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A Study to Improve Dissolved Oxygen Analysis Techniques to Facilitate Water Quality Field Survey Applications

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**A Study To Improve Dissolved
Oxygen Analysis Techniques
To Facilitate Water Quality
Field Survey Applications**

by

**R.W. RAIBLE
M.K. TESTERMAN**



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A STUDY TO IMPROVE DISSOLVED OXYGEN ANALYSIS TECHNIQUES
TO FACILITATE WATER QUALITY FIELD SURVEY APPLICATIONS

by

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June, 1973

ABSTRACT

A STUDY TO IMPROVE DISSOLVED OXYGEN ANALYSIS TECHNIQUES TO FACILITATE WATER QUALITY FIELD SURVEY APPLICATIONS

This report describes studies made of the temperature characteristics of dissolved oxygen electrodes having a large surface area. Large area electrodes proved to have much longer lifetime between rejuvenations. Many measurements of dissolved oxygen in water need to be made in field situations where recalibration techniques would be difficult and where making temperature corrections is time consuming for operators who may be making numerous measurements. This study was directed toward design of a compensation circuit for a dissolved oxygen electrode which will give the best possible measurement over a large water temperature range of 5° - 35°C without the necessity of recalibration.

Studies were made of the temperature characteristics of dissolved oxygen probes and several electronic circuits with different configurations and components are described. Experimental data using two of the circuits are reported. One method involved using an integrated circuit multiplier module. The best temperature compensation was obtained for a circuit based on a design in which two thermistors were incorporated.

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A STUDY TO IMPROVE DISSOLVED OXYGEN ANALYSIS TECHNIQUES TO FACILITATE FIELD SURVEY APPLICATIONS

I. INTRODUCTION

The measurement of dissolved oxygen in natural waters is of great importance. Membrane-covered oxygen electrodes can be used to determine the dissolved oxygen in natural waters. The membrane-covered electrode may be either polarographic or galvanic depending upon the choice of electrode materials and the external circuitry. Because of the use of a membrane, both of these types of electrodes exhibit a high temperature coefficient which results in variation of current output with temperature for the same oxygen concentration. Hence, it is necessary to compensate the measuring system to reduce the error in measurement due to the temperature characteristic of the probe.

This report covers work performed during the course of the WRRR-A-017-ARK project to achieve temperature compensation of membrane type electrodes. The aim of the work was to provide a temperature compensated dissolved oxygen measurement system for field use which would make the best possible measurements over a wide range of temperatures and dissolved oxygen concentrations. It was believed that it was very important for the inexperienced operator in field situations to have a system which did not require recalibration at the extremes of possible measurement situations, since the operator making measurements in a field situation has a variety of other readings to consider and is exposed to considerable difficulty in

other respects. This requirement is not nearly so stringent in a laboratory situation where the investigator has at his command facilities for making standardized measurements at various oxygen levels and the ability to check his results using the Winkler or other method. An effort was made to choose those electrodes which showed the longest possible lifetime once rejuvenated and calibrated.

From a large number of measurements on a series of electrodes made in this laboratory, it appears that the most likely electrodes to fulfill such conditions are those which have relatively large electrode surface areas and large electrolyte volumes. In spite of the fact that many companies have claimed long life times for probes with small electrode areas, in our studies no such electrode has proved to have a long life time compared to the lifetime of the larger probes.

The work described in this report includes studies of the temperature characteristic of dissolved oxygen probes, different methods of compensation, and testing the compensated system under actual conditions. The temperature compensated systems were used to measure dissolved oxygen concentration in water of various dissolved oxygen concentration levels and temperatures and the values were compared with values determined by Winkler tests as well as values determined by using a mixing system (Appendix I) capable of producing a given oxygen concentration with a high degree of accuracy and reproducibility.

II. BACKGROUND INFORMATION

A polarographic type dissolved oxygen probe consists of an anode and a cathode which are immersed in a conductive electrolyte solution. For the electrodes used in this study, the anode was silver and the cathode was gold.

A membrane is stretched over an opening in the electrode to separate the test solution from the electrolyte inside the probe. The membranes used are selectively permeable to oxygen. The membrane is stretched over the gold cathode and a thin film of electrolyte is trapped between the membrane and the cathode. This layer of electrolyte allows electrical conduction between the electrodes within the probe.

A polarizing potential is applied between the electrodes, and the oxygen diffusing through the membrane is reduced at the cathode. This provides a current flow in the external circuit which is proportional to the amount of oxygen reaching the cathode. Because oxygen is being consumed by reduction at the cathode, the partial pressure of oxygen in the electrolyte is always less than the partial pressure of oxygen in the test solution. Because of this difference in partial pressure, oxygen diffuses through the membrane. The current output of the probe is proportional to the diffusion rate of oxygen through the membrane. As the concentration of oxygen in the test solution varies, the partial pressure of oxygen, and hence the diffusion through the membrane varies, therefore, the current output also varies.

Probe current for membrane electrodes at constant temperature is given by Mancy, Okun, and Reilley¹ as

$$I = \frac{nFaPC}{b}, \quad (1)$$

where n is the number of electrons involved in the electrode reaction,

F is the Faraday,

a is the area of the polarized electrode,

P is the membrane permeability coefficient,

b is the membrane thickness, and

C is the oxygen concentration in the sample.

From this equation it can be seen that the probe current, I_t , is directly proportional to the concentration of dissolved oxygen. For the range of water temperatures of interest, temperature dependence of the probe current may be expressed by the equation

$$I_t = cAe^{kt}, \quad (2)$$

where, c is the concentration of oxygen,
 A is a constant of the probe,
 k is also a constant of the probe, and
 t is temperature in degrees centigrade.

The exponential nature of the current variation with temperature suggests utilization of thermistors to compensate the current output of the probe, since a thermistor's resistance decreases exponentially with temperature. If a circuit is designed to provide an exponentially decreasing voltage for an increase in temperature, then it should be possible to compensate for the exponential nature of the electrode current. Berthelot² designed a compensation circuit based on the above principle. The probe current, I_t , was converted to a voltage, V_t , through a current to voltage converter circuit yielding an equation of the form

$$V_t = Qce^{kt}, \quad (3)$$

Where, Q is a constant of the circuit and the probe,
 V_t is the voltage output of the current to voltage converter,
 c is the dissolved oxygen concentration,

k is the constant of the probe, and
t is the temperature in degrees centigrade.

If the resistance of a thermistor is assumed to follow an equation of the form

$$R_t = R_0 e^{-qt} \quad (4)$$

where R_0 is the resistance of the thermistor at 0°C , then by using an operational amplifier circuit, a voltage was developed

$$V_o = Ne^{qt}, \quad (5)$$

where V_o is the output voltage of the network,

N is a constant due to a particular thermistor and the network,

q is a constant of the thermistor, and

t is the temperature of the thermistor in degrees centigrade.

If a voltage V_t as given by Equation 3 is divided by voltage V_o as given by Equation 5 and if $q = k$ then the resultant voltage will be independent of temperature.

Logarithmic circuits were employed to divide one voltage by another. The logarithms of V_t and V_o are taken by using these two voltages as input to two independent logarithmic amplifiers. The outputs of the logarithmic amplifiers are connected to a difference amplifier. If V_3 is the output of the difference amplifier then, mathematically

$$\begin{aligned} V_3 &= \log V_t - \log V_o = \log \frac{V_t}{V_o} \\ &= \log \frac{cQe^{kt}}{Ne^{qt}} = \log \frac{Q}{N} ce^{(k-q)t}. \end{aligned} \quad (6)$$

If q and k are equal then

$$V_3 = \log \frac{Q}{N} c, \quad (7)$$

and it is seen that this voltage is independent of temperature and is dependent on the concentration only. If V_3 is the input of an anti-logarithmic circuit then the output V_4 will be

$$V_4 = \text{antilog} \left[\log \left(\frac{Q}{N} c \right) \right] = \frac{Q}{N} c. \quad (8)$$

Therefore, the output voltage is a linear function of concentration and is independent of temperature.

In the above method, two logarithmic and one antilogarithmic circuits were employed. These circuits drifted with variation in ambient temperature. To reduce this drift problem and to simplify the measuring circuitry, two other methods of temperature compensation were tested retaining the basic principle given by Berthelot. This report covers the work done in connection with these two methods.

III. TEMPERATURE COMPENSATION - METHOD I

The first method of temperature compensation attempted in this project utilized the principle given by Berthelot, and the basic aim was to simplify the measuring and compensating circuit as compared to the circuit used by Berthelot. The compensating voltage was multiplied by the output voltage of

the probe, instead of dividing, as was done in the original method. The compensating voltage was developed to decrease exponentially with temperature, i.e., where q is a constant

$$V_{\text{compensation}} = e^{-qt}. \quad (9)$$

Since the probe output increases exponentially with temperature, by multiplying these two voltages, the effect of temperature can be eliminated. This principle is illustrated in Figure 1.

As a first step the probe current is converted to a voltage by a simple current to voltage amplifier. For this circuit which is shown in Figure 2,

$$V_t = iR_3 = AR_3 (ce^{kt}) = Qce^{kt}, \quad (10)$$

where

R_3 is the feedback resistor in the current-voltage amplifier,

i is the current output of the dissolved oxygen probe,

c is the concentration of dissolved oxygen in ppm,

A and k are constants of the dissolved oxygen probe, and

$Q = AR_3$.

The resistors R_1 and R_2 form a voltage dividing network to provide 0.72 volts necessary for operation of the polarographic dissolved oxygen probe, and the operational amplifier serves as an isolating amplifier to maintain the constant voltage to the probe as probe current changes.

