

## Effects of Pressure on Oxygen Sensors\*†

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(Manuscript received 21 June 1995, in final form 14 March 1996)

### ABSTRACT

To measure the effects of pressure on the output of a membrane oxygen sensor and a nonmembrane oxygen sensor, the authors pressure cycled a CTD sensor package in a laboratory pressure facility. The CTD sensor package was cycled from 30 to 6800 db over a range of temperatures from 2° to 38°C. Pressure decreased the output of the membrane sensor and increased the output of the microhole sensor. The pressure terms for both types of oxygen sensors were affected by temperature. The effect of pressure on both types of sensors can be quantified as  $\exp(VP/R'T)$ , where  $V$  is a coefficient ( $\text{cm}^3 \text{mol}^{-1}$ ),  $P$  is decibars,  $R'$  is the gas constant ( $831.47 \text{ cm}^3 \text{mol}^{-1} \text{db K}^{-1}$ ), and  $T$  is kelvins. As water gets colder,  $V$  for both sensors increases. For temperatures less than 21°C,  $V$  for the membrane sensor is  $-33.7 \pm 0.54 \text{ cm}^3 \text{mol}^{-1}$ , and  $V$  for the microhole sensor is  $0.29 \pm 0.31 \text{ cm}^3 \text{mol}^{-1}$ . The  $V$ 's for calibrations of four oceanic casts had larger ranges than the laboratory experimental data:  $-27.6$  to  $-34.9 \text{ cm}^3 \text{mol}^{-1}$  for the membrane sensor, and  $-0.4$  to  $-2.9 \text{ cm}^3 \text{mol}^{-1}$  for the microhole sensor. At 10°C, increasing pressure to depths of 5000 m decreases current output of a membrane sensor approximately 50% and increases output of a microhole sensor about 0.6%. For field calibrations, the authors recommend using a constant  $V$  obtained by iterations of linear fits. The use of a pressure term with the form  $\exp(VP/R'T)$  appears to improve field calibrations of membrane oxygen sensors.

### 1. Introduction

Membrane oxygen sensors, or Clark "polarographic" oxygen sensors, are widely used for the measurement of oxygen in natural waters. These sensors are used on oceanic CTDs and are routinely taken to the great depths of the oceans. Typically these oxygen sensors exhibit differences in output between upcasts and downcasts; the quality of calibrations are also often depth dependent; that is, calibration coefficients of shallow casts are different than those for deep casts. Thus, there has been a need to improve the calibrations of oxygen sensors for routine use on oceanic CTDs (NSF, WOCE Program Announcement).

Increasing hydrostatic pressure on tetrafluoroethylene (FEP) Teflon-membrane oxygen sensors reduce their current output (Greene et al. 1970; Owens and Millard 1985). Greene reported a 44% decrease in the

output of a Teflon membrane oxygen sensor over 5000 psi (roughly 345 b). This decrease in the output of the sensor corresponds to a decrease in the permeability of the membrane, because the rate of diffusion of oxygen through the membrane is the rate-limiting step for the reduction of oxygen at the cathode of the sensor. Greene et al. (1970) formulated the effect of pressure on the output of a membrane-oxygen sensor as  $P_m = P_o \exp(-kP)$ , where  $P_m$  is the permeability of the membrane at a given pressure  $P$  and  $P_o$  is the permeability of the membrane at the reference pressure. Owens and Millard (1985) incorporated this formulation of the pressure effect on current output in their now widely used calibration equation, naming Greene's term " $k$ ," "p<sub>cor</sub>." Sea-Bird Electronics Inc., a manufacturer of CTDs, recommends using a constant  $p_{cor}$  with a value of  $-1.5 \times 10^{-4} \text{ db}^{-1}$ . Sea-Bird's value of  $p_{cor}$  is based on tests of pressure effects on their CTD oxygen sensor in isothermal fjords. The data reported by Greene et al. (1970) is equivalent to a  $p_{cor}$  of  $-1.68 \times 10^{-4} \text{ db}^{-1}$ . Thus,  $p_{cor}$  from Sea-Bird and the one derived from Greene et al. are similar in value and clearly demonstrate that the output of Teflon-membrane oxygen sensor decreases with increasing hydrostatic pressure.

Morild and Ølheim (1980) considered the effects of pressure on the electrochemistry of oxygen sensors and

\* Hawaii Institute of Marine Biology Contribution Number 1011.

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permeability of the membrane. Their analysis was based on thermodynamics, in which the effects of pressure followed a typical thermodynamic form: a change in rate equals  $\exp(VP/R'T)$  where  $P$  is pressure (db),  $R'$  is the gas constant ( $831.47 \text{ cm}^3 \text{ mol}^{-1} \text{ db K}^{-1}$ ),  $T$  is temperature (K), and  $V$  is a coefficient ( $\text{cm}^3 \text{ mol}^{-1}$ ). When applied to an equilibrium chemical reaction,  $V$  is a partial molar volume, but when applied to other processes, the coefficient is named an "activation volume" simply because it has the units of a volume per mass. Morild and Ølheim concluded that the change in permeability of the membrane was the limiting step, and for their data had an activation volume  $V$  of  $-58 \text{ cm}^3 \text{ mol}^{-1}$ . Adding this value to the partial molar volume of oxygen (about  $+32 \text{ cm}^3 \text{ mol}^{-1}$ ) gave an overall  $V$  for the sensor of  $-26 \text{ cm}^3 \text{ mol}^{-1}$ . A value of  $V$  of  $-26 \text{ cm}^3 \text{ mol}^{-1}$  at  $10^\circ\text{C}$  is equivalent to a pcor of  $-1.1 \times 10^{-4} \text{ db}^{-1}$ , only 27% less negative than the pcor of Sea-Bird. Although the theory was well developed, they had no direct measurements of the effects of pressure on the permeability of the membrane, nor did they measure the pressure effect on the whole sensor at different temperatures. The change in output of the sensor was measured only at one temperature,  $25^\circ\text{C}$ . The value of  $V$  for the permeability of the membrane was calculated from the overall change in sensor output. Thus, the theory was well developed but lacked experimental verification. Based on the Morild and Ølheim paper, Orbisphere Laboratories, an equipment manufacturer in Switzerland, recommends using a pressure term of  $\exp(VP/R'T)$ .

