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Characteristics of the OTOX Model CTL Oxygen Sensor

By J. E. Chilton, G. H. Schnakenberg, Jr.,
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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	mL	milliliter
cm^3	cubic centimeter	mm	millimeter
° C	degree Celsius	mV	millivolt
g	gram	Pa	pascal
in	inch	pct	percent
K	kelvin	sec	second
min	minute		

CHARACTERISTICS OF THE OTOX MODEL CTL OXYGEN SENSOR

By J. E. Chilton,[1] G. H. Schnakenberg, Jr.,[2] and L. Spinetti[3]

ABSTRACT

The Bureau of Mines has examined the operation of an oxygen sensor manufactured by the City University, London, England. The sensor produces a current proportional to the oxygen concentration by reacting oxygen at a nonconsumable cathode. The sensor design is unique in that the primary mode of oxygen transport to the cathode is by diffusion through a capillary. The sensor using this design has a stability of 0- to 0.02-pct reading change per day over a 4.7-month test, small temperature coefficient of 0.29-pct reading change per ° C, and small pressure coefficient of 0.34-pct reading change per 1,000-ft altitude change. If this sensor were incorporated into an oxygen detector or monitor, this would be a distinct improvement in electrochemical-type oxygen analyzers and would be useful to the mining industry.

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INTRODUCTION

An oxygen detector is used in mining operations for verifying that there is an adequate supply of oxygen for life support of miners. The Code of Federal Regulations requires a supply of air containing not less than 19.5 vol-pct O_2 for underground coal mine ventilation (30 CFR 75.301). To verify that ventilation air meets this specification, oxygen in air of underground coal mines should be measured by the use of an oxygen detector with certain properties:

1. Certified by the Mine Safety and Health Administration (MSHA) (i.e., permissible) for use in combustible atmospheres such as methane in air.

2. Have a range covering the concentrations encountered in practice (0 to 25 pct O_2).

3. Meet human related factors--size and weight considerations, readability, ruggedness.

4. Meet certain instrument parameter values--response time, accuracy, precision, and stability.

5. Meet environmental instrument parameters--temperature, pressure, humidity, and electrical and chemical interference.

The measurement of some of the oxygen sensor properties noted in items 4 and 5 are described in this Bureau of Mines report.

Many commercial oxygen detectors have sensors that operate as a galvanic cell. The cell anode is a reactive metal such as zinc or lead. The cell cathode is a noncomsumable metal or graphite structure catalyzed with silver to promote oxygen reduction. The cell electrolyte is usually a potassium hydroxide solution in water. Oxygen travels to the cell cathode through a porous membrane. The porous membrane limits the mass transport of oxygen from the air sample to the cell cathode and results in a sensor response that is proportional to the oxygen partial pressure. For a given oxygen volume concentration, the oxygen response of these cells, because of the membrane-diffusion-limited system, depends directly on oxygen partial pressure (and hence, an ambient pressure) and also is strongly dependent on ambient temperature. Detectors using such cells must use an electronic circuit that senses cell temperature and corrects for the temperature effect of the sensor output. Usually no pressure corrections are made electronically. The detector output is usually set to read 21 pct in air known to be fresh. From then on altitude or barometric pressure changes will affect the reading even if the actual oxygen concentration remains at 21 pct. Tests of performance of some of these oxygen detectors were reported.[4]

A galvanic oxygen sensor has been developed in England that uses a different principle for limiting the diffusion of oxygen to the cathode--that of diffusion through a capillary. This sensor, the OTOX model CTL,[5] developed at the City University, Chemistry Department, St. John St., London, was reported to have no dependence on atmospheric pressure and small dependence on temperature. The evaluation of this oxygen sensor was undertaken in the quest for improved oxygen detectors for mining use, and five OTOX model CTL oxygen sensors were obtained from the National Coal Board for study.

The sensor (fig. 1) is assembled in a cylindrical case, 43 mm high by 23 mm in diameter (C flashlight cell size). Although the mass transport of oxygen must pass through an air gap and two membranes, it is primarily limited by

[4]Ray, R. M., and F. B. Armstrong. An Evaluation of Several Direct Reading Electrochemical Oxygen Meters. Bartlesville Energy Research Center (BERC) RI 76/7, 1976, 50 pp.

[5]Reference to specific products does not imply endorsement by the Bureau of Mines.

diffusion through a fine capillary. The current produced by the cell is proportional to the oxygen volume concentration in the air at the sensor and is approximately 1 ma at 20.9 pct O_2.

THEORY

The OTOX sensor operates by the gas-diffusion-limited mass transport of oxygen, and the sensor current is determined by the overall movement of oxygen as follows:

1. Oxygen molecules move to the sensor face.

2. Oxygen molecules diffuse through the capillary into the sensor interior.

3. Oxygen within the sensor reacts at the cathode surface.

The mass transport of oxygen (S, g-mole/sec) is limited by diffusion through the cell capillary. This flow will follow Fick's law for steady state diffusion in a single dimension and can be written as follows:

$$S = \frac{DA}{L} C, \qquad (1)$$

where D is the diffusion coefficient, cm^2/sec,

A is the surface area, cm^2, through which diffusion occurs,

L is the diffusion zone thickness, cm,

and C is the ambient oxygen concentration, $g\text{-mole}/cm^3$.

This equation assumes a rapid reaction of oxygen at the cell cathode. The current in amperes, i, from the galvanic cell with limiting cathode reaction is related to the oxygen transport rate, S, as follows:

$$i = n F S, \qquad (2)$$

where n is the number of g equivalents per g-mole of reaction (for oxygen n = 4),

and F is the Faraday constant, 96,480 amp-sec/g equivalent.

The molar concentration (C, $g\text{-mole}/cm^3$) is related to C', the oxygen concentration in percent, as follows:

$$C = C' \, 10^{-2} \, P/RT, \qquad (3)$$

where P is the pressure, atm,

R is the gas constant, 82.06 $\frac{atm\ cm^3}{mole\ K}$,

and T is the absolute temperature, K.

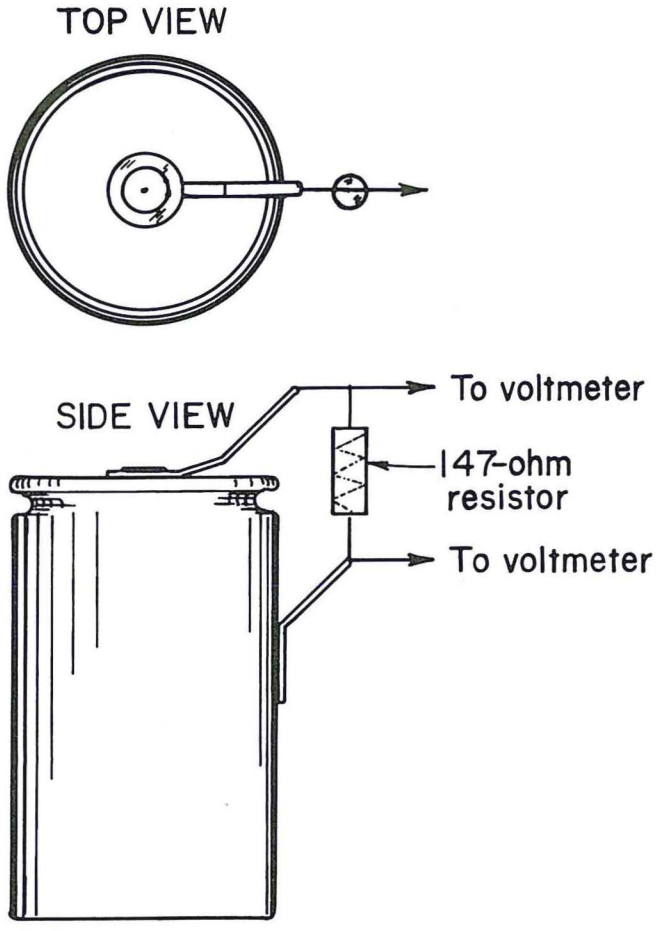

FIGURE 1. - OTOX oxygen sensor.