The next step was to find a multiplier circuit which would multiply the

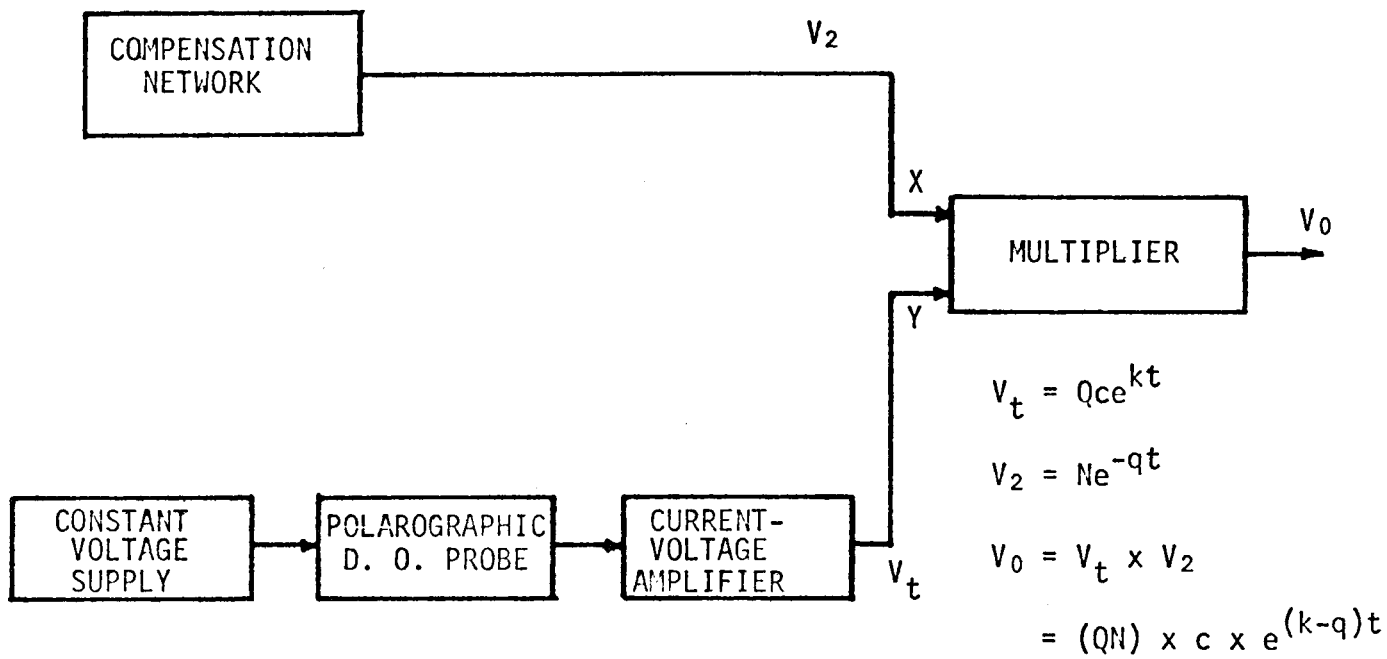


FIGURE 1

BLOCK DIAGRAM REPRESENTATION OF TEMPERATURE COMPENSATION UTILIZING A MULTIPLIER

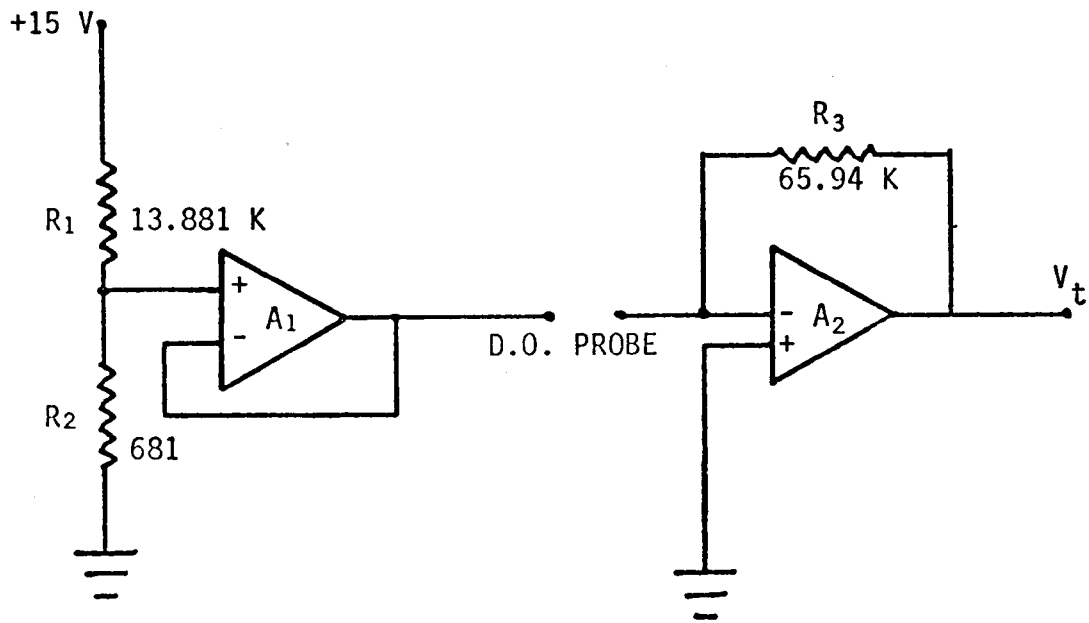


FIGURE 2

PROBE CIRCUIT TO MEASURE PROBE CURRENT

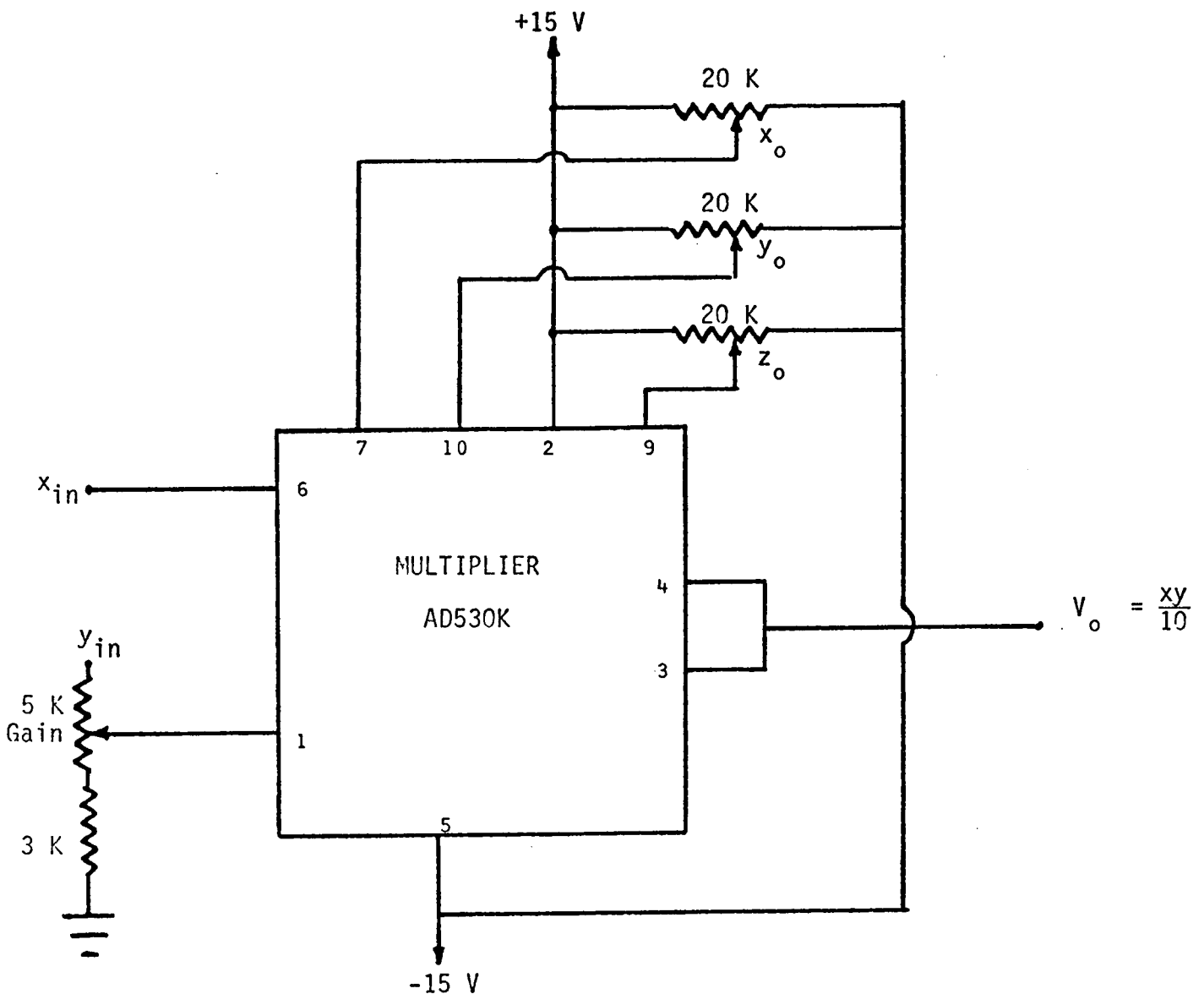


FIGURE 3
MULTIPLIER ALIGNMENT CIRCUIT

ALIGNMENT PROCEDURE:

1. $x_{in} = y_{in} = 0$ volts adjust z_o for minimum output.
2. $y_{in} = 5$ volts dc, $x_{in} = 0$ adjust x_o for minimum output.
3. $x_{in} = 5$ volts dc, $y_{in} = 0$ adjust y_o for minimum output.
4. Repeat steps 1,2, and 3 until $x_{in} = y_{in} = 0$, output = 0 and output is minimum in Steps 2 and 3.
5. $x_{in} = y_{in} = 5$ volts dc adjust gain until $V_o = 2.5$ volts dc.
6. Repeat Steps 1 and 5, if necessary. If it is not possible to adjust repeat Steps 2,3, and 4.

TABLE I
CUMULATIVE DRIFT FOR MC1494L

Time (Days)	Output of the Multiplier (Volts)
0.0	0.004
1.0	0.008
2.0	0.011
3.0	0.018
4.0	0.022
5.0	0.023
6.0	0.031

TABLE II
CUMULATIVE DRIFT FOR AD530K

Time (Days)	Output of the Multiplier (Volts)
0.0	0.002
1.0	0.001
2.0	0.007
5.0	0.004

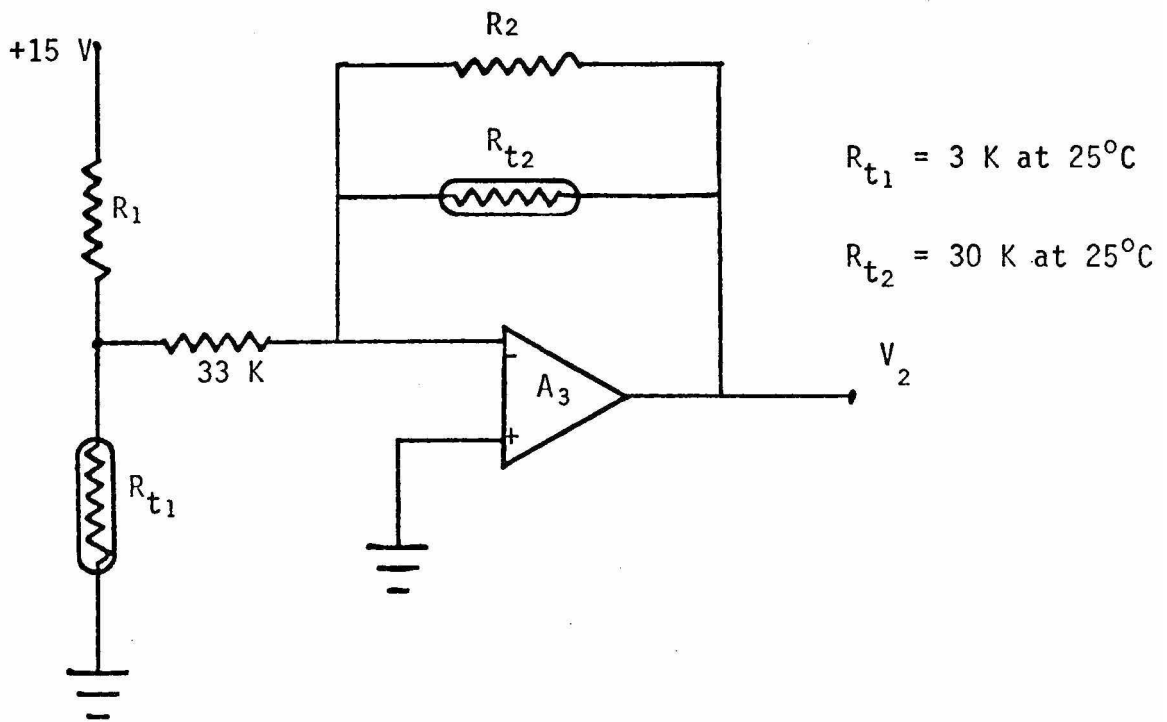


FIGURE 4
COMPENSATION NETWORK I

probe output voltage and the compensating voltage with minimum drift and offset. For this purpose different multipliers were tried and their performances compared. The multipliers which were chosen for comparison were MC1594L, MC1494L, and AD530K.

