSION

Preliminary measurements using a cell assembly with only one thermocouple showed that the emf obtained with a gas mixture at one electrode and oxygen at the other was a function of the gas flow rates. With a given flow rate in each electrode chamber, the measured emfs were asymmetric with respect to zero when the gases were reversed. Emfs were also observed with identical gases in each chamber. These emfs varied with gas composition, flow rate and temperature.

Based on these observations it appeared that the emf dependence on the flow rate may have been caused by thermal diffusion, thermoelectric, or nonisothermal galvanic cell effects produced by a variation in the temperature gradient in the furnace or across the electrolyte. The three experiments described below were employed in an attempt to determine the relative contributions of each of these phenomena. The cell assembly was modified to include two thermocouples as shown in Fig. 1 to measure the temperature difference at the electrodes. The emf measurements were made in the vicinity of 1000°C because polarization effects were negligible. In addition the sensitivity of the voltage measuring instrumentation was high because of low cell resistance.

In the first experiment the emf was studied as a function of flow rate using identical gases at both electrodes. The gas flow rate at one

electrode was fixed while that at the other was varied. The results of these measurements using analyzed-premixed tank mixtures of 0.1% O_2 -99.9%Ar and 1%CO-99% CO_2 are shown in Fig. 2.

The behavior of the emf as a function of flow rate when using air or the Ar- O_2 mixtures at both electrodes under the conditions of low flow rates can be explained on the basis of thermal diffusion. Darken and Gurry¹⁴ state that the heavier gases in mixtures tend to diffuse to the lower temperature region under the influence of a temperature gradient. With high flow rates in the outer chamber complete mixing should be obtained whereas with low flow rates in the inner chamber the oxygen would diffuse toward and argon away from the inner electrode region. Thus the thermal separation of the 0.1% O_2 -99.9%Ar gas mixture in the inner chamber should produce a larger value of the P_{O_2} at the inner electrode and a corresponding positive* emf.

On the other hand if the flow rate were high enough in the inner electrode chamber to eliminate thermal diffusion and low enough in the outer electrode chamber that thermal separation were to occur there, then oxygen would diffuse toward the electrode in the outer chamber. The value of P_{O_2} at this electrode would then increase and the emf of the cell would be negative. With increasing flow rates in the outer chamber mixing effects would increase and the emf should approach zero.

Similarly, if thermal separation were to occur using air, the changes in emf should be just the reverse of that observed for Ar- O_2 mixtures because N_2 is lighter than O_2 . Although the predicted dependence of emf on flow rate for air was observed, the results were not shown in Fig. 2 because the change in emf with flow rate was so small that it would be difficult to see on this plot. The results with oxygen at both electrodes were not shown in Fig. 2 because the emf was independent of flow rates.

Thus the observed results for oxygen, air and Ar- O_2 mixtures at low flow rates appear to be consistent with a model based on thermal diffusion. As shown in Fig. 2 a flow dependence was observed for a 0.01%CO-99.9% CO_2 mixture. The results for 52.4%CO-47.6% CO_2 and 96.9%CO-3.1% CO_2 gas mixtures were not shown because the emf was relatively insensitive to flow rate.

*The sign convention adopted in this study was that the emf was positive if the inner electrode was positive.

Fig. 2 emf vs flow rate with identical gases at both electrodes.

No attempt was made to analyze the sign of the emf since three different gases, CO, CO₂ and O₂, which are interrelated through the reaction $\text{CO} + 1/2\text{O}_2 \rightleftharpoons \text{CO}_2$ were present in these mixtures.

The small emf measured at high flow rates where thermal separation was negligible appeared to be due to thermal electric effects. It is interesting to note that the temperature at the electrodes appeared to be independent of flow rate over the range of flow rates investigated (i.e. 0-400cc/min). It should also be noted that in the initial studies an increase in the emf with increasing flow rate was observed when the flow rate in the inner chamber was varied in the high flow rate region. This behavior was observed for pure oxygen, air and Ar-O₂ mixtures. A manometer was connected to the inner chamber to measure the variation of pressure with flow rate. The increase in emf with increasing flow rate was correlated with the observed increase in pressure. This problem was eliminated by increasing the size of both the gas inlet tube and the exit port.