By combining the three equations, the cell current, i, is equal to the following expression:

$$i = \frac{1}{100} \frac{nFA}{L\ R} \frac{DP}{T} C', \qquad (4)$$

With the cell capillary physical parameters fixed, the equation may be written:

$$i = K \frac{DP}{T} C', \qquad (5)$$

where K is a constant.

The gas diffusion coefficient (D, cm^2/sec) is a function of the average gas molecule velocity and the mean free path of the gas molecule. In free space it is a function of $T^{3/2}\ P^{-1}$, and thus the cell current i expressed as a function of temperature and pressure becomes equal to the following expression:

$$i = K'\ T^{1/2}\ C', \qquad (6)$$

where K' is a constant.

The equations for gas diffusion are applicable to this system since the OTOX cell has a capillary with a size much greater than the oxygen mean free path. When the oxygen reaching the cathode is limited by gas diffusion rather than membrane diffusion, the cell current is a function only of the square root of the absolute temperature, and not of pressure. Thus, the OTOX sensor current should be directly proportional to the oxygen percent concentration and not to oxygen partial pressure as in many other oxygen sensors that have been investigated.

EXPERIMENTAL SYSTEMS

A load resistor was connected to the sensor leads, and the OTOX sensor current was measured by reading the voltage across the load resistor using a Keithley model 172 DMM digital multimeter. A 147-ohm resistor was chosen for the load since this value of resistance yielded maximum sensor power output and matched the internal sensor resistance. Room air (20.9 pct O_2) was used at local temperatures and pressures for stability testing. An Aminco environmental chamber was used for controlled-temperature experiments. A Boekel chamber was used for controlled-pressure measurement, with differential pressure readings taken from a mercury manometer. Oxygen and nitrogen from cylinders were mixed to form concentrations of oxygen above 20.9 pct. Cylinder nitrogen was used to dilute air to form oxygen concentrations below 20.9 pct. A Taylor Servomex model A0272 oxygen analyzer and an Edmont-Wilson amperometric membrane sensor both were used to measure the oxygen concentrations of the prepared air mixtures.

A Hewlett-Packard model 7100 strip chart recorder was used to record sensor response for subsequent measurement of response times, as follows: A sensor, initially in air, was plunged into nitrogen gas flowing at 50 mL/min by placing over the sensor a polyethylene cylinder connected by tubing to a nitrogen cylinder. The nitrogen flowed past the sensor and exited through 1/8-in-diameter holes in the cylinder to prevent pressure increase at the sensor. The response time for the sensor for a step decrease in oxygen was measured from the strip chart recording as the time from the initial change in response to 90 pct of the final response. By flowing air from a cylinder through a similar fitting, the response time for a step increase in oxygen was determined. In this procedure the cell, initially in nitrogen, was rapidly immersed in a flowing air atmosphere (20.9 pct O_2), and the cell current was recorded.

DISCUSSION

STABILITY

Five OTOX sensors were tested in room air (20.9 pct O_2) for a 13-day period during which the millivolt output of the sensors was monitored under a continuous 147-ohm load. The room temperatures and pressures varied during the test. The data obtained are summarized below, in millivolts:

Sensor	Initial	Average	Std. dev.
1.....	146.0	145.5	0.5
2.....	162.0	163.3	1.0
3.....	146.0	144.9	.4
4.....	151.0	154.0	1.6
5.....	163.0	164.6	1.4

The data were taken over 13 days with fluctuations of temperature from 18° to 24° C. The maximum coefficient of variation (the standard deviation divided by the average value) is 1.04 pct. The measured values are plotted in figure 2. The data indicated no general increase or decrease of the values of the sensor response to 20.9 pct O_2 for this brief test.

The OTOX sensor stability was also measured over a 146-day (4.7-month) period. These data were analyzed to obtain information on the drift or long-term change in sensor output. The drift is expressed as a linear function of time using a least squares regression analysis. The precision of the data can be estimated from the standard deviation of the observed data about the calculated drift line. The OTOX sensor outputs for 20.9 pct O_2 and room temperature (19° through 23° C) are summarized in table 1, and the data are plotted in figure 3. Table 2 summarizes the equation parameters for a least squares regression analysis.

It is apparent from both the graph and the calculated slopes of the stability data that sensor 1 is significantly different over long time observations from the other sensors. The measured output of sensor 1 in room air shows almost a ten-fold greater negative drift than that of the other sensors. The average response of the other sensors gave little variation over the 4.7-month period. The average of the slopes of the curves for

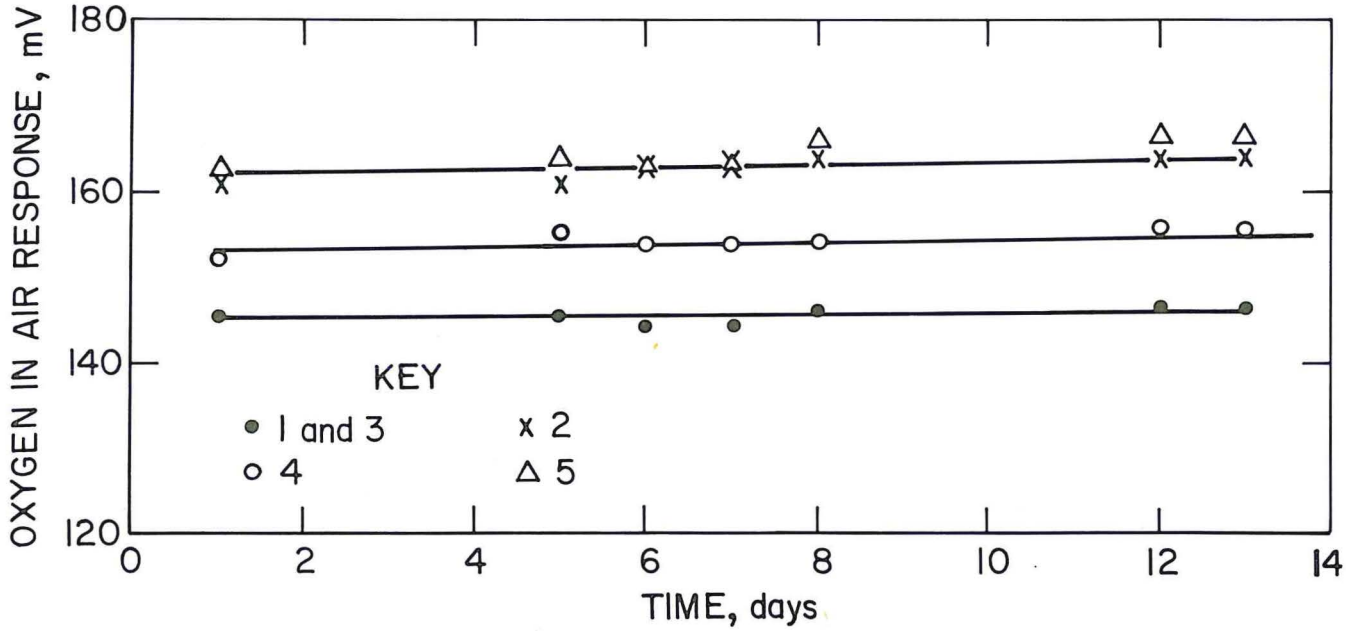

FIGURE 2. - OTOX sensor initial stability.