The multipliers were subjected to temperature variation to check for stability with temperature. Each multiplier was aligned as shown in Figure 3 at 25°C. Then it was placed in a temperature controlled oven and the oven temperature was varied from 0° to 50°C after which the multiplier was returned to 25°C. The output of each multiplier was measured with zero input for x and y. The output should be zero volts but drift caused it to be different from zero. This test was carried out for each multiplier. As a result of this test the multiplier, MC1594L, was rejected since it was found to have high temperature drift characteristics.

The next test was to check for drift over a period of time while the temperature was maintained at a constant value. In this test the AD530K multiplier performed better than the MC1494L multiplier while both of them were equally accurate in multiplication. The cumulative drift of these multipliers is shown in Tables I and II. Hence, based on these tests the AD530K multiplier was chosen for use in the circuit.³

The thermistor circuit was designed to provide the proper compensating voltage. The thermistor circuit shown in Figure 4 was tested. The circuit was simulated with potentiometers for testing prior to construction of the actual circuit with thermistors. The potentiometers were adjusted so that the resistance values were the same as those of the thermistors at a particular temperature $t^{\circ}\text{C}$. In each case the thermistor resistance at $t^{\circ}\text{C}$ was noted from the values provided by the manufacturer. The output voltage V_2 was the simulated compensating voltage at this temperature. This voltage is the "x" input to the multiplier.

For the same temperature $t^{\circ}\text{C}$ the probe output current was calculated with the knowledge of the probe constants. The value of voltage from the current to voltage amplifier was calculated from the value of the current in Equation 10. This voltage was simulated using a variable dc power supply and was the "y" input to the multiplier.

The measured output voltage V_o then became,

$$V_o = V_t V_2 \quad (11)$$

and was the compensated output at the temperature $t^{\circ}\text{C}$. In a similar manner the compensated output voltages at other temperatures were measured by simulating the thermistors and the probe. The value of R_1 was varied and in each case the voltage output of the multiplier was measured for various temperatures for a fixed value of R_2 . This test was repeated for different values of R_2 . The values are given in Tables III, IV, V, and VI. The data are plotted in Figures 5 to 8. It can be seen that the best compensation is achieved in Figure 7.

A different thermistor circuit was considered and a diagram of this circuit is shown in Figure 9. As before, in this case the multiplier output was measured at various temperatures with simulated values for the probe current and the thermistor resistances. The value of R_1 was varied to obtain different sets of data. The data are given in Table VII and are plotted in Figure 10.

With the data available from the two different type thermistor circuits, it was found that the circuit shown in Figure 9 gave a better fit and this circuit was used in testing the system under actual conditions.

A Beckman Model 191605 dissolved oxygen electrode was utilized. The

TABLE III

DATA FROM CIRCUIT FIGURE 4

 $R_2 = \infty$, CONC 8 ppm

TEMP (°C)	R_{t_1} (Kilohms)	R_{t_2} (Kilohms)	$R_1 = 2K$ Multiplier Output (Volts)	$R_1 = 3K$ Multiplier Output (Volts)	$R_1 = 5.49K$ Multiplier Output (Volts)	Probe Output (Volts)
14.3	4.855	47.78	5.29	5.01	3.67	2.74
20.2	3.721	37.18	5.38	4.35	3.10	3.71
25.0	3.000	30.00	5.00	3.99	2.85	4.77
31.5	2.281	22.91	4.84	3.89	2.86	6.69

TABLE IV
 DATA FROM CIRCUIT FIGURE 4

$R_2 = 464K$, CONC 8 ppm

TEMP (°C)	R_{t_1} (Kilohms)	R_{t_2} (Kilohms)	$R_1 = 2K$ Multiplier Output (Volts)	$R_1 = 3K$ Multiplier Output (Volts)	$R_1 = 5.49K$ Multiplier Output (Volts)	Probe Output (Volts)
14.3	4.855	47.78	5.28	4.48	3.26	2.74
20.2	3.721	37.18	4.95	4.00	2.85	3.72
25.0	3.000	30.00	4.67	3.74	2.67	4.77
31.5	2.281	22.91	4.64	3.73	2.75	6.69

TABLE V
 DATA FROM CIRCUIT FIGURE 4

$R_2 = 309.3K$ CONC 8ppm

TEMP (°C)	R_{t_1} (Kilohms)	R_{t_2} (Kilohms)	$R_1 = 2K$ Multiplier Output (Volts)	$R_1 = 3K$ Multiplier Output (Volts)	$R_1 = 5.49K$ Multiplier Output (Volts)	Probe Output (Volts)
14.3	4.855	47.78	5.18	4.25	3.08	2.74
20.2	3.721	37.18	4.76	3.84	2.73	3.72
25.0	3.000	30.00	4.55	3.62	2.59	4.77
31.5	2.281	22.91	4.54	3.65	2.70	6.69

TABLE VI
 DATA FROM CIRCUIT FIGURE 4

$R_2 = 203K$ CONC 8ppm

TEMP (°C)	R_{t_1} (Kilohms)	R_{t_2} (Kilohms)	$R_1 = 2K$ Multiplier Output (Volts)	$R_1 = 3K$ Multiplier Output (Volts)	$R_1 = 5.49K$ Multiplier Output (Volts)	Probe Output (Volts)
14.3	4.855	47.78	4.79	3.93	2.83	2.74
20.2	3.721	37.18	4.48	3.61	2.57	3.72
25.0	3.000	30.00	3.34	3.46	2.47	4.77
31.5	2.281	22.91	4.40	3.54	2.62	6.69