There are disparities in the literature regarding the effects of pressure on polarographic oxygen sensors. Forster and Gnaiger (1983) in their book on polarographic oxygen sensors state that (p. 232), "Hydrostatic pressure has little effect on solubility (of oxygen), but with increasing head the escaping tendency of the gas increases. Therefore, at constant concentration, a polarographic oxygen sensor gives a higher reading at depth." The last statement is simply not true, but it is based on the well-known fact that the fugacity of oxygen at equilibrium with a gas space increases with hydrostatic pressure according to the Krichevsky-Kasarnovsky equation (Enns et al. 1965; Millero 1983; Prausnitz et al. 1986). Forster and Gnaiger neglected the effects of increasing gas pressure and increasing hydrostatic pressure on permeability of the membrane. They implicitly assumed that the permeability of a Teflon membrane remained constant as pressure increased. This assumption is incorrect and will be discussed later. Grasshoff (1981) summarized the effects of pressure on output of polarographic oxygen sensors by writing (p. 404), "Therefore, the effect of pressure on the diffusion process is reduced to its effect on the permeability of oxygen in the membrane. This effect remains largely unexplored."

Teflon membranes are semiglassy polymers, which have three structural components: rigid crystalline

structures, amorphous polymer chains, and empty void spaces. Gas molecules either stick in the crystalline and amorphous structures or diffuse through the voids. The relative amount of gas that diffuses through the polymer is related to temperature (Pasternak et al. 1971) and partial pressure of the gas within the membrane. Permeability of the membrane (where permeability  $P_m$  is defined as solubility  $S$ , times diffusivity  $D$ ,  $SD = P_m$ ) is also related to the relative composition of the gases and the total pressure of those gases (Koros et al. 1981; Jordon and Koros 1990). Gases compete for binding sites and diffusion spaces. Increases in absolute pressure of gases increase or decrease the permeability of a component gas through the polymer (Jordon and Koros 1990). Apparently, the effect of temperature on pressure effects have not been well studied. Thus, there are potentially two ways that increases in hydrostatic pressure alter permeability of FEP membranes: 1) by rearranging void spaces and changing the permeability of the membrane, and 2) altering the total pressure of the gases in the membrane, thereby changing the relative solubility of various gases in the membrane.

There are no measurements of the effects of temperature on the pressure term for membrane oxygen sensors. The reported data of Greene et al. (1970) are not over a large enough pressure difference to determine a temperature effect.

We recently developed and tested an oxygen sensor that has no membrane (Atkinson et al. 1995; Thomas and Atkinson 1995). The rate-limiting step for reduction of oxygen is diffusion of oxygen through water near the cathode surface. At the outset of the field testing of this sensor, it was not apparent how pressure might affect sensor output. One might postulate that output would increase simply because fugacity of oxygen increases with increasing hydrostatic pressure. However, these nonmembrane sensors measure oxygen concentration, not partial pressure (Morita and Shimizu 1989; Atkinson et al. 1995). The rate of diffusion through the boundary layer is directly related to the concentration gradient, not the partial pressure gradient. The Gibbs free energy for diffusion is proportional to the log of the ratio of fugacity at the relevant pressure conditions. Thus, the coefficients of fugacity cancel, leaving the ratio of concentrations as the driving force for diffusion.

We fit field data to a calibration equation that had a pressure term of the form  $\exp(VP/RT)$ . Data from both membrane and nonmembrane sensors fit this pressure term very well (standard deviation of error between Winklers and calibrated output was better than those with Owen and Millard equation); however, the values of  $V$  for the two sensors were very different. The membrane sensor had a mean  $V$  of around  $-33 \text{ cm}^3 \text{ mol}^{-1}$ , and the microhole sensor had a  $V$  of  $-1 \text{ cm}^3 \text{ mol}^{-1}$ . Considering the difficulty of separating effects of temperature and pressure in the ocean, it became apparent that we should perform laboratory pres-

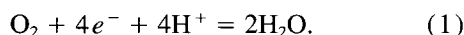
sure tests on these sensors to verify the pressure terms. Thus, our goal in this research was 1) to determine the effects of pressure on a typical membrane sensor and on our new microhole sensor, and 2) to determine whether temperature influences the pressure term.

## 2. Background

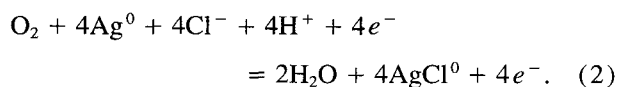
### a. Polarographic membrane sensors

The polarographic membrane oxygen sensor is an amperometric sensor in which a hydrophobic membrane hemetically separates a gold or platinum cathode from the environment. Oxygen dissolved in the water diffuses through a viscous boundary layer at the external surface of the membrane and then diffuses into the membrane. Oxygen crosses the membrane as a gas because water is excluded from the membrane. The gas diffuses through the membrane and then into a very thin layer of electrolyte trapped between the membrane and the electrode surface. Oxygen is reduced relatively rapidly at the electrode surface, creating a gradient in concentration of oxygen from the outer edge of the membrane to the electrode surface. The gradient drives the flux of oxygen from the water to the cathode.