TABLE 1. - Stability of OTOX sensors; sensor response for 20.9 pct O_2, mV

Day	No. 1	No. 2	No. 3	No. 4	No. 5
0.....	146.34	161.70	146.18	151.46	162.75
6.....	144.92	162.89	144.57	153.82	164.74
7.....	145.57	164.01	144.93	154.50	165.98
12.....	144.90	165.13	145.50	156.23	166.53
13.....	144.82	162.14	143.28	154.03	163.77
39.....	139.56	164.21	144.49	153.62	165.04
49.....	139.30	163.92	144.70	153.24	166.04
84.....	132.56	163.94	144.61	153.27	165.52
88.....	132.46	166.30	146.46	155.73	167.28
98.....	135.76	164.33	146.90	155.76	165.48
101.....	136.48	164.16	147.96	152.33	162.63
103.....	136.83	163.45	144.69	152.31	164.75
104.....	137.63	163.92	145.33	156.32	164.63
111.....	134.39	163.97	147.34	157.24	164.88
115.....	133.71	165.37	147.47	156.26	164.79
116.....	134.38	164.59	146.58	152.76	165.45
118.....	136.66	164.32	148.14	152.73	166.49
119.....	134.49	165.63	148.08	153.69	165.38
124.....	135.35	164.17	146.36	153.60	165.52
125.....	134.51	164.04	146.34	152.86	165.00
126.....	133.60	163.43	145.69	152.36	164.29
130.....	133.99	163.88	145.99	151.50	164.82
131.....	131.65	162.57	145.18	151.02	164.12
136.....	129.42	163.61	146.24	151.77	164.63
138.....	129.35	163.18	146.16	150.98	164.44
142.....	129.44	163.89	146.30	152.28	164.74
144.....	126.61	163.94	146.73	152.36	165.19
146.....	126.62	164.38	147.02	152.21	165.22

TABLE 2. - Linear regression analysis for stability data on OTOX sensors[1]

Sensor	Least squares analysis		Squared regression coefficient, mV	Standard deviation, mV	
	Slope, mV/day	Intercept, mV		Slope	Regression
1.....	-0.10700	145.8	0.85200	0.0088	2.18
2.....	.00525	163.5	.06740	.0038	.96
3.....	.01430	144.7	.31900	.0041	1.02
4.....	-.01080	154.5	.08800	.0068	1.70
5.....	.00009	165.0	.00002	.0041	1.03

[1]Equation response (mV) = slope × elapsed time + intercept.

sensors 2 through 5 is nearly zero. Limits of the values for true slope β may be estimated at a given risk α (say, $\alpha = 5$ pct) from the experimental data for calculated slope b from sample data as follows:

$$b - t\left(\frac{S_{yx}}{S_x}\right) \leq \beta \leq b + t\left(\frac{S_{yx}}{S_x}\right),$$

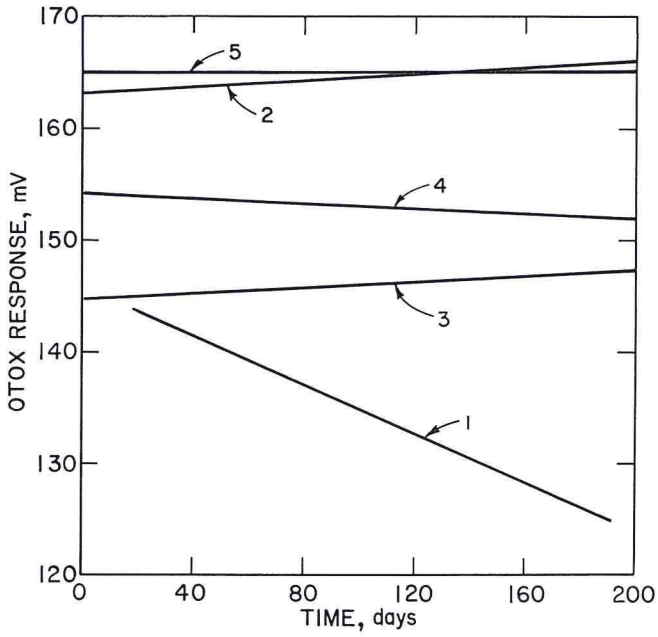

FIGURE 3. - OTOX sensor long-term stability.

where t is the value taken from the Student t tables at the n-2 (26) sample level, where $\alpha = 0.05$ and the ratio $\left(\frac{S_{yx}}{S_x}\right)$ is the standard error of the slope with values given in table 2. The following estimates for the limits of values of the true slope β are obtained:

Sensor	β limits	
	Upper	Lower
1.....	-0.860	-0.128
2.....	.014	-.0038
3.....	.024	.0045
4.....	.0054	-.027
5.....	.0098	-.0097

From data on measurements taken on sensors 2, 4, and 5, the true slope could be zero. For sensors 1 and 3 the data taken do not support the hypothesis that the true slope is zero; however, the slope of sensor 3 is small.

The square of the regression coefficient, a measure of the dependence of the sensor response on time, was large for sensor 1 but approximated zero for the other sensors. The coefficient of variation for the regression line or the scatter of the data about the calculated line ranged from 0.6 to 1.5 pct for the five sensors.

The original response data and the calculated intercepts show that the sensors are not identical and could not be directly interchanged in a commercial oxygen detector without electrical compensation for sensitivity and zero offset. This nonuniform response may be due to variation in construction and differences in dimensions of materials used in the sensor.

BIAS OVER RANGE

The response of the OTOX sensors, placed in an environmental chamber, was measured while the atmosphere was changed in steps from 0 to 40 pct O_2. The measured sensor responses are listed in table 3 for different oxygen concentrations. Since the sensor responses were not zero in nitrogen, or 0 pct O_2, the data were corrected by subtracting the measured response in nitrogen from the measurements taken at the other oxygen concentrations. A graph made from this data is given in figure 4.

The data are linear for lower values of oxygen and deviate from a straight line above 35 pct O_2. This nonlinearity of the complete data was confirmed by a least squares analysis of the data for the five sensors.

The average sensor sensitivity (millivolts per percent oxygen) in normal air (20.9 pct O_2) follows:

Sensor 1.....	6.18
Sensor 2.....	7.75
Sensor 3.....	6.93
Sensor 4.....	7.20
Sensor 5.....	7.81

The sensor response data were normalized to yield values of indicated percent oxygen by dividing the zero corrected response data for each sensor by the corresponding sensor average response ratio.