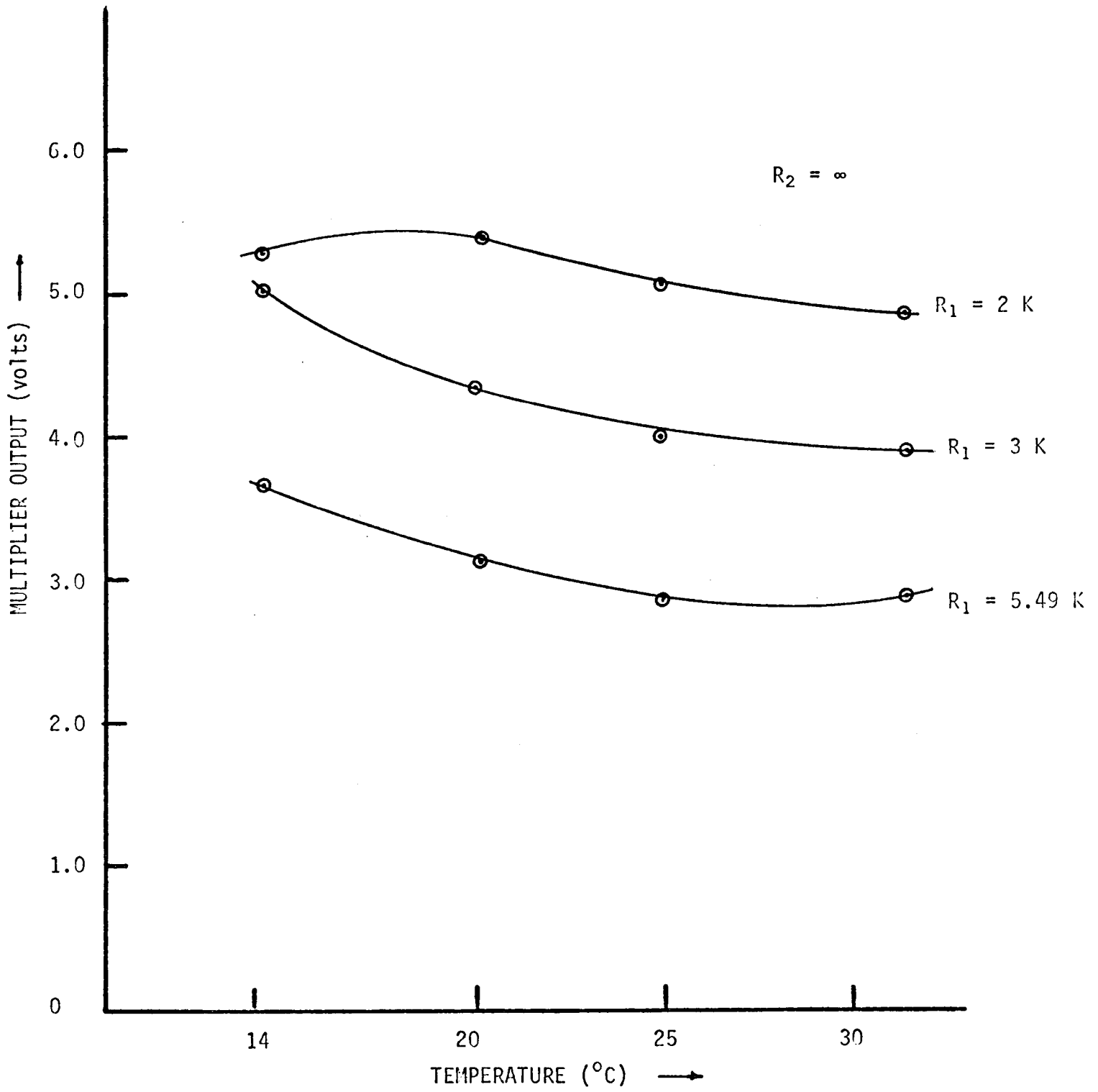


FIGURE 5

COMPENSATED MULTIPLIER OUTPUT FOR FIGURE 4, $R_2 = \infty$

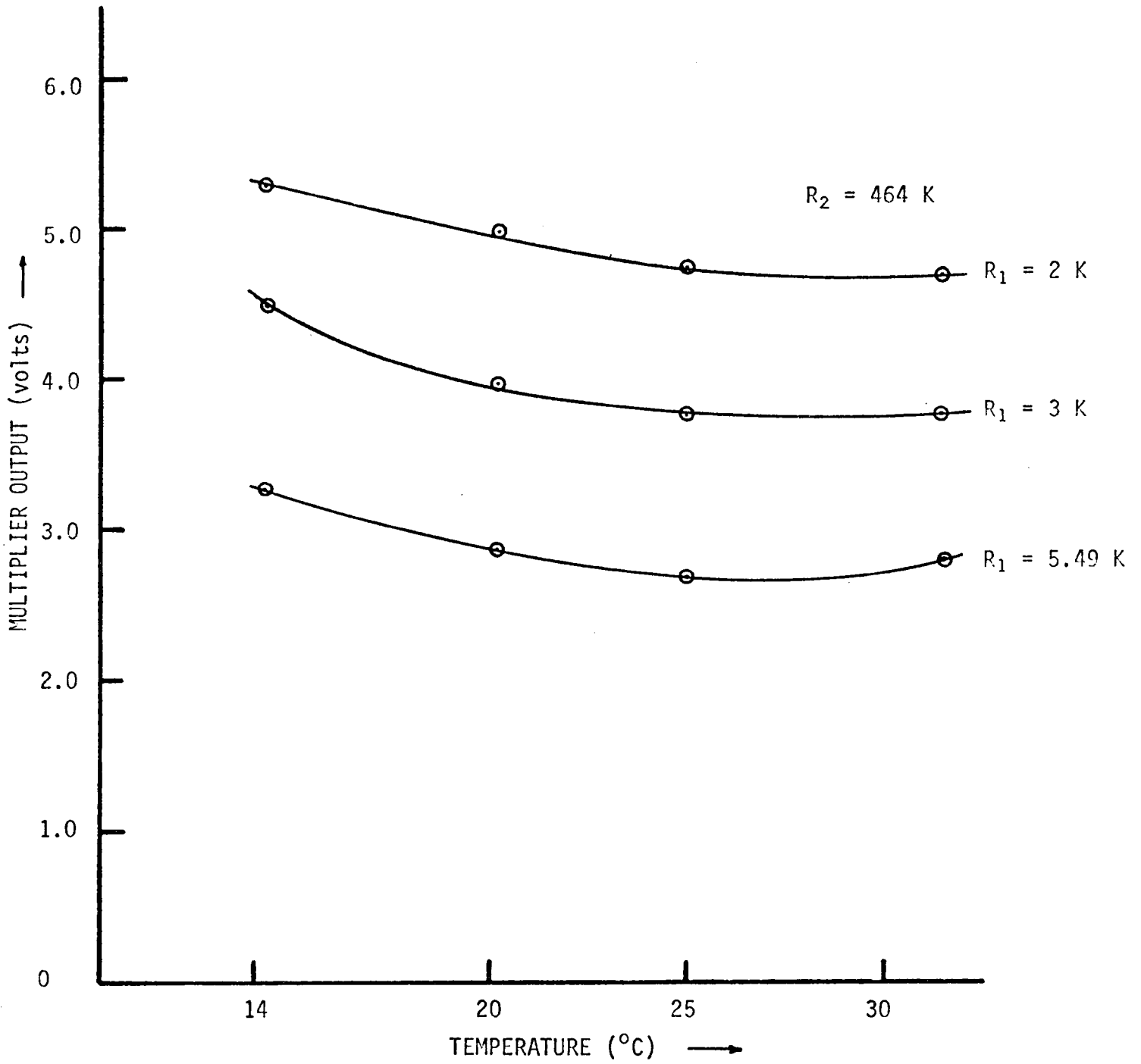


FIGURE 6

COMPENSATED MULTIPLIER OUTPUT FOR FIGURE 4, $R_2 = 464$ K

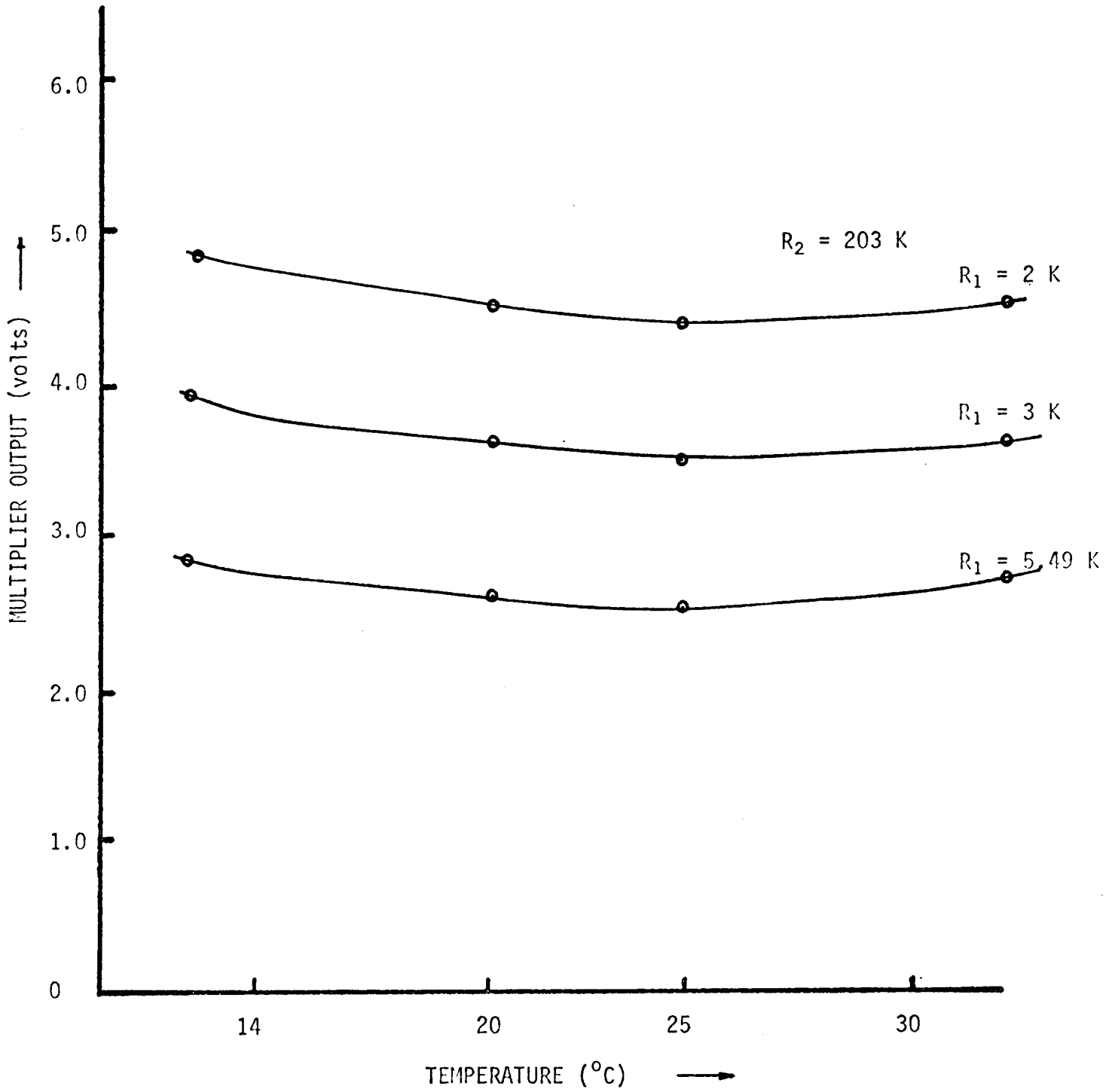


FIGURE 7

COMPENSATED MULTIPLIER OUTPUT FOR FIGURE 4, $R_2 = 203$ K

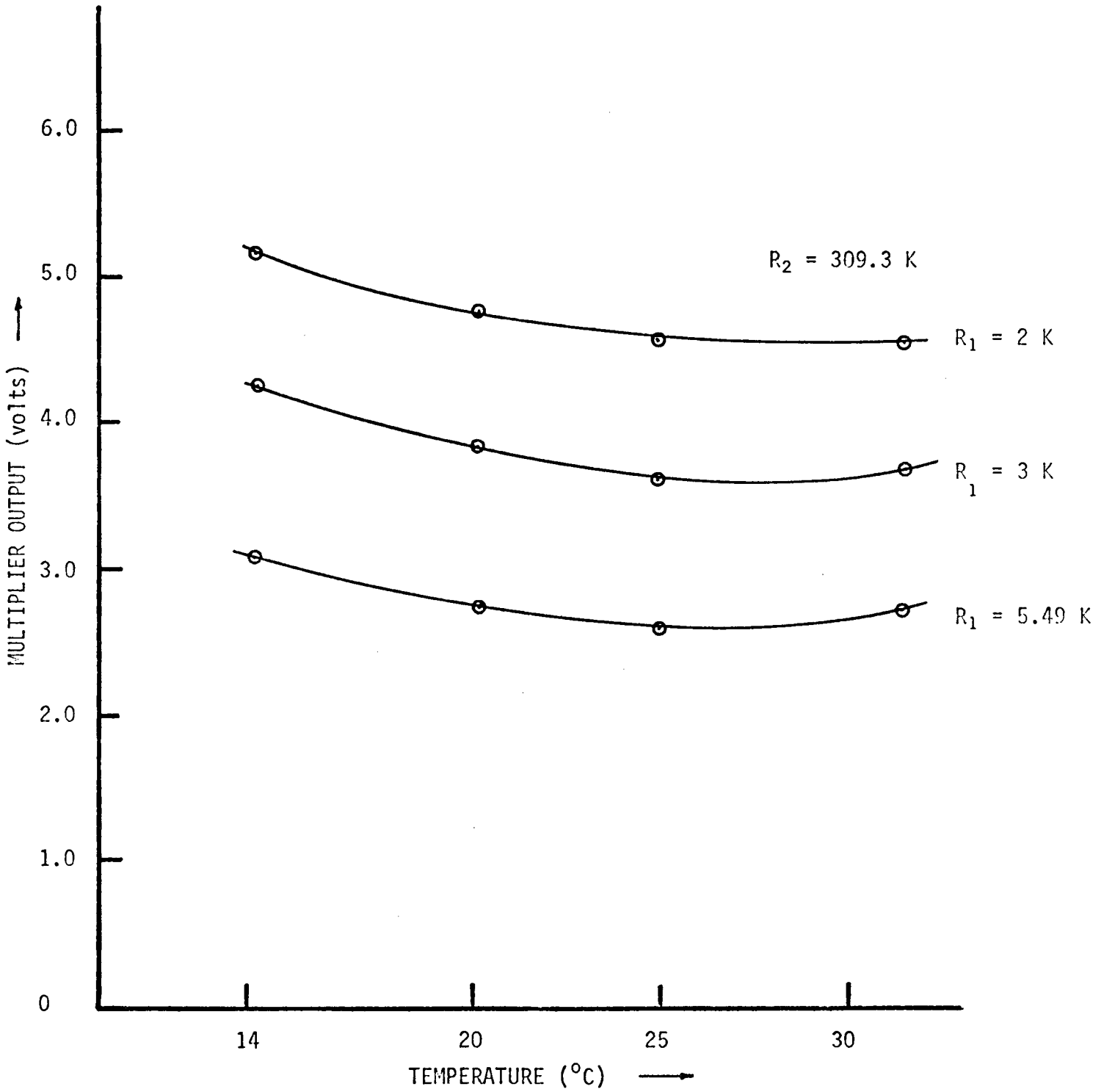


FIGURE 8

COMPENSATED MULTIPLIER OUTPUT FOR FIGURE 4, $R_2 = 309.3\text{ K}$

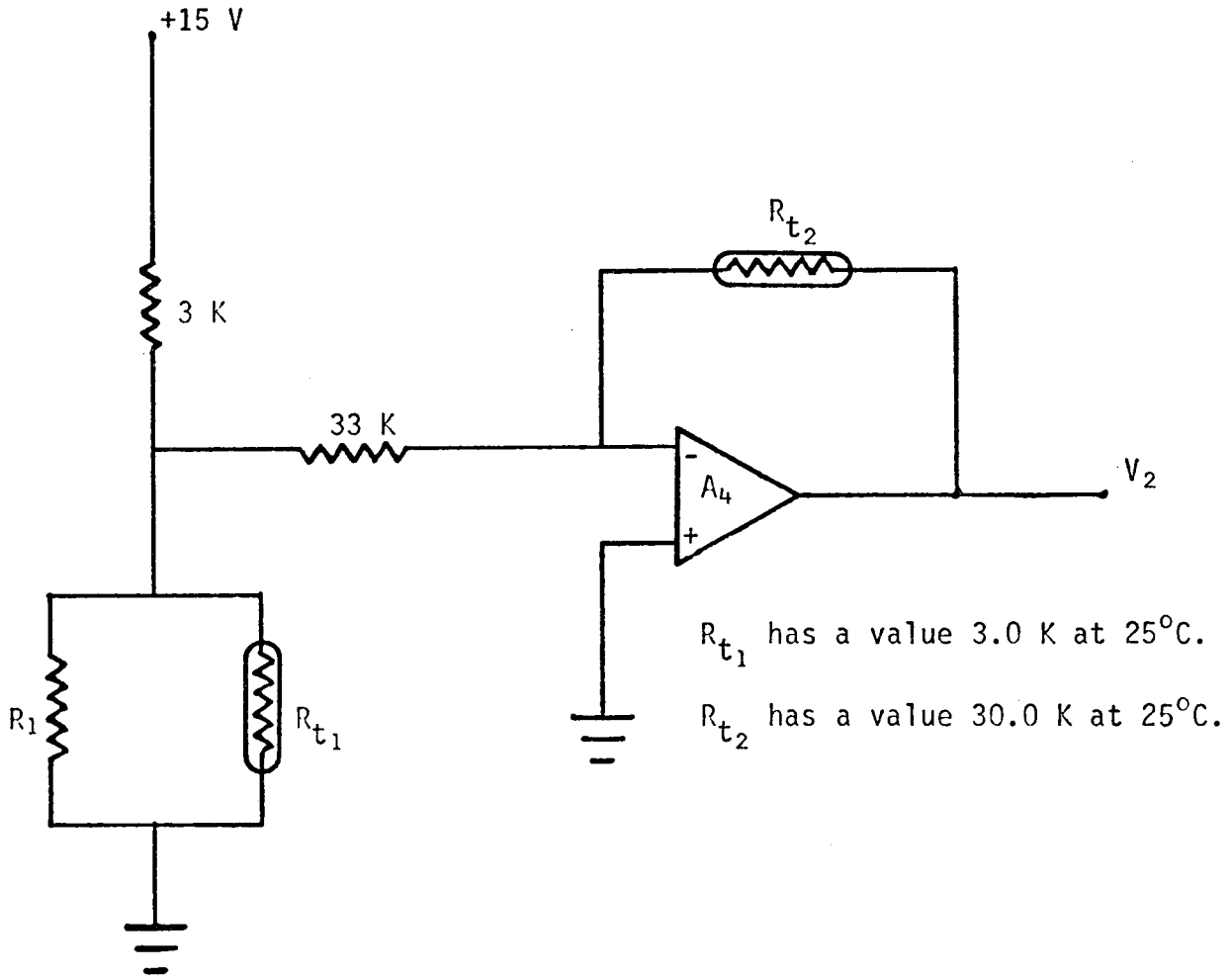


FIGURE 9
COMPENSATION CIRCUIT II

Table VII

DATA FROM CIRCUIT FIGURE 9

TEMP (°C)	R_{t_1} (Kilohms)	R_{t_2} (Kilohms)	R = 15K Multiplier Output (Volts)	$R_1 = 30K$ Multiplier Output (Volts)	$R_1 = 53.6K$ Multiplier Output (Volts)	$R_1 = \infty$ Multiplier Output (Volts)	Probe Output (Volts)
14.3	4.855	47.78	2.53	2.65	2.70	2.77	2.74
20.2	3.721	37.18	2.43	2.52	2.56	2.62	3.72
25.0	3.000	30.00	2.42	2.49	2.52	2.57	4.77
31.5	2.281	22.91	2.59	2.69	2.67	2.70	6.69

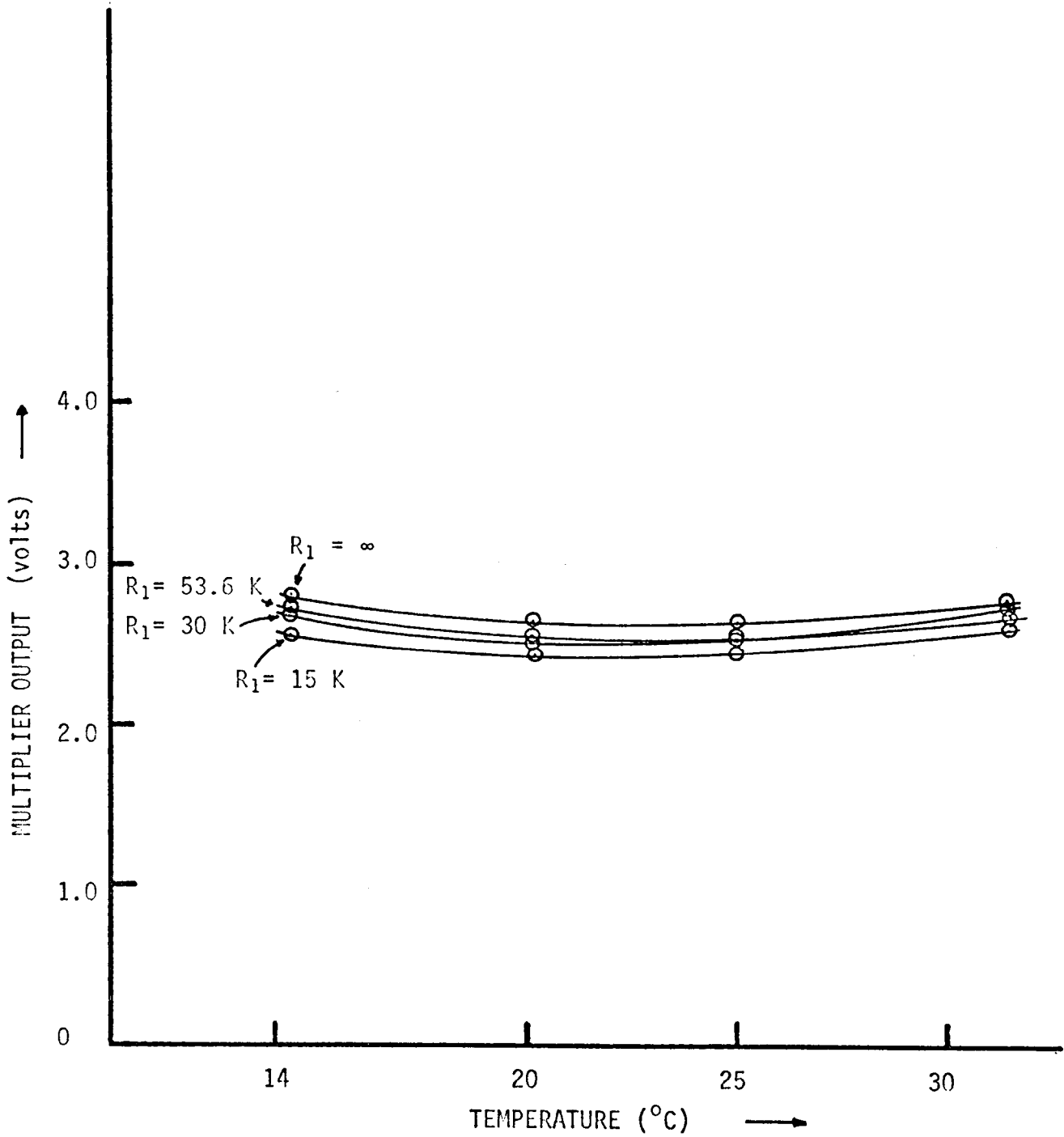