The complete reduction of oxygen at the cathode surface is according to the following equation, in which  $\text{OH}^-$  and  $\text{H}_2\text{O}_2^*$  are intermediates (Hitchman 1978):



The chemical pathway to  $\text{H}_2\text{O}$  varies depending on pH and the characteristics of the metal surface; the details of these reaction pathways are not well described in the literature. Oxygen can be reduced on the cathode at potentials from  $-0.6$  to  $-0.9$  V relative to the reference electrode, usually Ag/AgCl. Most commercially available amperometric oxygen sensors operate in the middle of this range, between  $-0.7$  and  $-0.8$  V. The reaction at the reference electrode, usually Ag/AgCl ( $\text{Ag}^+ + \text{Cl}^- = \text{AgCl}$ ), balances the electrochemical cell and an electrical current flows between reference and cathode; thus, the reference also acts as the anode. The overall chemical reaction can be written as



Electrical current from the sensor is proportional to the rate of oxygen reduction, which is limited by the rate of oxygen diffusion through the membrane and secondarily through the diffusive boundary layer of oxygen at the outer edge of the membrane. Water velocity affects the thickness of this viscous boundary layer; thus, water flow past the sensor affects the diffusion of oxygen and the output of the sensor.

Current output  $i$  at one atmosphere pressure of these sensors can be predicted with the following equation (Greene et al. 1970; Hitchman 1978; Grasshoff 1981),

which is well established in electrochemistry (Atkins 1980):

$$i = nFA \left( \frac{SD}{z} \right) \exp \left( - \frac{E}{RT} \right) p\text{O}_2 + c, \quad (3)$$

where  $n = 4$  [Eq. (2)];  $F = 96490$  A s mol  $\text{O}_2^{-1}$ ;  $A$  is the area of cathode ( $\text{m}^2$ );  $S$  is solubility of the membrane [ $\text{mol O}_2 \text{m}^{-3}$  (of membrane)  $\text{atm}^{-1}$ ];  $D[\exp(-E/RT)]$  is diffusivity ( $\text{m}^2 \text{s}^{-1}$ ) through the membrane at a given temperature;  $E$  is activation energy for diffusion through the membrane ( $\text{cal mol}^{-1}$ );  $R$  is the gas constant ( $1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$ );  $T$  in kelvins;  $z$  is thickness (m) of the oxygen diffusion path, typically dominated by the membrane;  $p\text{O}_2$  is the partial pressure of oxygen  $\{[\text{O}_2]/44.615B$  where  $B$  is the Bunsen coefficient (Weiss 1970; Benson et al. 1979); conversion of milliliters per liter to moles per cubic meter is by assuming oxygen behaves as an ideal gas at STP}; and the intercept  $c$  in Eq. (3) is merely the current output of the sensor when  $p\text{O}_2 = 0$ . A well-designed and well-calibrated sensor will have a value of  $c$  equal to zero. Membrane permeability  $P_m$  is defined as  $SD[\exp(-E/RT)]$ . In this study we hypothesized that the pressure term is affected by temperature according to  $\exp(VP/R'T)$ ; thus, the full equation that describes the current output of the sensor is

$$i = nFA \left( \frac{SD}{z} \right) \exp \left( - \frac{E}{RT} \right) p\text{O}_2 \exp \left( \frac{VP}{R'T} \right) + c, \quad (4)$$

where  $V$  is the reaction volume of oxygen ( $\text{cm}^3 \text{mol}^{-1}$ ),  $P$  is pressure (db), and  $R'$  is the gas constant ( $831.47 \text{ cm}^3 \text{mol}^{-1} \text{db K}^{-1}$ ).

Equation (4) describes the output of the membrane sensor at steady state, it does not include a term to sharpen response (Thomas et al. 1995) or a term for the effect of changing temperature of the bulk water on the actual temperature of the membrane. The calibration equation of Owens and Millard (1985) has a first derivative term of calculated oxygen concentration to sharpen response and a temperature weighting term to compensate for the difference between internal and external temperatures of the Beckman polarographic oxygen sensor.

### b. Microhole potentiostatic oxygen sensor

The microhole potentiostatic oxygen sensor has three electrodes, a cathode, a reference, and an anode (Morita and Shimizu 1989). The cathode of the sensor is a bundle of about 1000 carbon fibers embedded in an epoxy matrix. The tips of the carbon fibers are recessed  $50 \mu\text{m}$  from the end of the epoxy tip, and the tips of the fibers are electroplated with platinum. The cathode tips are at the bottom of these  $50\text{-}\mu\text{m}$ -deep,  $3\text{-}5\text{-}\mu\text{m}$ -wide channels. Seawater fills these channels. For a detailed description of the design of the oceanic sen-