TABLE 3. - OTOX sensor oxygen response, mV

Oxygen,pct	No. 1	No. 2	No. 3	No. 4	No. 5
0.0.....	1.58	1.72	1.65	1.58	1.73
5.0.....	28.18	32.75	28.90	32.12	31.76
10.0.....	51.24	63.15	56.09	59.77	63.49
15.0.....	85.13	105.64	94.39	99.99	106.60
17.0.....	97.01	120.39	107.69	113.21	121.54
18.0.....	108.42	133.87	119.24	126.51	134.41
20.0.....	117.42	145.70	130.34	137.31	146.96
20.9.....	130.25	164.62	147.12	152.84	165.58
20.9.....	130.87	163.11	146.16	151.35	164.42
22.0.....	130.73	162.82	147.28	152.45	166.04
25.0.....	149.17	185.98	167.24	174.30	188.27
30.0.....	184.21	229.03	207.73	211.99	232.54
35.0.....	222.76	270.52	252.79	248.93	277.23
40.0.....	240.74	286.57	272.48	263.25	294.36
45.0.....	260.64	302.20	292.30	277.84	311.40

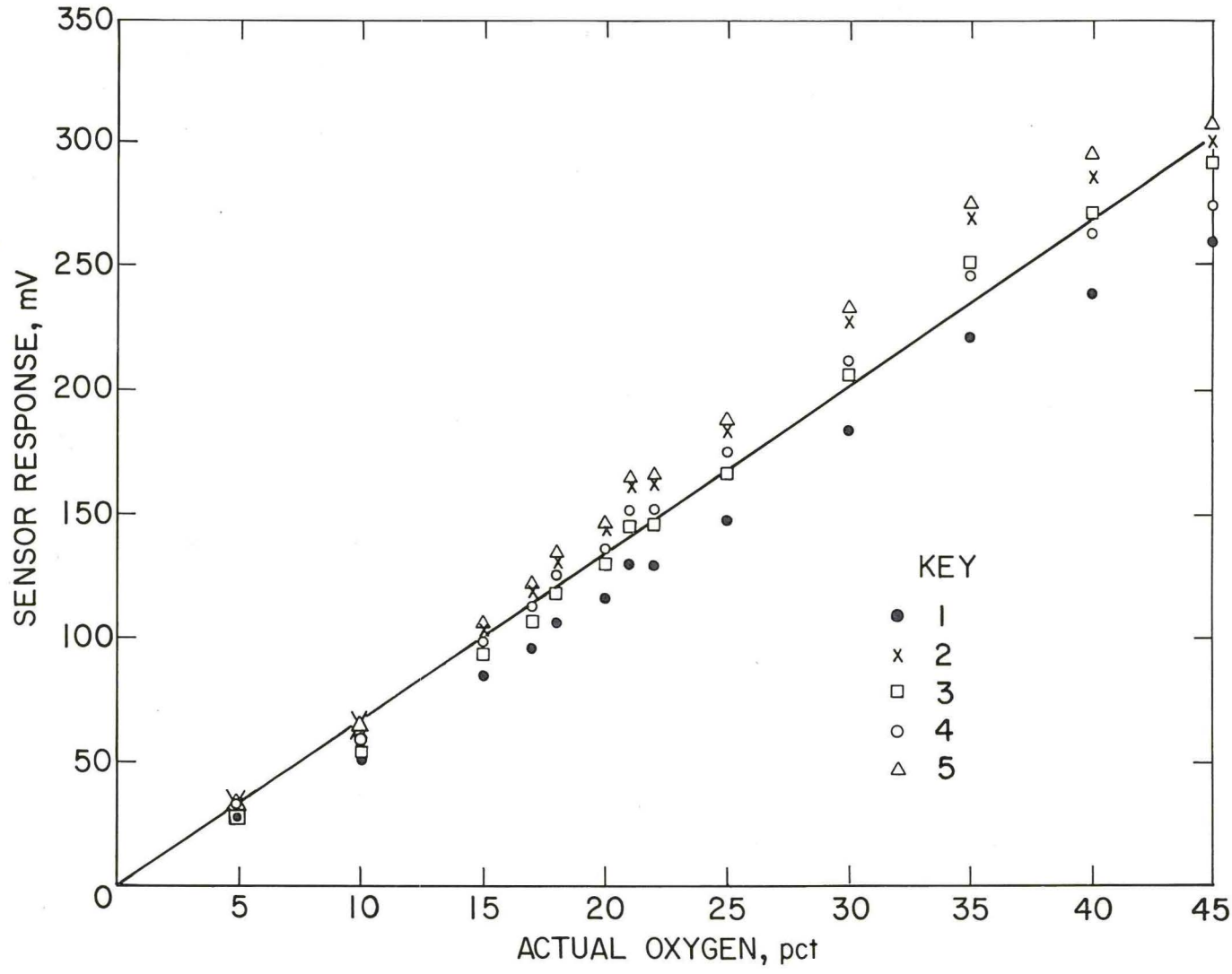

FIGURE 4. - Zero-corrected oxygen response for the OTOX sensor.

Table 4 summarizes this normalized sensor response data, giving the actual percent oxygen as determined by the reference instruments and the indicated percent oxygen values for each sensor. Figure 5 is a graph of the normalized responses of the sensors for varying oxygen concentrations to 30 pct. Figure 5 also contains the line calculated from the least squares analysis of the data. Table 5 summarizes the values of the slope, intercept, and standard deviation for the derived curves. The slopes of the calculated curves are close to 1.0, indicating equivalency of the actual and indicated percent oxygen values. The excellent fit of the experimental data to a straight line is indicated by the near-unity value for the square of the regression coefficient.

TABLE 4. - OTOX sensor normalized oxygen response data, pct

Oxygen, pct	No. 1	No. 2	No. 3	No. 4	No. 5
0.0..	0.00	0.00	0.00	0.00	0.00
5.0..	4.30	4.00	3.93	4.24	3.84
10.0..	8.03	7.92	7.85	8.08	7.90
15.0..	13.51	13.40	13.38	13.66	13.42
17.0..	15.44	15.31	15.30	15.50	15.34
18.0..	17.28	17.05	16.96	17.35	16.98
20.0..	18.74	18.57	18.57	18.85	18.59
20.9..	20.82	21.01	20.99	21.00	20.97
20.9..	20.92	20.82	20.85	20.80	20.83
22.0..	20.89	20.78	21.01	20.95	21.03
25.0..	23.88	23.77	23.89	23.98	23.88
30.0..	29.55	29.33	29.73	29.22	29.55

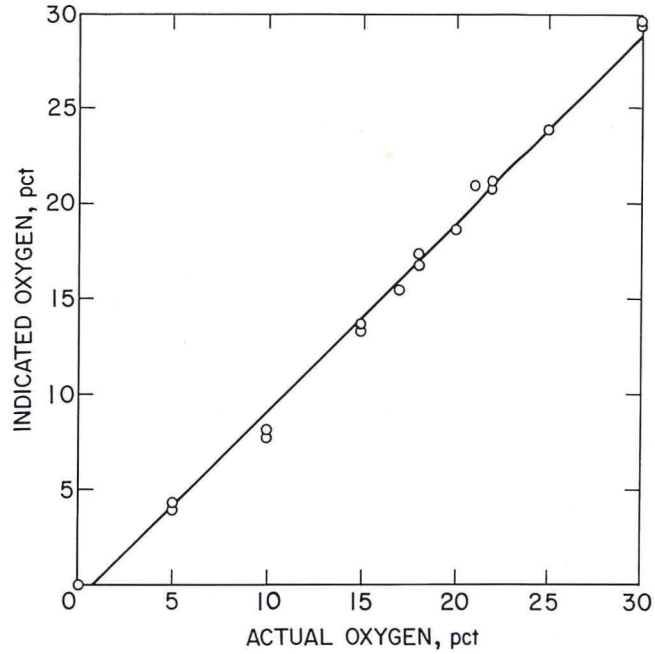

FIGURE 5. - Normalized oxygen response for the OTOX sensor.