In the second experiment the effect of thermal emfs was investigated. For this study a high flow rate (230-280 cc/min) was used at both electrodes to avoid problems arising from thermal diffusion. The same gas mixture was used at both electrodes and a small temperature gradient (1 to 10°C) was imposed across the electrolyte by passing current through the small auxiliary furnace. The emf was then measured as a function of ΔT . These results and the values of the thermal electric power calculated from the slopes of these curves are shown in Fig. 3 for pure oxygen, air and Ar-O₂ mixtures and Fig. 4 for CO-CO₂ mixtures. It is interesting to note that the sign of the thermal electric power exhibits a negative or positive value depending on the gas mixture used. For the gas mixtures used, the sign of the thermal electric power is consistent with that reported by Ruka, et al¹⁵ except that the magnitudes are only in fair agreement.

The third experiment was conducted in order to estimate the error due to the presence of a temperature difference at the electrodes when oxygen was used at one electrode and a gas mixture at the other. High flow rates (approximately 230-280 cc/min) were used at both electrodes to avoid problems arising from thermal diffusion. The results of these

Fig. 3 emf vs ΔT for identical gases at both electrodes; for O₂ at one electrode and O₂-inert gas mixtures at the other.

Fig. 4 emf vs ΔT for identical gases at both electrodes; for O₂ at one electrode and CO-CO₂ mixtures at the other..

experiments are shown in Figs. 3 and 4 where the emf is plotted as a function of ΔT . The effect of a temperature gradient is quite small when dealing with mixtures of oxygen in an inert gas. According to Fig. 3, a positive ΔT increases the magnitude of the negative emf and decreases the magnitude of the positive emf. Since the slopes of these curves are almost equal the average emf of a cell with an oxygen-inert gas mixture at one electrode remains relatively constant even for large values of ΔT . A temperature gradient of one degree causes a deviation in calculated oxygen partial pressures of $\pm 0.1\%$ or less.

The effect of a temperature gradient with a CO-CO₂ mixture at one electrode is much larger. A positive ΔT decreases the magnitude of both the positive and negative emfs. Therefore, as ΔT increases the average emf decreases causing large deviations in calculated oxygen partial pressures. A one degree ΔT causes the calculated oxygen partial pressures to increase by 3.6, 2.6 and 2.7% for the 10,000 ppm CO, 50% CO and 97% CO-CO₂ mixtures respectively. These percent deviations are approximately linear for values of ΔT to ten degrees.

No attempt was made to separate thermal electric effects from nonisothermal galvanic cell effects for this experiment because the sign and the magnitude of the thermal electric power is a function of $\bar{S}_{O_2}$, and different gases with different values of $\bar{S}_{O_2}$ were used at both electrodes.¹⁵ Large errors in the calculated results could also occur if the cell temperatures were not measured accurately. The magnitudes of these errors obviously increase as the magnitudes of the measured emfs increase. Errors arising from the inaccuracy of the measuring system are negligible when compared to those involving temperature.

The data from the above experiments were then used in investigating the accuracy of the results obtained using the gauge as an oxygen analyzer. The compositions of several analyzed-premixed gases were calculated from the data obtained using the gauge. These results were compared to the analyses supplied with the mixtures.

Before these tests were begun, the following change was made in order to minimize errors due to temperature differentials across the electrolyte. The cell was located in the furnace such that the two thermocouples measured the same temperature with oxygen at both electrodes. The measured

emf at this time was $0.0 \pm 0.05\text{mv}$. A nonzero temperature difference was later measured at the electrode. This may have been due to a lack of complete thermal equilibrium or to a change in the furnace temperature gradient with the use of gases other than oxygen. However, these temperature differences were generally less than 1°C . Gas flow rates of 230 - 280 cc/min were used. These flow rates corresponded to regions in which the emfs were independent of the flow rate.

The results of several analyses using the oxygen gauge are presented in Table I. The gases present at each electrode with the measured temperatures of the electrodes are listed for each run. A measured emf for each electrode condition with a corresponding calculated oxygen partial pressure and gas composition are also tabulated. An average calculated composition is listed for each run. Analyses supplied by the Matheson Company complete the table. The Matheson Company claims an accuracy for these analyses of $\pm 3\text{-}5\%$ of the reported value for mixtures containing 10% or less O_2 or CO and $\pm 2\text{-}3\%$ of the reported value for mixtures with O_2 or CO contents greater than 10%. The temperature used in calculating a value of the P_{O_2} for each set of electrode conditions was obtained by averaging the temperatures measured at the inner and outer electrodes.