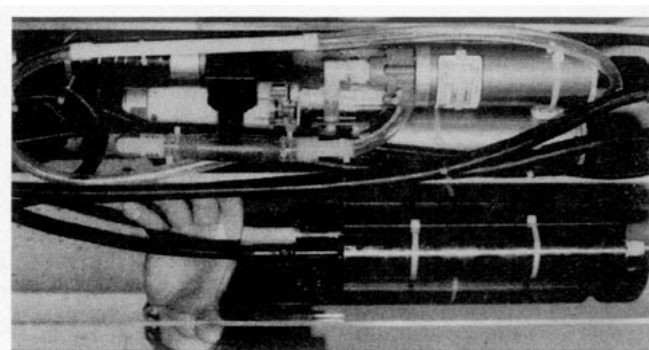
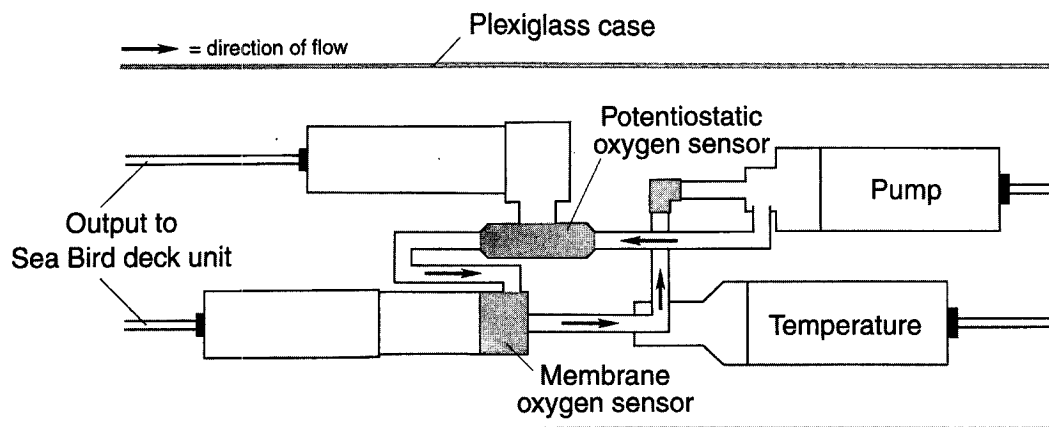


FIG. 1. Diagram (a) and photograph (b) of the experimental apparatus and pressure tank.

sor see Atkinson et al. (1995). Oxygen diffuses through the water in the channels and reacts at the platinum surface. The reduction of oxygen at the cathode surface is according to Eq. (1) and is the same as the membrane sensor. The reaction at the anode is generally considered to be the formation of oxygen from water [the reverse reaction of Eq. (1)], but  $\text{Cl}^-$  can also react with gold or platinum anodes to balance the electron flow. Thus, sensor output is proportional to rate of diffusion of oxygen to the cathode surface and is proportional to oxygen concentration, not partial pressure as with the membrane sensors. The calibration equation is similar in form to the membrane sensor [Eq. (4); Atkinson et al. 1995], except  $p\text{O}_2$  is replaced by  $\text{O}_2$  concentration,  $[\text{O}_2]$ , and the solubility of the diffusion channels is mole  $\text{O}_2$  in the diffusion space per mole  $\text{O}_2$  in the bulk solution:

$$i = nFA \left( \frac{SD}{z} \right) \exp\left(-\frac{E}{RT}\right) [\text{O}_2] \exp\left(\frac{VP}{R'T}\right) + c. \quad (5)$$

The term  $(SD/z) \exp(-E/RT)$  is the effect of temperature on the permeability of oxygen in the diffusion channels. The form of this term is the activation energy for diffusion of oxygen through seawater. The effects of pressure on these types of sensors have not been described. Assuming that the solubility of oxygen in

the diffusion channels does not change, then the only effects that pressure can have is on the diffusivity of oxygen through water. Diffusivity changes as the inverse of viscosity (Li and Gregory 1974).

### 3. Methods

#### a. Laboratory experiments

Experiments were designed to determine a change in the exponent of the pressure term as a function of temperature. We hypothesized that output of the sensor is proportional to  $\exp(VP/R'T)$ :

$$i = \alpha \exp\left[\left(\frac{V}{R'T}\right)P\right] [\text{O}_2]. \quad (6)$$

Thus, given a constant temperature and  $\text{O}_2$  concentration, the slope of  $\ln i$  versus  $P$  should have a value of  $V/R'T$ . The plot of  $V/R'T$  versus  $1/T$  should yield a line with the slope of  $V/R'$ .

An instrument package containing a Sea-Bird pump, a Sea-Bird pressure sensor, a Sea-Bird temperature sensor, a YSI membrane oxygen sensor packaged by Sea-Bird, and the microhole potentiostatic oxygen sensor, also packaged by Sea-Bird, was designed to fit into a cylinder that could be pressurized to 7000 db (Fig. 1).

Seawater was circulated past the sensors in a loop, from the pump to the microhole oxygen sensor, then to the YSI membrane sensor, and finally past the temperature sensor. The Tygon tubing joining the sensors was approximately 1.5 m long, with a volume of 112 mL. The consumption of oxygen in this small volume of seawater is significant and can be approximated using Eq. (3). The output of a YSI oxygen sensor at saturation and 25°C is about 30  $\mu$ A. Dividing the output by Faraday's constant and the number of electrons involved in the reaction, Eq. (3) [ $30 \times 10^{-6} \text{ C s}^{-1} / (4 \times 96490 \text{ C mol O}_2^{-1})$ ], gives an estimate of the rate of O<sub>2</sub> consumption, or  $3 \times 10^{-12} \text{ mol O}_2 \text{ s}^{-1}$ . This rate is not negligible and represents a 2  $\mu$ M O<sub>2</sub> change (1% of saturation) in the circulating seawater within 23 min. Thus, we pressure cycled the sensors over periods of less than 5 min.