TEMPERATURE EFFECT

The OTOX sensors were placed in the environmental chamber, and the temperature was varied in steps from 5° to 40° C. The sensor responses were measured while in air (20.9 pct O_2) at the different temperatures and were corrected to percent oxygen readings by dividing by the measured responses value (millivolts) at 22° C and multiplying by 20.9 pct. Table 6 lists the data obtained, and figure 6 shows the data. Sensor 1 data are not included in the figure since the curve was not the same as for the other

TABLE 5. - Linear regression analysis for OTOX response to oxygen concentration[1]

Sensor	Least squares analysis		Squared regression coefficient, pct	Standard deviation, pct	
	Slope[2]	Intercept, pct		Slope	Regression
1.....	0.9998	-0.864	0.994	0.0245	0.687
2.....	.9998	-.979	.993	.0264	.739
3.....	1.0109	-1.126	.993	.0274	.767
4.....	.9969	-.791	.995	.0231	.648
5.....	1.0086	-1.097	.993	.0263	.735

[1]Normalized response = slope × true oxygen pct + intercept.

[2]$\frac{\text{pct oxygen reading}}{\text{pct gaseous oxygen}}$.

TABLE 6. - OTOX sensor temperature response in air, pct

Temperature, ° C	No. 1	No. 2	No. 3	No. 4	No. 5
5.....	18.66	19.53	19.88	18.49	19.56
10.....	20.30	20.26	20.50	19.65	20.22
15.....	20.83	20.57	20.81	20.25	20.59
20.....	20.83	20.74	20.93	20.61	20.74
22.....	20.90	20.90	20.90	20.90	20.90
25.....	20.30	21.02	21.13	21.08	20.98
30.....	19.45	21.21	21.30	21.40	21.17
35.....	19.12	21.32	21.36	21.62	21.26
40.....	19.04	21.25	21.23	21.65	21.20

four sensors. The maximum changes for the readings are 2 pct of oxygen response increase for a 35° C temperature increase.

If the principal mechanism limiting the transport of oxygen is by diffusion through a fine capillary, then, as indicated in equation 6, a plot of the square root of the absolute temperature versus sensor response should yield a straight line. Figure 7 shows such a plot. This relationship gives a curve that is apparently no more linear than that of figure 6. The curvature in this plot could be due to the diffusion of oxygen being limited, by transport through a membrane as well as by the capillary. Upon disassembly of a sensor, we found two Teflon membranes within the cell separating the capillary from the cathode, which are used with the capillary and dead air space to form the total diffusion transport system for the oxygen sensor.

PRESSURE EFFECT

The sensors' response to change of air pressure was measured with ambient air (20.9 pct O_2) at an average pressure of

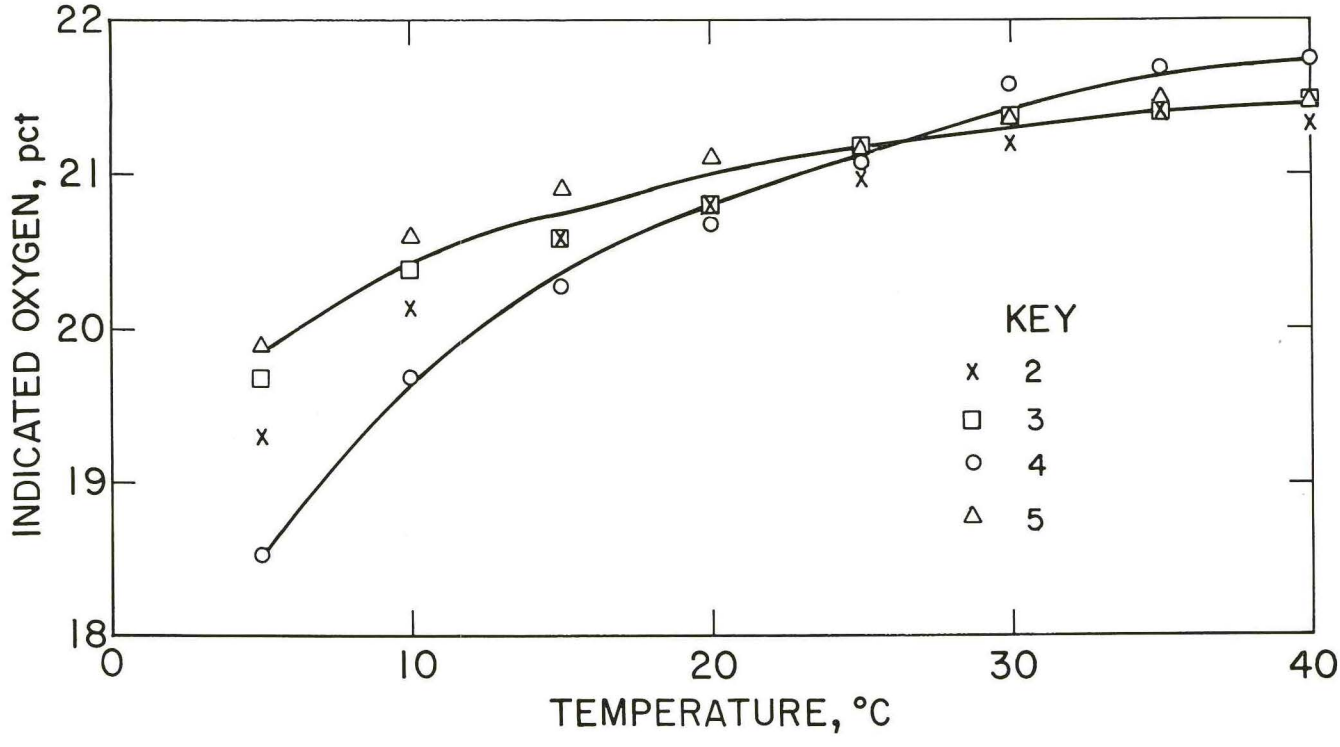

FIGURE 6. - OTOX sensor temperature response.

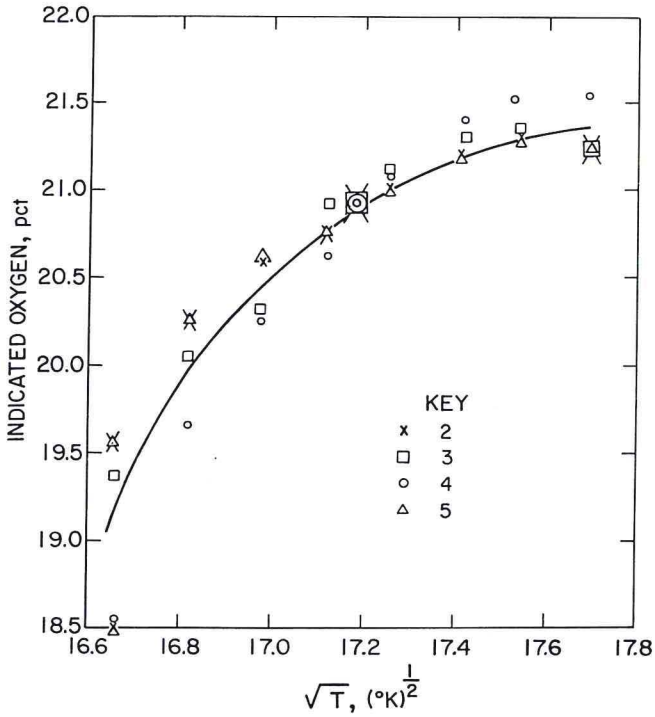

FIGURE 7. - OTOX sensor temperature response for the square root of the absolute temperature.