The average calculated compositions for all runs with the exception of number 4 are in agreement with the Matheson analyses within their reported limits of accuracy. However the results for run 4 should be the most accurate of all the results because of the equality of the temperatures of the inner and outer electrodes during the measurement of both emfs. In all cases the values of the two calculated compositions for a given run are within $\pm 0.0 - \pm 0.4\%$ of the average calculated composition for that run. The average deviation for all runs is less than $\pm 0.2\%$ of the average calculated composition.

The accuracies of the calculated results shown in Table I were estimated on the basis of Figs. 3 and 4 after assuming 1) that the use of an average temperature in the calculations was valid and 2) that the measured temperatures were accurate. The validity of this second assumption is supported by the fact that both thermocouples were constructed from the same spools of reference grade wire. In addition the Pt in both hot junctions came from the same location on the spool of Pt as did the Pt + 13% Rh from its

TABLE I

EXPERIMENTAL DATA WITH COMPARISON OF CALCULATED COMPOSITIONS TO GAS ANALYSES
FURNISHED BY THE MATHESON COMPANY

INNER ELECTRODE		OUTER ELECTRODE		emf (mv)	calc. P_{O_2} (atm)	calc. comp.	avg. calc. comp.	Matheson Analysis
Gas	Temp. (°C)	Gas	Temp. (°C)					
1	0.1% O_2			-190.5	1.033×10^{-3}	0.1033% O_2	0.1034% O_2	0.1% O_2
	O_2	0.1% O_2	1013.3	+190.5	1.035×10^{-3}	0.1035% O_2		
2	50% O_2			-21.70	4.553×10^{-1}	45.53% O_2	45.58% O_2	45.6% O_2
	O_2	50% O_2	1013.7	+21.65	4.563×10^{-1}	45.63% O_2		
3	0.3% CO			-570.3	1.170×10^{-9}	0.3587% CO	0.3587% CO	0.36% CO
	O_2	0.3% CO	1012.2	+571.3	1.105×10^{-9}	0.3587% CO		
4	3% CO			-687.7	1.704×10^{-11}	2.909% CO	2.915% CO	2.61% CO
	O_2	3% CO	1012.1	+689.2	1.551×10^{-11}	2.920% CO		
5	10% CO			-759.0	1.296×10^{-12}	9.747% CO	9.791% CO	9.78% CO
	O_2	10% CO	1013.3	+759.2	1.272×10^{-12}	9.835% CO		
6	50% CO			-890.9	1.096×10^{-14}	53.64% CO	53.76% CO	52.4% CO
	O_2	50% CO	1013.1	+890.7	1.109×10^{-14}	53.88% CO		
7	75% CO			-947.9	1.378×10^{-15}	76.32% CO	76.29% CO	75.9% CO
	O_2	75% CO	1014.2	+947.0	1.490×10^{-15}	76.25% CO		
8	97% CO			-1074.6	1.466×10^{-17}	96.96% CO	96.95% CO	96.9% CO
	O_2	97% CO	1013.6	+1074.1	1.517×10^{-17}	96.94% CO		

spool. Thus the average oxygen pressures corresponding to the O_2 -Ar mixtures should be accurate to $\pm 0.10\%$ of the reported value. The average oxygen pressures corresponding to all CO-CO₂ mixtures should be accurate to $\pm 3\%$. This corresponds to an error in the CO content of the mixtures of $\pm 0.5\%$ or less with the maximum error corresponding to the mixture with the lowest CO content.

It should be noted that the calculated CO contents for runs 4 through 8 are larger than those reported by the Matheson Company. This would indicate that electronic conductivity in the electrolyte was not a problem even at the lowest oxygen pressures used in this investigation.

These results show that the oxygen gauge can be a valuable research tool for accurately measuring oxygen pressures over a wide range at 1000°C if 1) gas flow rates are high enough to eliminate thermal diffusion, 2) equal absolute pressures exist at both electrodes when measuring O_2 -inert gas mixtures, 3) no temperature differences are present across the electrolyte and 4) calibrated thermocouples are used.

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