Pressure cycling created adiabatic heating of the seawater, which was about 1°–2°C depending on the temperature of the experiment. The effect of temperature on the output of the sensors was removed from the data by dividing  $i$  by  $\exp(-E/RT)$  [see Eq. (4) or (5) in background] before correlating  $\ln i$  to  $P$ . The value of  $E$  used for the microhole sensor was 4665 cal mol<sup>-1</sup> (Thomas and Atkinson 1995) and for the YSI membrane sensor  $E$  was 5485 (Pasternak et al. 1971; M. Atkinson 1996, unpublished manuscript). Temperature of the pressure bomb was varied from 2° to 38°C. Temperature, pressure, and output of the oxygen sensors were acquired with a Sea-Bird deck unit and writ-

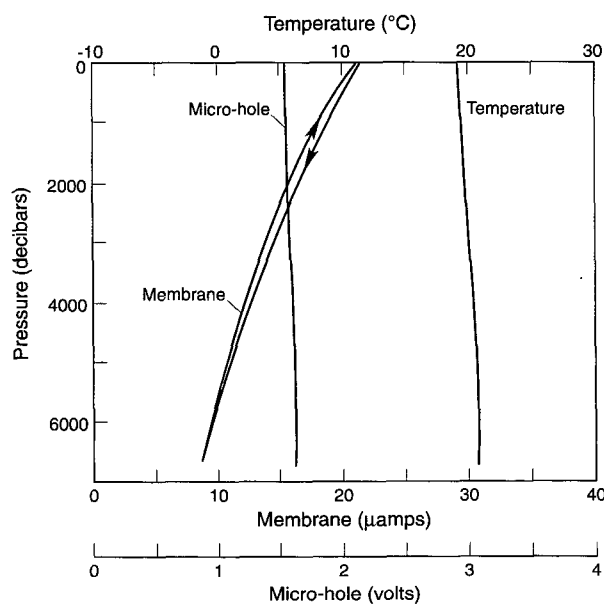


FIG. 2. Temperature, output of membrane sensor, and output of microhole potentiostatic sensor versus pressure. Pressure was increased to either 4800 or 6800 db over 2–5 min. Table 1 is a summary of the slopes of  $\ln i$  versus pressure for all experiments.

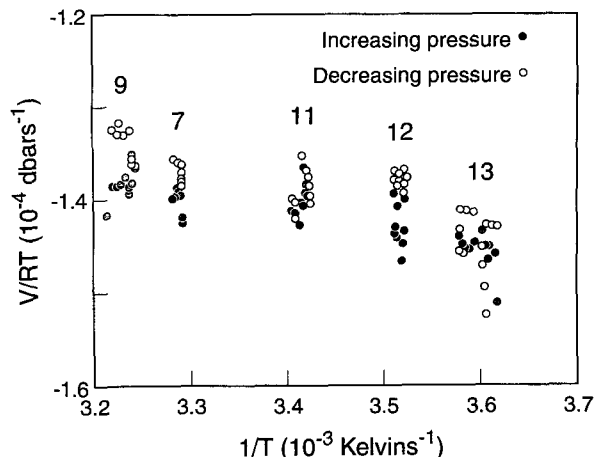


FIG. 3. The  $V/RT$  for membrane sensor output ( $\ln i$  vs db). There is a significant difference between increasing and decreasing pressure cycles.

ten to hard disk on a laptop computer. Pressure was cycled from 30 db to either 4800 or 6800 db.

*b. Fits to ocean casts*

Fits to oceanic casts were done to verify the value of the pressure coefficient  $V$ . Field data for this study were from the WOCE-GOFS, Hawaii Ocean Time-Series (Chiswell et al. 1990) deep-water stations 100–150 km north of Oahu (22°45' N, 158°W and 23°25' N, 158°W). Oxygen concentrations were determined by Winkler titration (Carpenter 1965). To determine the redox endpoint, a Metrohm Dosimat was used in conjunction with a redox probe. Temperature, salinity, and pressure data were taken with a Sea-Bird SBE-09 CTD when Niskin bottles were tripped. Niskin bottles were tripped during the upcast after stopping at depth for at least 1 min.

Casts were to 4600 m and at some depths had duplicate or triplicate bottles. Some triplicate bottles had relatively large errors and were omitted from analysis. To reduce the chance that a single bottle with large error influenced the calculation of  $V$ , all single bottles were removed from some calibrations, and the fit recalculated with just duplicate and triplicate bottles. Also, because a mismatch between the response of the temperature sensor and the oxygen sensor can create large errors, we recalculated  $V$ 's after removing depths in which the variability of the sensors over the sampling interval had changes in oxygen or temperature above 0.3%. Most of the depths that were omitted for this reason were from regions of high vertical structure in the thermocline. Normally, a response term in the calibration is used to match temperature and oxygen output (Owens and Millard 1985); however, Thomas et al. (1995) showed that temperature influences the response-time constant, and the response-time terms are

TABLE 1. Pressure terms for membrane and microhole oxygen sensors. Here  $V/R'T$  (or  $pcor$ ) is the mean slope of  $\ln i$  versus decibars for each experimental temperature ( $\times 10^{-6} \text{ db}^{-1}$ );  $V$  is in units of cubic centimeter per mole; "95%" refers to the 95% confidence interval of  $V$  based on  $n$  number of measurements.

| $T$<br>(°C) | $1/K$<br>( $\times 10^{-3}$ ) | $n$ | Membrane |       |      | Microhole |        |       |
|-------------|-------------------------------|-----|----------|-------|------|-----------|--------|-------|
|             |                               |     | $V/R'T$  | $V$   | 95%  | $V/R'T$   | $V$    | 95%   |
| 4.85        | 3.597                         | 26  | -145     | -33.6 | 0.28 | +3.03     | +0.70  | 0.067 |
| 11.11       | 3.518                         | 24  | -140     | -33.1 | 0.29 | +1.47     | +0.35  | 0.056 |
| 20.25       | 3.408                         | 6   | -141     | -34.4 | 0.19 | +0.44     | +0.11  | 0.59  |
| 19.22       | 4.420                         | 16  | -139     | -33.8 | 0.25 | +0.006    | +0.001 | 0.067 |
| 30.97       | 3.288                         | 14  | -139     | -35.1 | 0.35 | -4.57     | -1.16  | 0.19  |
| 36.30       | 3.232                         | 18  | -136     | -35.1 | 0.37 | -4.15     | -1.07  | 0.083 |

not consistently stable to less than 10%. We decided not to rely on unvalidated response-time terms for these field determinations of  $V$ .