97.923 × 10^3 Pa (28.92 in Hg). Table 7 lists the measured response changes, and figure 8 plots the responses over a range of air pressures. Measurements were also taken of the pressure response of the Edmont Wilson membrane-amperometric oxygen analyzer (membrane-limited transport) and of the Taylor Servomex paramagnetic oxygen analyzer, model A0272, used as reference analyzers. Each of the reference analyzers has a pressure response of 3.46 pct of reading per 33.864 × 10^2 Pa (1 in Hg) change in pressure. The pressure unit of 1 in Hg was chosen since this is equivalent to 1,000 ft of altitude change. The -3.46-pct change in response would also be found on transporting either of the reference oxygen analyzers from sea level to a 1,000-ft elevation.

For sensors with a membrane-limited transport system, the sensor response to pressure changes was given previously in equation 5. For gas diffusion through a membrane, the gas diffusion coefficient D is proportional to $T^{1/2}$ and not dependent on pressure P; thus, by substitution for D in equation 5 we obtain

$$i = K' T^{-1/2} PC' \qquad (7)$$

or $$i = K' P C' \text{ for constant temperature,} \qquad (8)$$

where, again, i is the sensor response current, amp,

P is the pressure, atm,

and C' is the oxygen concentration, pct.

The change in response Δi for a change in pressure ΔP is

$$\Delta i = K \Delta P C', \qquad (9)$$

TABLE 7. - Effect of static pressure on sensor response, OTOX CTL, pct

Air pressure change, in Hg	No. 1	No. 2	No. 3	No. 4	No. 5	ED[1]	TY[2]
-8.....	19.90	20.54	20.26	20.09	20.41	15.1	15.2
-6.....	20.12	20.69	20.46	20.50	20.58	16.7	16.7
-4.....	20.33	20.84	20.70	20.56	20.73	18.2	18.1
-2.....	20.52	20.93	20.92	20.79	20.77	19.4	19.5
0.....	20.53	21.08	21.09	20.99	20.91	20.9	20.9
2.....	20.90	21.11	21.23	21.15	21.05	22.5	22.3
4.....	21.02	21.18	21.31	21.28	21.12	24.0	23.8
6.....	21.16	21.29	21.49	21.42	21.17	25+	25.5
8.....	21.31	21.38	21.58	21.57	21.22	([3])	([3])

[1]Edmont Wilson oxygen sensor.
[2]Taylor Servomex A0272 oxygen analyzer.
[3]Off scale.

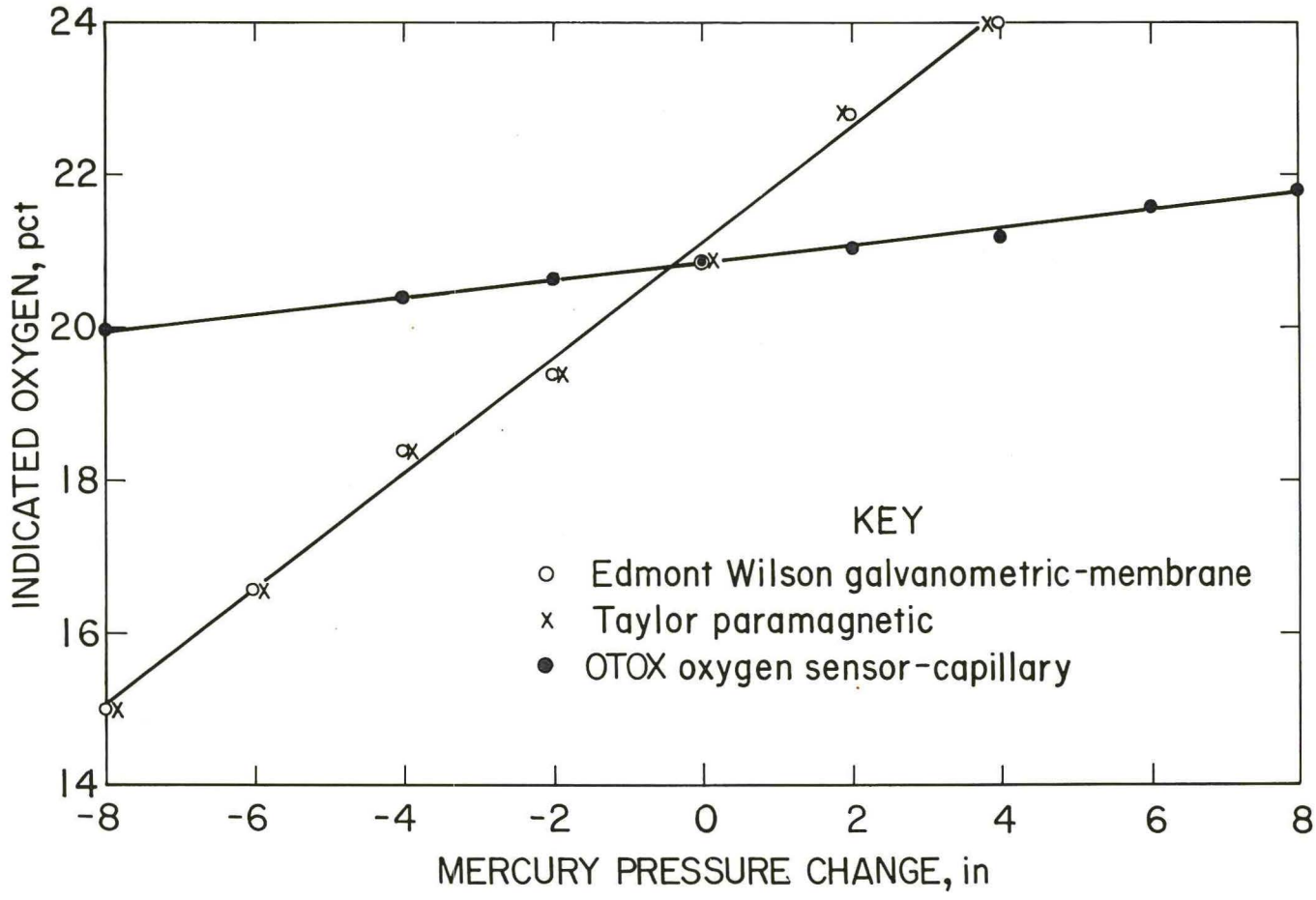

FIGURE 8. - OTOX sensor pressure effect.

and the relative percent change in response is obtained by dividing equation 9 by equation 8 and multiplying by 100 as follows:

$$\frac{\Delta i}{i} \cdot 100 \text{ pct} = \frac{\Delta P}{P} \cdot 100 \text{ pct.} \quad (10)$$

Thus, the calculated relative percent change in percent sensor response is equal to the percent pressure change. A pressure change of 33.864×10^2 Pa (1 in Hg decrease) is a 3.46-pct change at our test elevation of 1,000 ft above sea level.