FIGURE 10

TEMPERATURE COMPENSATION FOR CONSTANT OXYGEN CONCENTRATION

compensating circuit with the two thermistors was assembled and the output of this circuit and the probe circuit was fed into the multiplier. The overall circuit is shown in Figure 11. The system used to vary oxygen concentration and water temperature is shown in Figure 12. The temperature of the water was varied from 14.4°C to 31°C in increments of 2°C. In each case the oxygen concentration was measured using the Modified Winkler Method⁴ and the multiplier output was measured. The data given in Table VIII is for air saturated water.

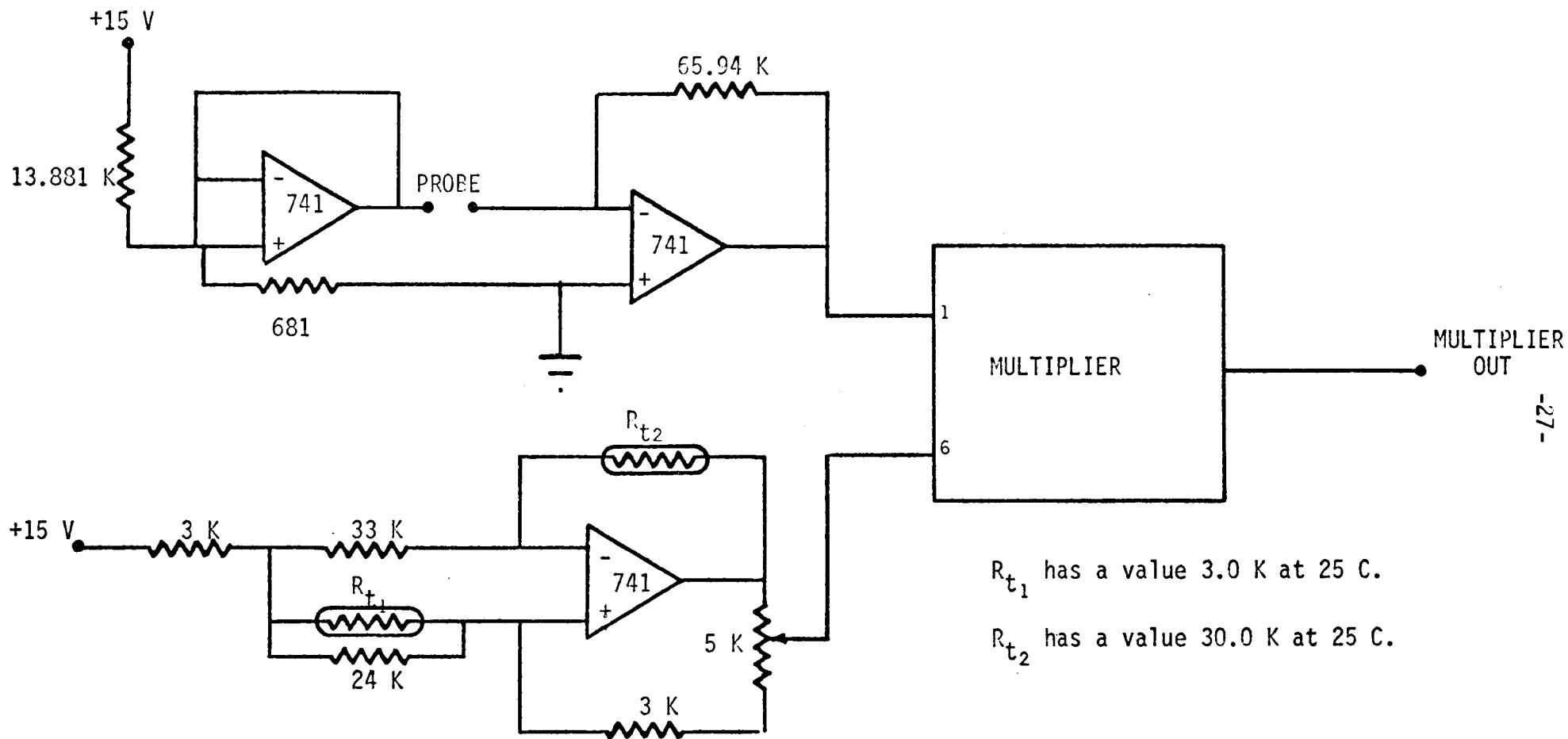
Next the oxygen concentration was varied by bubbling nitrogen into the water at a constant temperature. For each concentration the multiplier output was measured and the oxygen concentration was determined by the Winkler method. This run was repeated for different temperatures. The experimental data are given in Table IX.