To predict oxygen concentration from a linear regression, Eq. (5) was rearranged so that oxygen was the dependent variable and current output was the independent variable;

TABLE 2. Summary of the oceanic casts. "All" refers to casts with all bottles used to fit for  $V$ , "2-3" means only bottles that were duplicate or triplicate, and "best" means only bottles with less than 0.3% drift at the mark;  $n$  refers to the number of depths. "Sum devs" is the sum of all plus or minus deviations divided by  $n$ ; this number should be zero for a perfectly balanced fit; the listed values are exponents of base 10 ( $\mu\text{M}$ ). "Std error" is the standard deviation of the error ( $\mu\text{M}$ ). Activation energy  $E$  and the partial molar volume  $V$  were determined by iterating  $E$  at steps of  $10 \text{ cal mol}^{-1}$  and  $V$  at steps of  $0.1 \text{ cm}^3 \text{ mol}^{-1}$ . Values of  $V$  and  $E$  are reported for the highest  $r^2$ .

| Cast             | Bottles | $n$ | $r^2$  | Sum<br>devs | Std<br>error | $E$  | $V$   |
|------------------|---------|-----|--------|-------------|--------------|------|-------|
| <b>Membrane</b>  |         |     |        |             |              |      |       |
| 34-2-14          | all     | 23  | 0.9997 | -2          | 1.50         | 5270 | -28.8 |
|                  | 2-3     | 8   | 0.9999 | -2          | 1.21         | 5260 | -28.8 |
|                  | best    | 7   | 0.9998 | -2          | 1.30         | 5260 | -28.8 |
| 34-2-17          | all     | 21  | 0.9974 | -2          | 3.40         | 5650 | -30.9 |
|                  | 2-3     | 7   | 1.0000 | -3          | 0.41         | 5650 | -30.7 |
|                  | best    | 7   | 1.0000 | -3          | 0.41         | 5650 | -30.7 |
| 35-2-12          | all     | 23  | 0.9984 | -2          | 3.16         | 5400 | -27.6 |
|                  | 2-3     | 10  | 0.9994 | -2          | 2.32         | 5550 | -27.4 |
|                  | best    | 5   | 0.9999 | -4          | 0.98         | 6470 | -21.5 |
| 35-3-1           | all     | 23  | 0.9983 | -3          | 3.72         | 4670 | -34.9 |
|                  | 2-3     | 7   | 0.9984 | -2          | 3.68         | 4640 | -34.9 |
|                  | best    | 4   | 1.0000 | -3          | 0.01         | 6610 | -22.8 |
| <b>Microhole</b> |         |     |        |             |              |      |       |
| 34-2-14          | all     | 23  | 0.9997 | -14         | 0.98         | 4850 | -0.9  |
|                  | 2-3     | 8   | 0.9999 | -13         | 0.64         | 4810 | -0.9  |
|                  | best    | 7   | 0.9999 | -14         | 0.62         | 4770 | -1.0  |
| 34-2-17          | all     | 23  | 0.9960 | -14         | 3.87         | 4980 | -0.4  |
|                  | 2-3     | 7   | 1.0000 | -14         | 0.39         | 4920 | 0.0   |
|                  | best    | 7   | 1.0000 | -14         | 0.39         | 4920 | 0.0   |
| 35-2-12          | all     | 23  | 0.9989 | -14         | 2.24         | 4520 | -0.7  |
|                  | 2-3     | 10  | 0.9995 | -14         | 1.40         | 4610 | -0.4  |
|                  | best    | 5   | 1.0000 | -13         | 0.14         | 4840 | +0.8  |
| 35-3-1           | all     | 23  | 0.9971 | -14         | 3.54         | 4130 | -2.9  |
|                  | 2-3     | 7   | 0.9966 | -14         | 3.54         | 4000 | -2.9  |
|                  | best    | 4   | 1.0000 | -14         | 0.02         | 4640 | +0.3  |

$[\text{O}_2]$  or  $p\text{O}_2$

$$= b \left\{ i \left[ \exp\left(-\frac{E}{RT}\right) \exp\left(\frac{VP}{R'T}\right) \right]^{-1} \right\} + c'. \quad (7)$$

A computer program was written to iterate values of  $V$  and  $E$ , then solve for the best  $b$ . The iteration interval for  $E$  was  $10 \text{ cal mol}^{-1}$ , and the interval for  $V$  was  $0.1 \text{ cm}^3 \text{ mol}^{-1}$ . Here  $V$ ,  $E$ , and statistics for the fit with the highest  $r^2$  were reported.

#### 4. Experimental results

The output of the membrane sensor decreased with pressure and the output of the microhole sensor increased with pressure (Fig. 2). Temperature of the water in the sensor package increased due to adiabatic heating (Fig. 2).