The paramagnetic analyzer does not rely on oxygen diffusion, and the paramagnetic sensor response is simply proportional to the oxygen concentration (gram-mole per unit volume) and thus proportional to oxygen pressure. The calculated sensor response change per inch of mercury pressure for the paramagnetic sensor is 3.46 pct, the same as calculated in equation 10. The measured sensor response change per unit pressure of both reference instruments was approximately equal to this calculated value. On the other hand, the OTOX sensors have a pressure response change of only 0.34 pct per 33.864×10^2 Pa (1 in Hg). This is 1/10 of the change for the reference units, and the deviation of this number from zero again may be due to the presence of the two mechanisms for diffusion control used in the OTOX sensor, that of a capillary air space and the membranes within the sensor.

Table 8 summarizes the results of the statistical tests for the effect of pressure on the sensor response. The values for the square of the regression coefficient approach unity and show the excellent fit for a linear dependence of

TABLE 8. - Linear regression analysis for OTOX response to change in static pressures[1]

Sensor	Least squares analysis		Squared regression coefficient, pct	Standard deviation of regression, pct
	Slope, pct/in Hg	Intercept, pct		
1.....	0.088	20.64	0.99	0.06
2.....	.05	21.00	.98	.05
3.....	.08	21.00	.98	.07
4.....	.09	20.93	.98	.08
5.....	.05	20.89	.97	.11
Taylor Servomex	.73	21.01	1.00	.04
Edmont Wilson..	.71	20.90	1.00	.04

[1]Equation: Indicated O_2, pct = slope × Δp inch Hg + intercept.

response on pressure. The OTOX sensors give oxygen response readings proportional to the oxygen concentration rather than to the oxygen partial pressure as do the reference detectors. This response to gas concentrations is unique since all other electrochemical sensors, and almost all other sensors using infrared absorption or refractive index measurements, respond to partial pressure of the sensed gas. The ANDROS handheld CO_2 or CH_4 detector using a pressure modulated infrared absorption technique is the only other sensor we have found with the ability to read the concentration of gas directly.[6]

PRESSURE SURGE TESTS

The OTOX sensor contains free space or dead volume within the cell interior between the end of the capillary and the membranes. The oxygen in this volume must be reacted before equilibrium oxygen concentrations and stable sensor response values can be obtained. Pressure surges up to 24.90 × 10^2 Pa (10-in water pressure) may occur when a miner moves through airlocks (sealed doors) separating aircourses in underground mines. Figure 9 shows a plot of data obtained from the response measurements for a sensor encountering a pressure change from +270.91 × 10^2 Pa (8 in Hg) to atmospheric pressure. The initial response change is due to reduction of oxygen quantity in the capillary by the outward flow of oxygen-defficient from the space in the cell. Equilibrium diffusion and a stable response are reestablished at atmospheric pressure in 30 sec (time to reach 90 pct of final value).

Figure 10 shows the reponse change for an air pressure change from -270.91 × 10^2

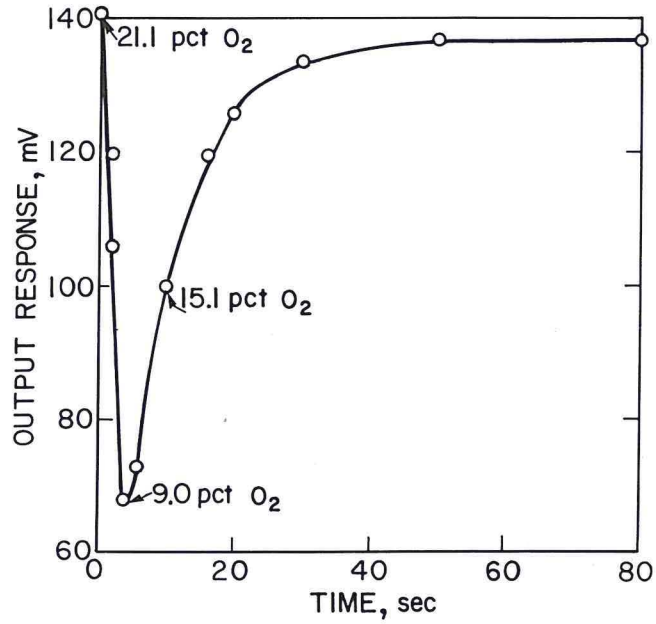

FIGURE 9. - OTOX sensor pressure surge effect: Initial pressure +8 in Hg above atmospheric pressure.

[6]Chilton, J. E., C. R. Carpenter, and G. H. Schnakenberg. Improvements in Gas Detector Instrumentation. Proc. 5th WVU Conf. on Coal Mine Electrotechnology, Dept. of Elec. Eng., W. Va. Univ., Morgantown, W. Va., July 30-Aug. 1, 1980, pp. 19-1 to 19-17.

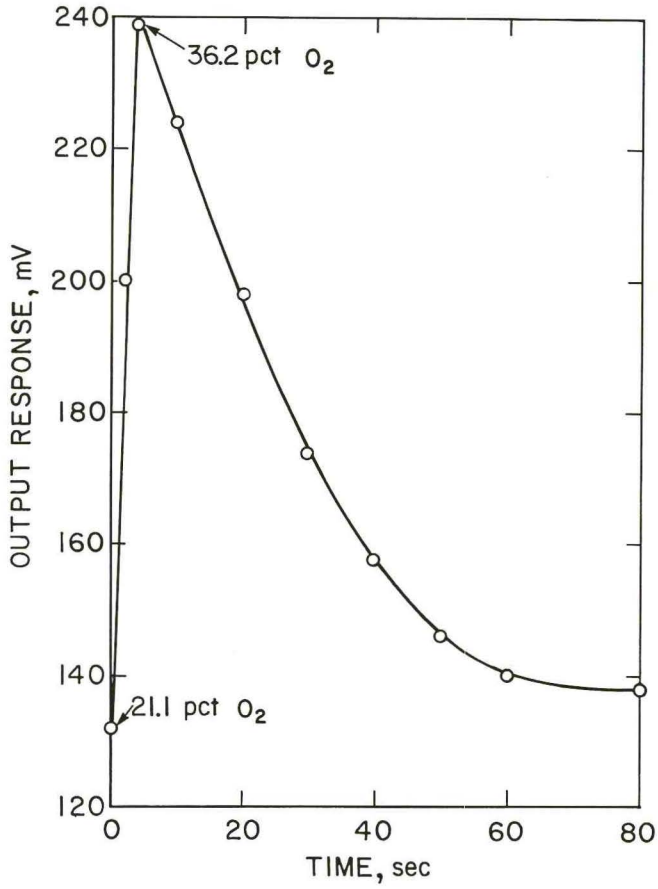

FIGURE 10. - OTOX sensor pressure surge effect: Initial pressure -8 in Hg below atmospheric pressure.