The data were reduced as follows for analysis. Because of the very large number of readings only the reduced data will be given following the example exploring the method used.

For each temperature a linear curve fitting was done from the data utilizing the linear regression program provided in the Hewlett-Packard 9100 Program Library No. 70803. The general formula for the data is

$$\text{Multiplier voltage} = (a)\text{concentration} + b. \quad (12)$$

The program calculates the values of a and b. The values of a and b were calculated for each temperature. One temperature, preferably from the middle of the temperature range covered was chosen for calibration. The values for a and b at this temperature were used for calculation of the indicated and actual concentrations at other temperatures. The calculation is shown below.



R_{t1} has a value 3.0 K at 25 C.
 R_{t2} has a value 30.0 K at 25 C.

FIGURE 11

OVERALL CIRCUIT FOR COMPENSATED D.O. PROBE

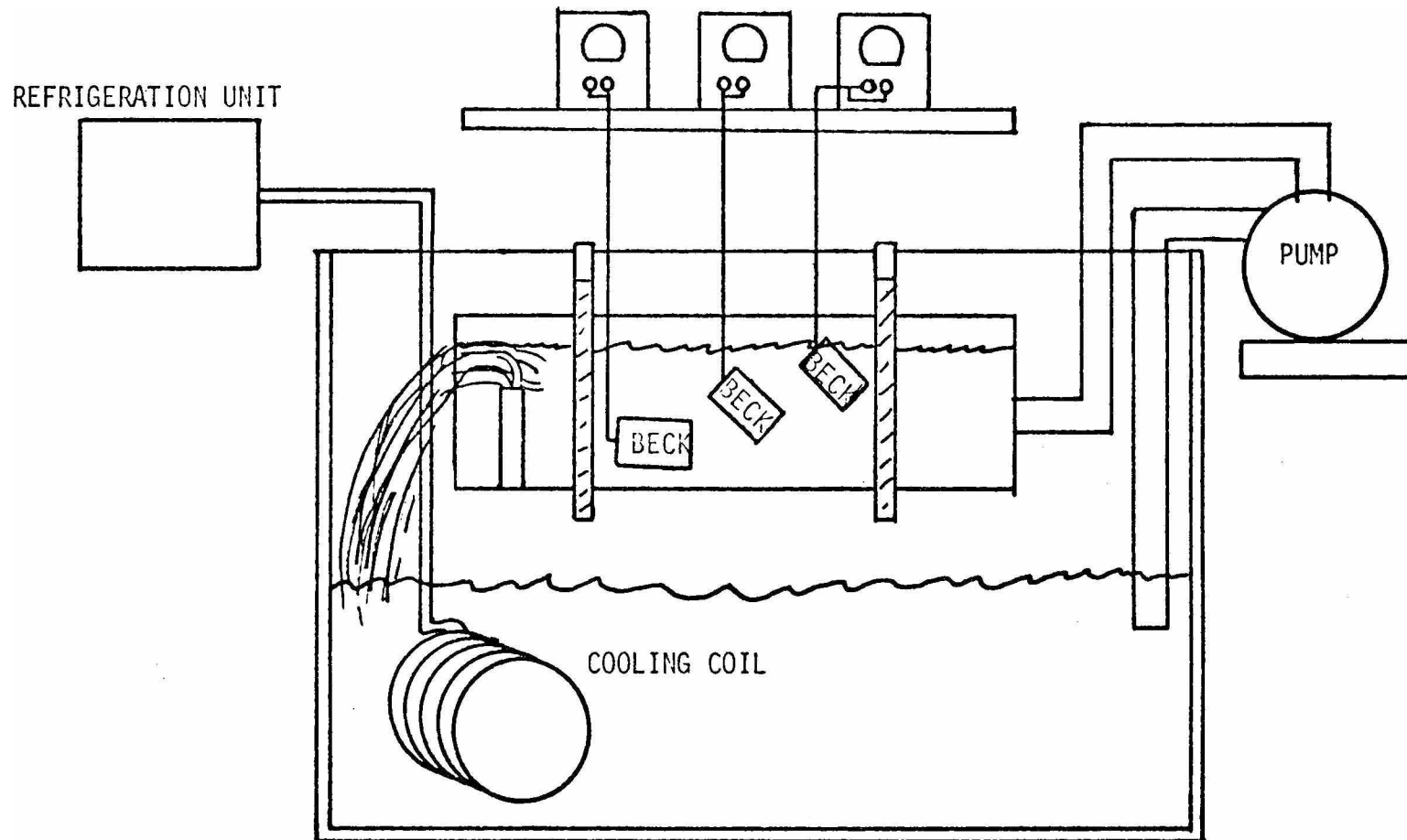


FIGURE 12

WATER BATH FOR MEASURING ELECTRODE CONSTANTS AND FOR TESTS INVOLVING TEMPERATURE COMPENSATION

TABLE VIII
TEMPERATURE COMPENSATED D. O. PROBE OUTPUT AT
DIFFERENT TEMPERATURES FOR AIR SATURATED WATER

<u>TEMP °C</u>	<u>Multiplier Output (Volts)</u>	<u>Concentration (ppm)</u>
14.4	3.54	10.4
16.2	3.32	10.1
18.4	3.10	9.6
20.0	2.91	9.2
22.0	2.79	9.0
24.0	2.52	8.5
26.0	2.25	7.9
28.3	2.05	7.8
31.0	1.86	7.6

TABLE IX
TEMPERATURE COMPENSATED D.O. PROBE OUTPUT AT
DIFFERENT TEMPERATURES AND DIFFERENT CONCENTRATIONS

<u>Temperature °C</u>	<u>Concentration ppm</u>	<u>Multiplier Output volts</u>
14.3	2.2	0.6
	3.3	0.95
	3.8	1.18
	4.5	1.46
	5.3	1.74
	5.9	1.99
	6.6	2.25
	7.3	2.49
	8.3	2.83
9.7	3.33	
<hr/>		
20.3	0.9	0.16
	1.9	0.51
	3.1	0.92
	4.1	1.28
	5.3	1.59
	5.8	1.82
	6.7	2.13
	7.4	2.38
<hr/>		
28.6	0.9	0.09
	0.8	0.02
	0.8	0.04
	0.9	0.07
	1.2	0.08
	1.2	0.00
	2.6	0.49
	4.2	0.94

<u>Temperature °C</u>	<u>Concentration ppm</u>	<u>Multiplier Output volts</u>
28.6	5.3	1.34
	5.9	1.59
	6.7	1.75
	7.3	1.87
<hr/>		
33.0	0.2	0.08
	1.5	0.28
	2.8	0.62
	3.9	0.88
	4.6	1.08
	5.3	1.28
	6.3	1.50
7.0	1.65	

If $t_1^{\circ}\text{C}$ is the calibration temperature and $t_2^{\circ}\text{C}$ is the temperature at which the indicated values are compared, the output voltage V_1 was calculated for 2 ppm at t_1 using

$$V_1 = 2a_1 + b_1. \quad (13)$$

V_1 was substituted into the equation for temperature $t_2^{\circ}\text{C}$ as

$$V_1 = a_2c_2 + b_2, \quad (14)$$

and the concentration c_2 was calculated. In this case c_2 was the actual concentration while 2 ppm was the indicated concentration. Similar calculations were repeated for 4, 6, 8, and 10 ppm oxygen concentrations and for other temperatures. The reduced data are given in Table X.

The data showed that the compensation was not perfect. As a next step the compensation circuit was modified as shown in Figure 13. With this modified circuit runs were made for the Beckman probe by varying the concentrations for three temperatures. The data are given in Table XI. During this run, the thermistor in the probe started malfunctioning due to a heat dissipation problem. To avoid this problem a YSI thermistor No. 44108 was used with the resistance at 25°C being equal to 30 kilohms.

In the next run the resistance R_2 was changed to 1.5 kilohms as shown in Figure 14 and the 196.3 kilohm resistor in parallel to the thermistor was removed. Three more runs were made after realigning the multiplier. The data from these tests are shown in Tables XII, XIII and XIV.