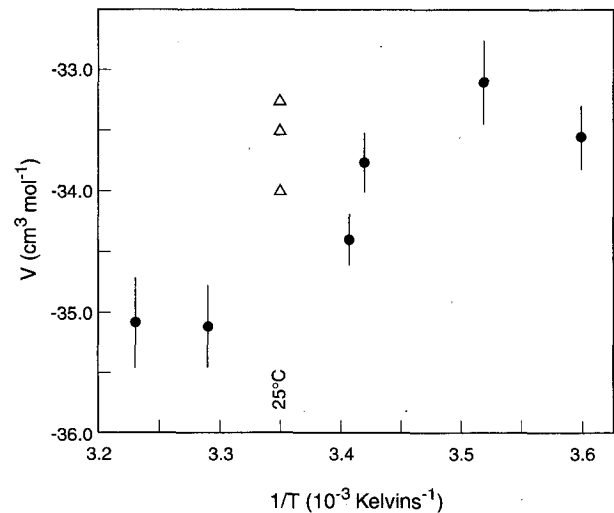


FIG. 4. Mean  $V$  for membrane sensor output ( $\ln i$  vs  $\text{db}$ ) at each temperature. Error bars are the 95% confidence limits. The upper two open triangles are values of the partial molar volumes of nitrogen. The lower open triangle represents the proposed effect of nitrogen on the permeability of the membrane ( $-33.5$ ) plus the effect of viscosity on oxygen diffusivity in the boundary layer ( $-0.5$ ) or  $-34$ .

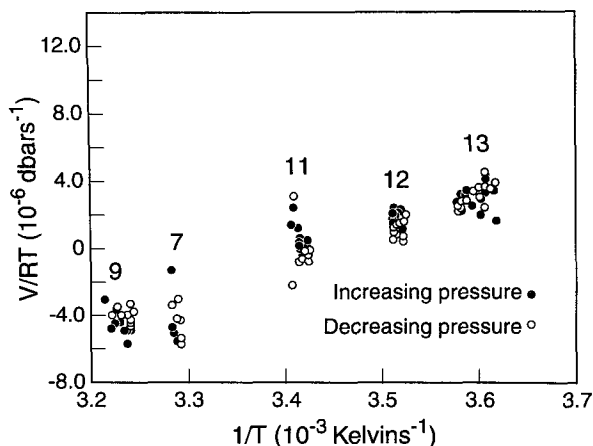


FIG. 5. The  $V/RT$  for microhole sensor output ( $\ln i$  vs  $\text{db}$ ). There is no significant difference between increasing and decreasing pressure cycles.

Values of  $V/RT$  (pcor) for the membrane sensor ranged from  $-1.3 \times 10^{-4} \text{ db}^{-1}$  at the warmest temperatures to  $-1.5 \times 10^{-4} \text{ db}^{-1}$  at coldest temperatures (Fig. 3). Values of  $V/RT$  for increasing pressure cycles are more negative than for decreasing pressure ( $-1.42 \times 10^{-4} > -1.39 \times 10^{-4} \text{ db}^{-1}$ ; paired  $t$  test,  $p < 0.001$ ,  $n = 52$ ; Fig. 3, Table 2). The mean values of  $V$  ( $V/RT$  is multiplied by  $R'T$ ) at each temperature range from  $-33.1$  to  $-35.1 \text{ cm}^3 \text{ mol}^{-1}$  (Table 1 and Fig. 4). Here  $V$  significantly increased, or became less negative, as  $1/T$  increased [ $V_{\text{membrane}} = 5251(1/T) - 52.03$ ,  $r = 0.71$ ,  $n = 104$ ,  $p \ll 0.01$ ]. The  $V$ 's for temperatures less than  $21^\circ\text{C}$ , however ( $1/T$  greater than  $0.0034$ ), are not significantly different and average to  $-33.7 \pm 0.54$ . The range of  $V$ 's for the oceanic casts is from  $-27.6$  to  $-34.9 \text{ cm}^3 \text{ mol}^{-1}$  with a mean and standard deviation of  $-30.6 \text{ cm}^3 \text{ mol}^{-1}$  (Table 2). The  $V$ 's become less negative when the same casts are calibrated with duplicate/triplicate bottles or "best" bottles (Table 2).

Values of  $V/RT$  (pcor) for the microhole potentiostatic sensor range from  $-6 \times 10^{-6} \text{ db}^{-1}$  at warm temperatures to  $5 \times 10^{-6} \text{ db}^{-1}$  at cold temperatures (Table 1, Fig. 5). There are no significant differences of  $V/RT$  between increasing or decreasing pressure cycles. Mean values of  $V$  ( $V/RT$  is multiplied by  $R'T$ ) for the microhole sensor range from  $+0.70$  to  $-1.07 \text{ cm}^3 \text{ mol}^{-1}$  (Table 1, Fig. 6). Here  $V$  increased as  $1/T$  increased [ $V_{\text{microhole}} = 5171(1/T) - 17.85$ ,  $r = 0.93$ ,  $n = 104$ ,  $p \ll 0.01$ ]. The  $V$ 's for temperatures less than  $21^\circ\text{C}$  ( $1/T$  greater than  $0.0034$ ) average to  $0.29 \pm 0.31 \text{ cm}^3 \text{ mol}^{-1}$ . The range of  $V$ 's for the oceanic casts is from  $-0.4$  to  $-2.9 \text{ cm}^3 \text{ mol}^{-1}$  (Table 2) with a mean of  $-1.2 \text{ cm}^3 \text{ mol}^{-1}$ . The  $V$ 's changed to a mean of  $+0.025 \text{ cm}^3 \text{ mol}^{-1}$  when casts were calibrated with duplicate/triplicate bottles or "best" bottles.

### 5. Discussion

Increasing the pressure of seawater clearly decreases the output of a membrane sensor and only slightly increases the output of the microhole sensor. For example, at  $10^\circ\text{C}$  an increase in pressure of  $5000 \text{ db}$  will decrease the current output of the membrane sensor by  $50\%$ , whereas with the output of the microhole sensor will increase by  $0.6\%$ .