Pa (-8 in Hg) pressure to atmospheric pressure. The increase in cell response is due to the oxygen in air flowing into the sensor internal free space, and the equilibrium sensor response is reestablished in 60 sec (time to obtain 90 pct of final value). These experimental pressure surges are greater than would be found in operating mines, and response to upset from smaller pressure surges would more quickly return to the original value. Table 9 summarizes the times to recover obtained by the pressure surge test. The average time to recover to 90 pct of original response value is 22 sec for a negative pressure surge; full recovery occurs in an average of 55 sec. The average time to recover to 90 pct of the original response value is 61 sec for positive pressure surges; full recovery is in an average of 98 sec. The measured times depend both on quantity of oxygen to be consumed, which is a measure of sensor free space volume relative to the surge volume through the capillary, and on the sensor current, which controls the rate of oxygen consumption. This current is set by the value of the load resistor placed across the sensor.

TABLE 9. - Pressure surge response time data--time in seconds for recovery of response to 90 pct of initial value

Sensor	Pressure change	
	Negative (+8 in Hg to 0 in Hg)	Positive (-8 in Hg to 0 in Hg)
1.....	20	45
2.....	16	62
3.....	29	52
4.....	27	80
5.....	21	65

RESPONSE TIMES

Response times were measured for a step decrease in oxygen by first equilibrating the sensor in air and then flooding it with flowing nitrogen at constant ambient pressure. Response times were measured also for a step increase in oxygen concentration by equilibrating the sensor in nitrogen and then flooding it with flowing air at ambient pressure. Figure 11 shows the sensor response change for both conditions: The step increase and step decrease in oxygen. Table 10 reports the

TABLE 10. - Response times for step change in oxygen concentration to 90 pct of final value, sec

Sensor	Test sequence[1]	
	Step decrease in oxygen	Step increase in oxygen
1.....	70	76
2.....	50	28
3.....	26	32
4.....	28	32
5.....	45	25

[1]For a step decrease, the sensor is originally in air (20.9 pct O_2), then immersed in nitrogen (0 pct O_2); for a step increase, the sensor is originally in nitrogen, then immersed in air (20.9 pct O_2).

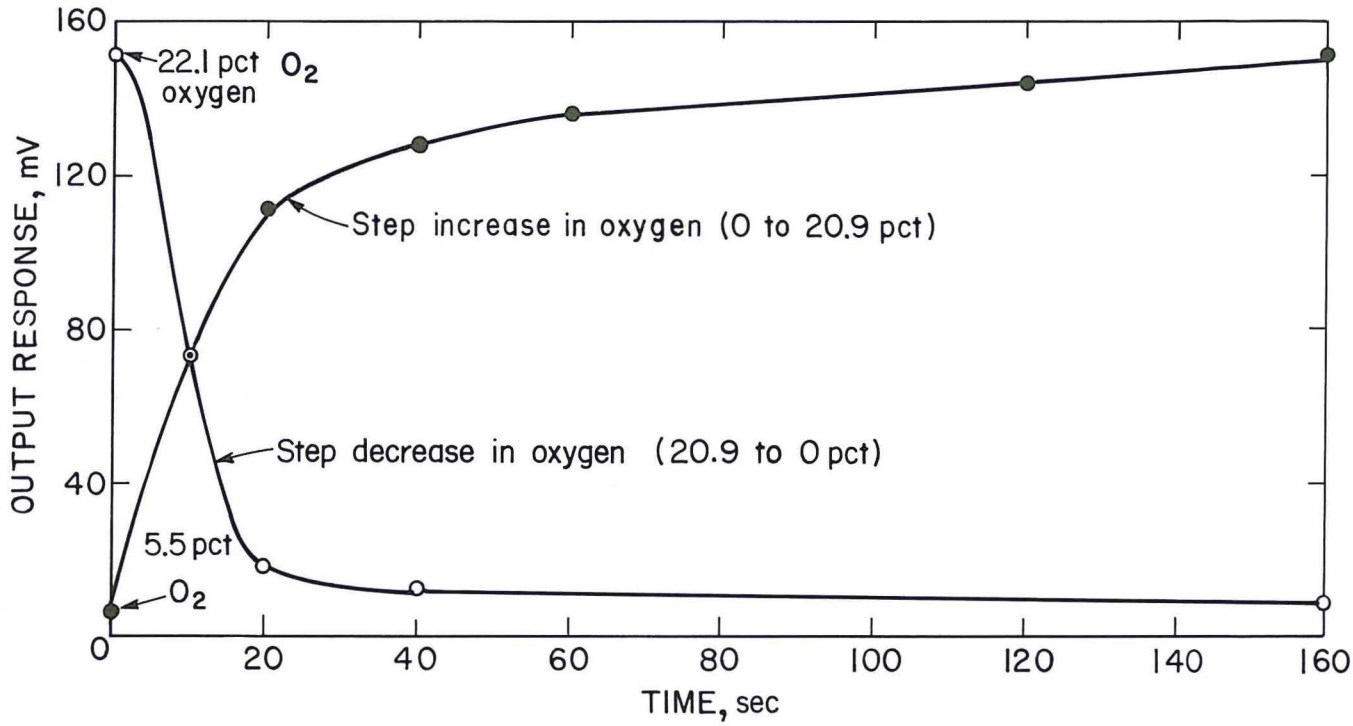

FIGURE 11. - Sample time responses for the OTOX sensor.

response times in seconds for both conditions as times for response to change to 90 pct of the final value. The average values of 44 sec for a step decrease and 39 sec for a step increase in oxygen concentration were measured. As noted in the last section, the response times are functions of sensor internal volumes and of the sensor currents generated by reaction of the oxygen. The sensor current is a function of sensor load resistance value. This current is maximized, and the response time is shortened by the use of smaller load resistors. However, sensor life is shortened by using small resistors as loads since the anode consumption is proportional to sensor output current. An operational amplifier coupled with the sensor to form a current-to-voltage converter can also yield minimum response times for this type of oxygen detector.

SUMMARY

The OTOX model CTL sensor is a unique electrochemical oxygen sensor. The limiting oxygen mass transport process is the diffusion of oxygen through a small-diameter capillary. Oxygen is rapidly consumed at an inert cathode, and the complete galvanic cell also contains a consumable metal anode with an alkaline electrolyte. Because of this design, the sensor has a response with a small temperature coefficient and very small pressure coefficient. The sensor responds to oxygen concentration rather than oxygen partial pressure because of the minimum pressure dependence. The stated sensor life is 6 months in ordinary air atmospheres, but operation in high oxygen concentrations (greater than 30 pct), with substantial quantities of acid gases (HCl or CO_2), or in very dry environments, and the use of electronic circuitry with small load resistances may shorten the operating life. A summary of the measured parameters follows:

1. Average response time to 90 pct of final value by step change of oxygen concentration is 42 sec.

2. Average response time to 90 pct of initial value by pressure shock of $+270.91 \times 10^2$ Pa to ambient pressure (+8 in Hg to ambient pressure) is 61 sec.

3. Sensor response change to temperature for 5° to 40° C range is +2.9 pct reading change per 10° C.

4. Sensor response change to pressure change in the range $\pm 270.91 \times 10^2$ Pa (+8 in Hg) is +0.34 pct reading change per 33.864×10^2 Pa (1 in Hg or 1,000 ft of altitude change).

5. Range is linear from 0 to 30 pct oxygen; the 95-pct confidence limit for indicated percent oxygen at 20.9 pct O_2 is ±2.84 pct of reading.

6. Interchangeability of sensors: The OTOX sensors have significantly different output. Sensor replacement with recalibration would be performed by gain and zero offset adjustment of the detector.

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