In all these runs, the compensation was found to be inadequate as is shown in Figure 15 which is a plot of the data from Table XIV. One reason for this was that the equations describing the probe current and the

TABLE X
TEMPERATURE COMPENSATED D.O. PROBE OUTPUT
AT DIFFERENT TEMPERATURES USING CIRCUIT IN FIGURE 11

Indicated Value of Oxygen Concentration Obtained From Compensated Dissolved Oxygen Probe ppm	Actual Value of Oxygen Concentration Based On Winkler Analysis ppm			
	at 14.3°C	at 20.3°C	at 28.6°C	at 33.0°C
2.0	2.0	2.0	2.6	2.3
4.0	3.9	4.0	4.9	5.2
6.0	5.7	6.0	7.2	8.0
8.0	7.5	8.0	9.5	10.8
10.0	9.4	10.0	11.8	13.6

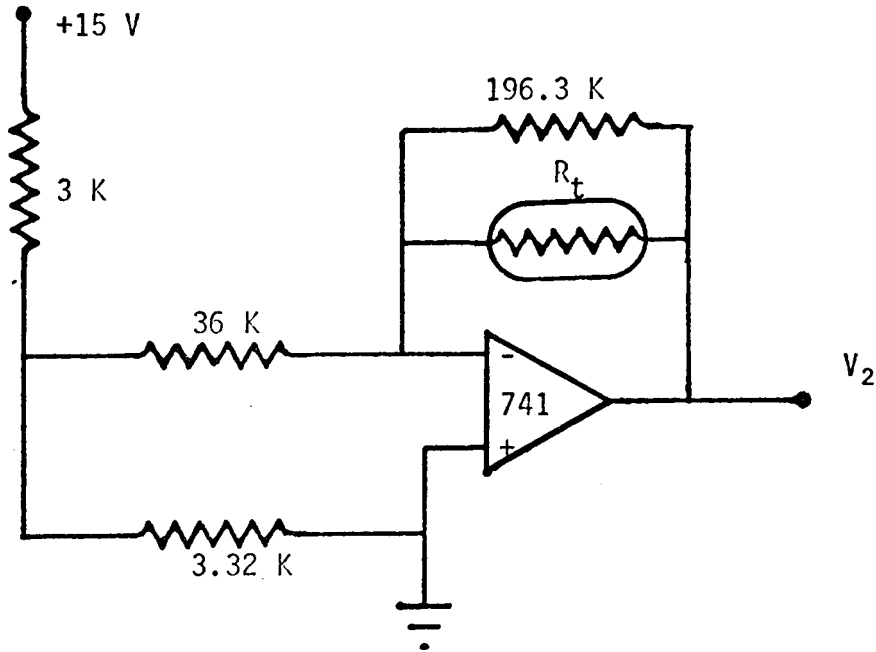


FIGURE 13

COMPENSATING CIRCUIT III R_t HAS A VALUE 30.0 K AT 25⁰ C

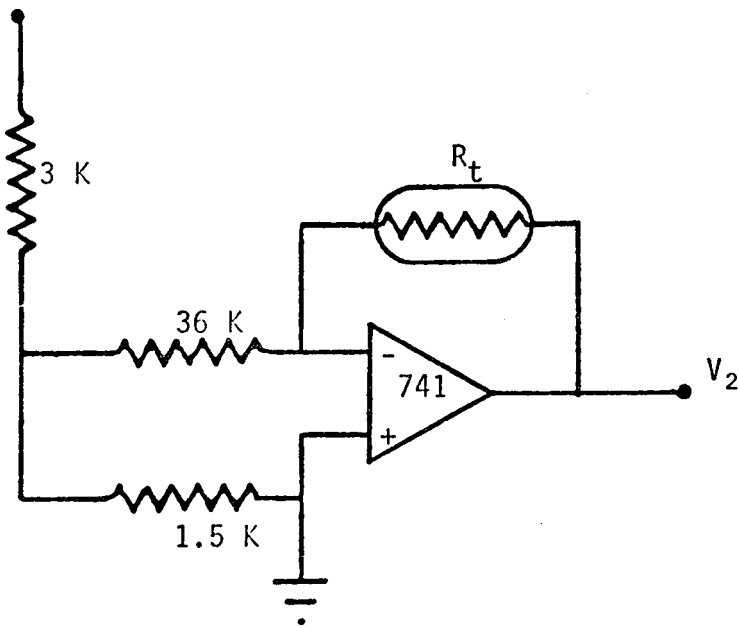


FIGURE 14

COMPENSATING CIRCUIT IV R_t HAS A VALUE OF 30.0 K AT 25⁰ C

TABLE XI
TEMPERATURE COMPENSATED D.O. PROBE OUTPUT
AT DIFFERENT TEMPERATURES USING CIRCUIT IN FIGURE 13

Indicated Value of Oxygen Concentration Obtained From Compensated Dissolved Oxygen Probe ppm	Actual Value of Oxygen Concentration Based On Winkler Analysis ppm		
	at <u>14.3°C</u>	at <u>22.7°C</u>	at <u>28.5°C</u>
2.0	1.9	2.0	2.0
4.0	4.3	4.0	4.0
6.0	6.7	6.0	6.0
8.0	9.0	8.0	7.9
10.0	11.4	10.0	9.9

TABLE XII

TEMPERATURE COMPENSATED D.O. PROBE OUTPUT

AT DIFFERENT TEMPERATURES, RUN 1

Indicated Value of Oxygen Concentration Obtained From Compensated Dissolved Oxygen Probe ppm	Actual Value Of Oxygen Concentration Based On Winkler Analysis ppm					
	at <u>11.4°C</u>	at <u>13.7°C</u>	at <u>19.6°C</u>	at <u>20.8°C</u>	at <u>24.1°C</u>	at <u>32.4°C</u>
2.0	2.0	2.5	2.0	2.2	2.1	2.0
4.0	4.1	5.1	4.0	4.6	4.0	4.0
6.0	6.3	7.7	6.0	7.0	6.0	6.0
8.0	8.4	10.4	8.0	9.4	8.0	8.0
10.0	10.6	13.0	10.0	11.7	9.9	10.0

TABLE XIII

TEMPERATURE COMPENSATED D.O. PROBE OUTPUT
 AT DIFFERENT TEMPERATURES, RUN 2

Indicated Value of Oxygen Concentration Obtained From Compensated Dissolved Oxygen Probe ppm	Actual Value of Oxygen Concentration Based On Winkler Analysis ppm						
	at 3.5°C	at 7.4°C	at 12.0°C	at 16.8°C	at 24.0°C	at 29.4°C	at 36.2°C
2.0	1.9	2.0	1.9	2.0	1.8	1.9	1.9
4.0	4.0	4.1	4.0	4.0	3.7	3.8	3.8
6.0	6.3	6.3	6.1	6.0	5.6	5.7	5.6
8.0	8.5	8.4	8.2	8.0	7.5	7.6	7.5
10.0	10.6	10.5	10.3	10.0	9.5	9.5	9.3

TABLE XIV
 TEMPERATURE COMPENSATED D.O. PROBE OUTPUT
 AT DIFFERENT TEMPERATURES, RUN 3

Indicated Value of Oxygen Concentration Obtained From Compensated Dissolved Oxygen Probe ppm	Actual Value of Oxygen Concentration Based on Winkler Analysis ppm						
	at <u>5.4°C</u>	at <u>10.8°C</u>	at <u>15.4°C</u>	at <u>23.4°C</u>	at <u>28.1°C</u>	at <u>32.4°C</u>	at <u>36.1°C</u>
2.0	1.7	1.7	2.0	2.0	1.8	2.0	1.9
4.0	3.9	3.8	4.0	3.9	3.8	3.8	3.8
6.0	6.0	5.9	6.0	5.8	5.7	5.7	5.7
8.0	8.2	8.0	8.0	7.7	7.6	7.6	7.6
10.0	10.3	10.1	10.0	9.6	9.5	9.4	9.5

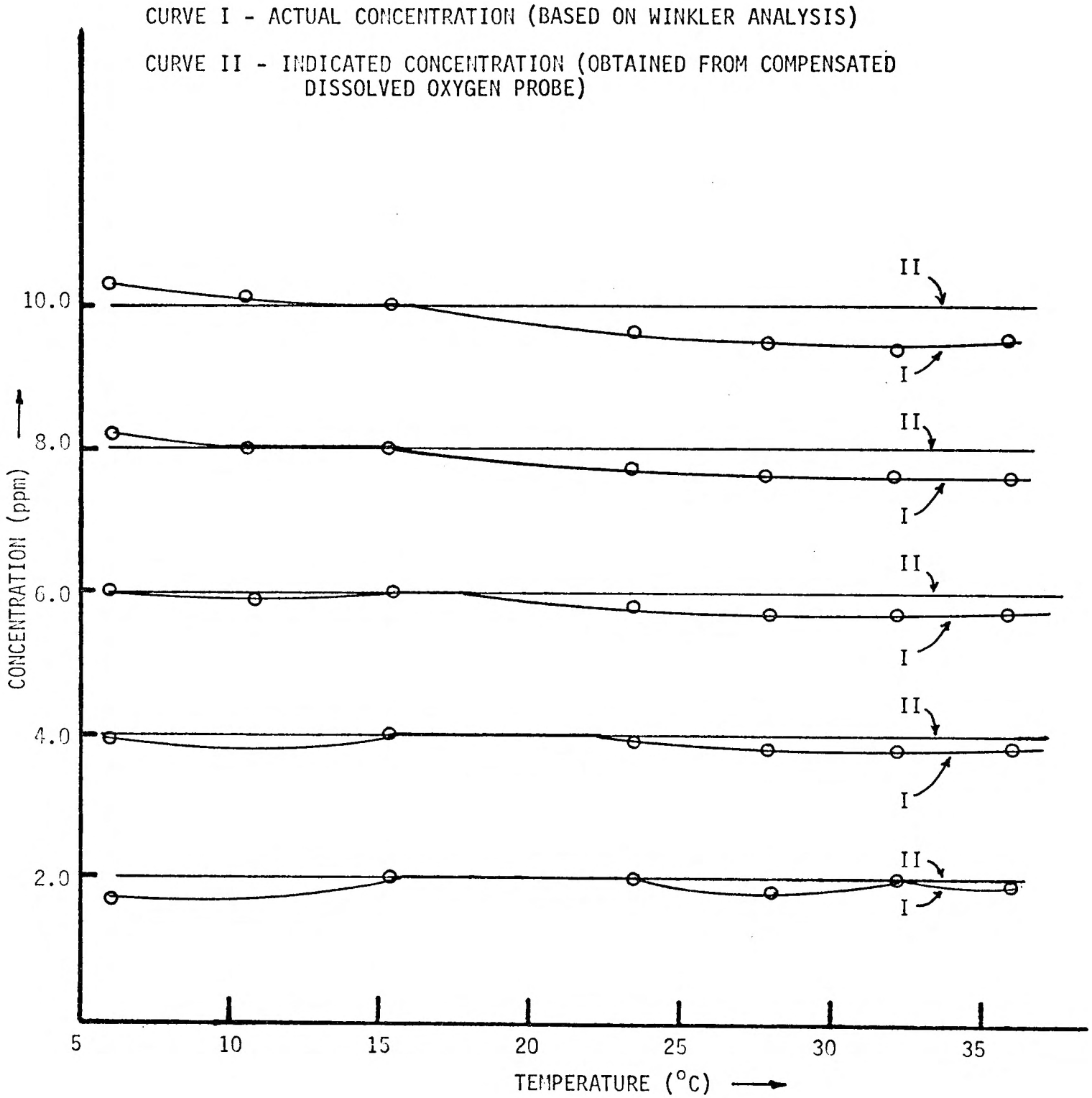


FIGURE 15

FINAL COMPENSATION USING MULTIPLIER CIRCUIT IN FIGURE 11

thermistor resistance as functions of temperature were not accurate over the entire temperature range. This point will be elaborated upon in the next section.

This method demonstrated that the temperature compensation is adequate within an accuracy of 6 percent. The logarithmic-antilogarithmic circuit has been avoided by using an analog multiplier. It was found that the procedures for adjusting the zero setting and the calibration of the multiplier circuit were tedious and time consuming. Therefore, efforts were directed toward methods of compensation not requiring multipliers.