The pressure term (pcor) is a function of temperature and can be described algebraically by using  $\exp(VP/R'T)$ . Interestingly, however,  $V$ 's for both membrane and microhole sensors are positively correlated to  $1/T$  (Figs. 4 and 6) by the same slope. Activation volume  $V$  increases  $2 \text{ cm}^3 \text{ mol}^{-1}$  as water gets colder from  $36^\circ$  to  $4^\circ\text{C}$ . Assuming the diffusivity of oxygen is proportional to viscosity of seawater (Li and Gregory 1974), then the diffusivity of oxygen through water would be affected by pressure in a way shown on Fig. 6. The open squares represent values of  $V$  calculated from the effects of pressure on viscosity of water (Stanley and Batten 1969). There appears to be an excellent match in both magnitude of  $V$  and its relationship with temperature. Changes in viscosity affect the rate of diffusion of oxygen through the diffusive boundary layers around both types of sensors. The membrane sensor has a diffusive boundary layer adjacent to the outer membrane, whereas the microhole sensor has a diffusive boundary layer within the diffusion channels.

At  $25^\circ\text{C}$ , the value of  $V$  for the microhole sensor is about  $-0.5 \text{ cm}^3 \text{ mol}^{-1}$ . Assuming this value of  $V$  represents the effect of viscosity on the diffusion of oxygen through diffusive boundary layers adjacent to the sensors, the effect of the Teflon membrane on the pressure term of the membrane sensor is the difference be-

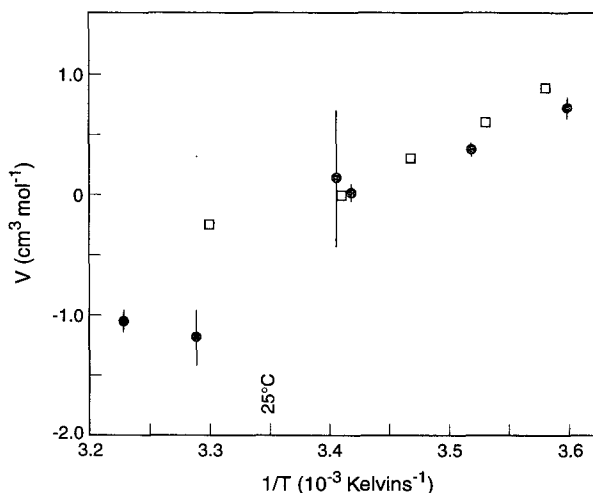


FIG. 6. Mean  $V$  for microhole sensor output ( $\ln i$  vs  $\text{db}$ ) at each temperature. Error bars are the 95% confidence limits. The open squares are values of  $V$  calculated assuming diffusivity of oxygen changes as the inverse of viscosity of seawater.

tween  $V_{\text{membrane}}$  and  $V_{\text{microhole}}$ , or about  $-34 - (-0.5) = -33.5 \text{ cm}^3 \text{ mol}^{-1}$ . The magnitude of this value is surprisingly close to the partial molar volumes of nitrogen ( $33.5 \text{ cm}^3 \text{ mol}^{-1}$ ) and oxygen ( $32 \text{ cm}^3 \text{ mol}^{-1}$ ) in seawater, but the sign is opposite! We suggest that the effect of pressure on the membrane is actually due to the increase in total pressure of nitrogen and oxygen in the membrane. This increased pressure within the membrane acts as a "compressor" and reduces permeability (Jordon and Koros 1990). This interpretation of the results would imply that hydrostatic pressure, or the crushing of the membrane from water has little effect on the permeability of the membrane.

Teflon FEP membranes vary in their relative proportions of crystalline, amorphous, and void spaces; each lot of membrane material is slightly different (J. F. Imbalzano, DuPont). This variability in the crystallinity of the membrane affects overall permeability. Assuming that our interpretation of the pressure term is correct, variability in structure should not affect how pressure alters permeability. Thus, the effect of pressure on a membrane sensor is related to 1) the increasing equilibrium total gas pressure in the membrane, and 2) the change in viscosity of the seawater. Both factors are related to physical chemistry of seawater.

The membrane sensor showed a difference between the increasing and decreasing pressure terms. The difference represents a  $4\text{-}\mu\text{M}$  change in oxygen concentration of the recirculating water, 20 times greater than the change from consumption of oxygen by the sensor. The 90% response time of the sensor is about 10 s, which over 5 min represents a pressure change of 227 db ( $10/300 \times 6800 \text{ db}$ ). A pressure change of 227 db is 3% change in output or about  $4 \mu\text{M}$ . Thus, we suggest the difference in increasing and decreasing pressure terms of the membrane sensor is due to the relatively rapid change in pressure in the laboratory facility compared to the slow response of the sensor.

The results of this research indicate that calibrations of oxygen sensors should be improved by employing a pressure term of  $\exp(VP/R'T)$ . Routine calibrations of HOTS data indicate the use of this pressure term reduces the mean error of calibrations from the use of the standard Owen and Millard treatment (1996 unpublished manuscript). At the temperatures of the ocean,  $V$  at present can be assumed to be constant; however, further work on field calibrations will have to be performed to determine the extent of improvement on fits using a  $V$  that is a linear function of temperature.

A distinct advantage of the microhole sensor over a membrane sensor is its relatively small pressure effect. Together with its inherently fast response, this sensor can be used for detailed profiling of the water column.

**Acknowledgments.** This research was supported by NSF Oceanic Technology Grant OCE 92-17590. Thanks to Roger Lukas for the CTD data and Dave Karl, Dale Hebel, and GOFS students for the field sam-

pling and Winkler titrations. Discussions with John Prausnitz (University of California, Berkeley) and John Koros (University of Texas at Austin) are greatly appreciated.

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