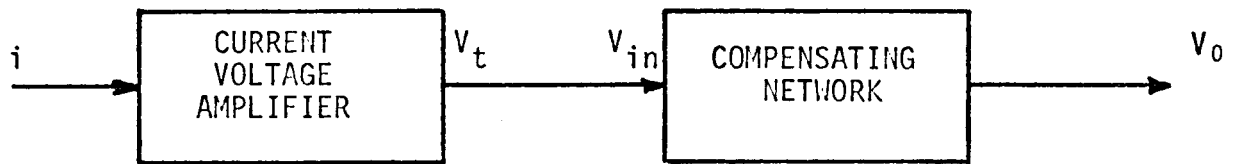
IV. TEMPERATURE COMPENSATION - METHOD II

In this method, the circuits are simplified as much as possible to reduce cost and drift problems. Neither logarithmic-antilogarithmic circuits nor multiplier circuits are used thereby reducing problems associated with earlier methods.

In the method using the logarithmic-antilogarithmic circuits, the probe output voltage was divided by the compensating voltage to achieve temperature compensation. In the method using the multiplier circuit the compensating voltage was of the form

$$V_2 = Ne^{-qt}, \quad (15)$$

and this voltage was multiplied by the probe output using a multiplier to achieve the temperature compensation. In the present method, compensation was achieved by multiplying the compensating voltage with the probe output as before but without using the analog multiplier. This principle is illustrated in block diagram form in Figure 16.



$$V_0 = V_{in} e^{-qt} = Qce^{kt} e^{-qt} = (QI)ce^{(k-q)t}$$

FIGURE 16

BLOCK DIAGRAM REPRESENTATION OF TEMPERATURE COMPENSATION - METHOD II

The probe current was of the form $I = cAe^{kt}$ and this current was converted into a voltage by means of a current-voltage amplifier as follows,

$$V_t = Qce^{kt}, \quad (16)$$

where,

V_t is the uncompensated output voltage

c is the concentration

Q is a constant of both the circuitry and the probe

k is a constant of the probe, and

t is temperature in degrees centigrade.

The compensating circuit utilized thermistors and was designed to give the relationship,

$$V_o = V_{in} Ne^{-qt}, \quad (17)$$

where,

N is a constant of the circuitry,

q is a constant of both the circuitry and thermistors,

V_{in} is the input voltage,

V_o is the output voltage, and

t is temperature in degrees centigrade.

If the input voltage V_{in} is the same as the output of the probe then,

$$V_{in} = V_t = Qce^{kt}. \quad (18)$$

The compensating circuit output voltage then becomes

$$V_{out} = Qce^{kt}Ne^{-qt} = (QN)ce^{(k-q)t}. \quad (19)$$

If q is made equal to k then,

$$V_{out} = (QN)c. \quad (20)$$

Since Q and N are constants depending upon the probe and the circuitry, the output voltage of the system is directly proportional to the concentration. It can be seen that the basic principle is the same as in Method I and the only difference is the manner in which the probe output and the compensating voltage are combined.

The current-voltage amplifier was the same as that used in other methods except for the difference in the amplification factor or gain of the system. The compensating circuit was designed to achieve the relation

$$\frac{V_{out}}{V_{in}} = Ne^{-qt} \quad (21)$$

with the facility to vary the constants N and q . The overall gain of the system could be changed by varying N which made it possible to adjust the output voltage level if necessary. Variation of q made it possible to adjust for variation in the probe constant k due to different membranes whenever the probe was rejuvenated. The aim then was to design the compensating circuit with components, preferably with potentiometers, so that N and q in the above equation could be set to different values.

The compensation circuit included thermistors as in other cases to

achieve a voltage with a negative temperature coefficient. The thermistors chosen for use in this circuit were YSI 44108 and YSI 44105 thermistors which have, respectively, 30 kilohms and 3 kilohms resistance at 25°C. These two thermistors have a low time constant and they have consistent resistance values from one thermistor to another and from one time to another. These requirements were determined in the previous compensation methods and this was the reason for utilizing these thermistors.

Different combinations of these two thermistors were tested to achieve the desired result. At first these circuits were analyzed analytically since the resistance values of the thermistors were available from the manufacturer. The resistance values are expressed as a function of temperature by an equation

$$R_t = R_o e^{-\alpha t} \quad (22)$$

for each of the thermistors. The values of R_o and α were calculated over a temperature range of 5° to 35°C for each thermistor. The equation for the resistance of the YSI 44108 thermistor was

$$R_{t_2} = 91449e^{-0.0442t} \quad (23)$$

and the resistance for YSI 44105 was

$$R_{t_1} = 9390e^{-0.0452t} \quad (24)$$

A circuit incorporating the two thermistors was designed and an expression for the ratio of output voltage V_o to the input voltage V_{in} was

developed. The value of V_o/V_{in} was calculated for different temperatures using the numerical values for the components. Then an equation of the form

$$\frac{V_o}{V_{in}} = Ne^{-qt} \quad (25)$$

was assumed and the values of the ratio V_o/V_{in} were substituted in the equation for different temperatures. The values of N and q were determined using the method of least square curve-fitting. The value of q was compared with the desired value which was the value of k given in Equation 16.

If the value of q was not the desired value, then a different combination of thermistors and circuit components was tried since the thermistors themselves were not changed. After studying different circuit configurations analytically, the one shown in Figure 17 was found to suit the problem at hand.

For this circuit,

$$\begin{aligned} \frac{V_o}{V_{in}} &= \frac{R_2 + (R_5 - R_6) + (R_6 || R_3 + R_{t_1})}{R_1 + R_2 + (R_5 - R_6) + (R_6 || R_3 + R_{t_1})} \cdot \frac{R_{t_2}}{R_4} \\ &= \frac{R_2 + (R_5 - R_6) + \{R_6(R_3 + R_{t_1})/R_6 + R_3 + R_{t_1}\}}{R_1 + R_2 + (R_5 - R_6) + \{R_6(R_3 + R_{t_1})/R_6 + R_3 + R_{t_1}\}} \cdot \frac{R_{t_2}}{R_4} \quad (26) \end{aligned}$$

The values of R_{t_1} and R_{t_2} given by Equations 23 and 24 were substituted into Equation 26. The values of V_o/V_{in} were calculated at different temperatures. From these values, the values of the constants N and q in the equation

$$\frac{V_o}{V_{in}} = Ne^{-qt} \quad (27)$$

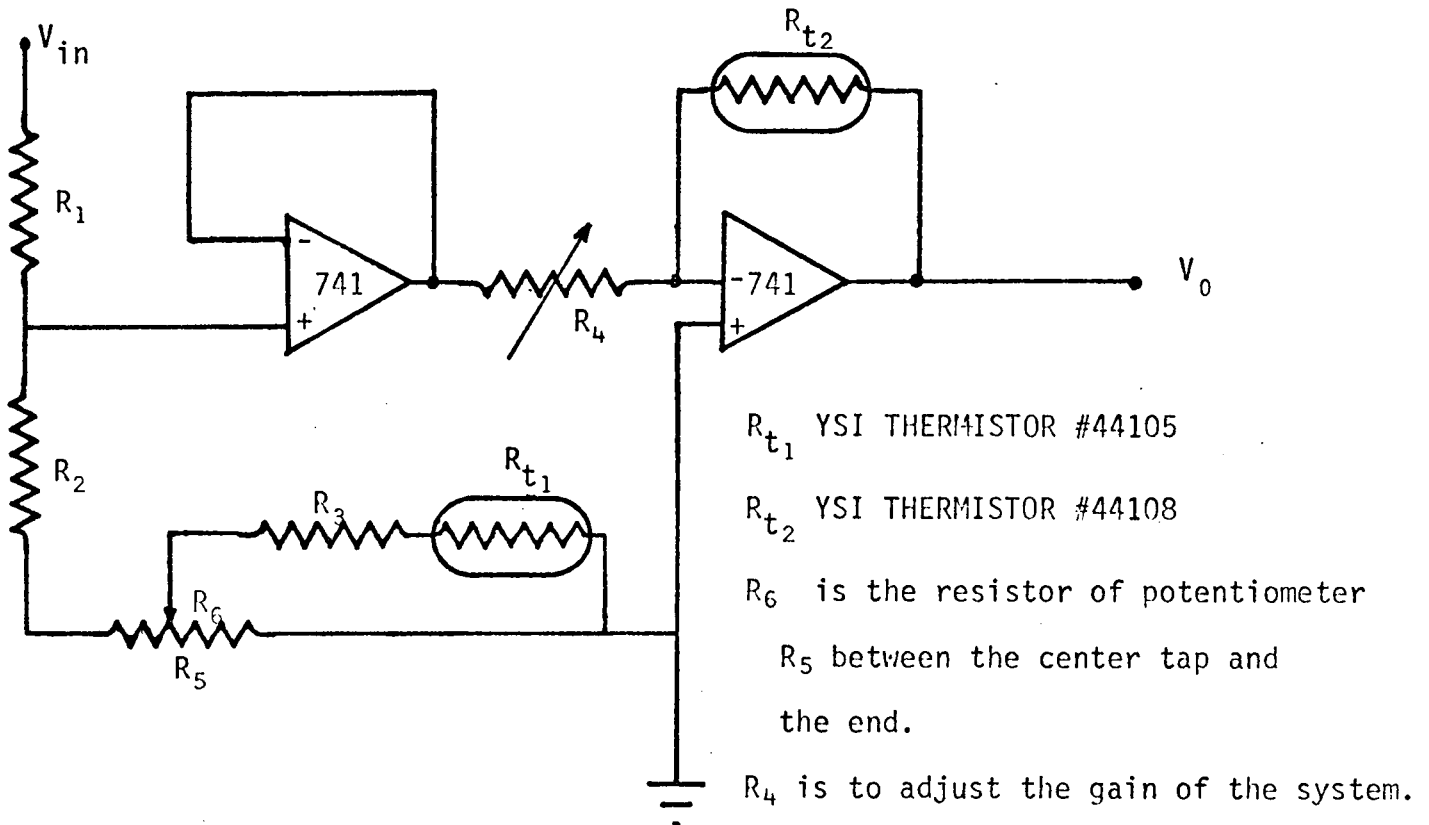


FIGURE 17

COMPENSATION CIRCUIT FOR TEMPERATURE COMPENSATION METHOD II

were calculated. It can be seen that by changing R_4 , the gain of the system, the value of N was changed since R_4 appears as an independent factor in the expression. By changing R_6 the value of Δq_1 was changed since R_6 is parallel to R_{t_1} , and the effect of R_{t_1} on the constant q was varied. R_6 and R_4 provided the capability for varying q and N which was the desired result. The values of the other components were chosen to get the exact numerical values desired to match the probe output. The circuit with the component values is shown in Figure 18.

The next step was to measure the true value of q by running an actual test on the circuit shown. For this purpose, the compensating circuit was assembled on a patch board the two thermistors were placed in a well agitated water bath. The ratio V_o/V_{in} was measured for different temperatures. The values of V_o/V_{in} and of temperature were then substituted in the equation

$$\frac{V_o}{V_{in}} = Ne^{-qt} \quad (28)$$

to obtain the values for N and q . The measured value of q was of interest in this work to confirm the manufacturer's quoted values.

The procedure was repeated for different values of R_6 and in each case the value of Δq_1 was calculated. The value of Δq_1 versus R_6 is plotted in Figure 19. The values of Δq_1 for different values of R_6 are given in Table XV. If k has a known value in the equation

$$V_o = QNce^{(k-q)t}, \quad (29)$$

a suitable value of R_6 may be selected from Figure 19 to make q exactly equal to k .

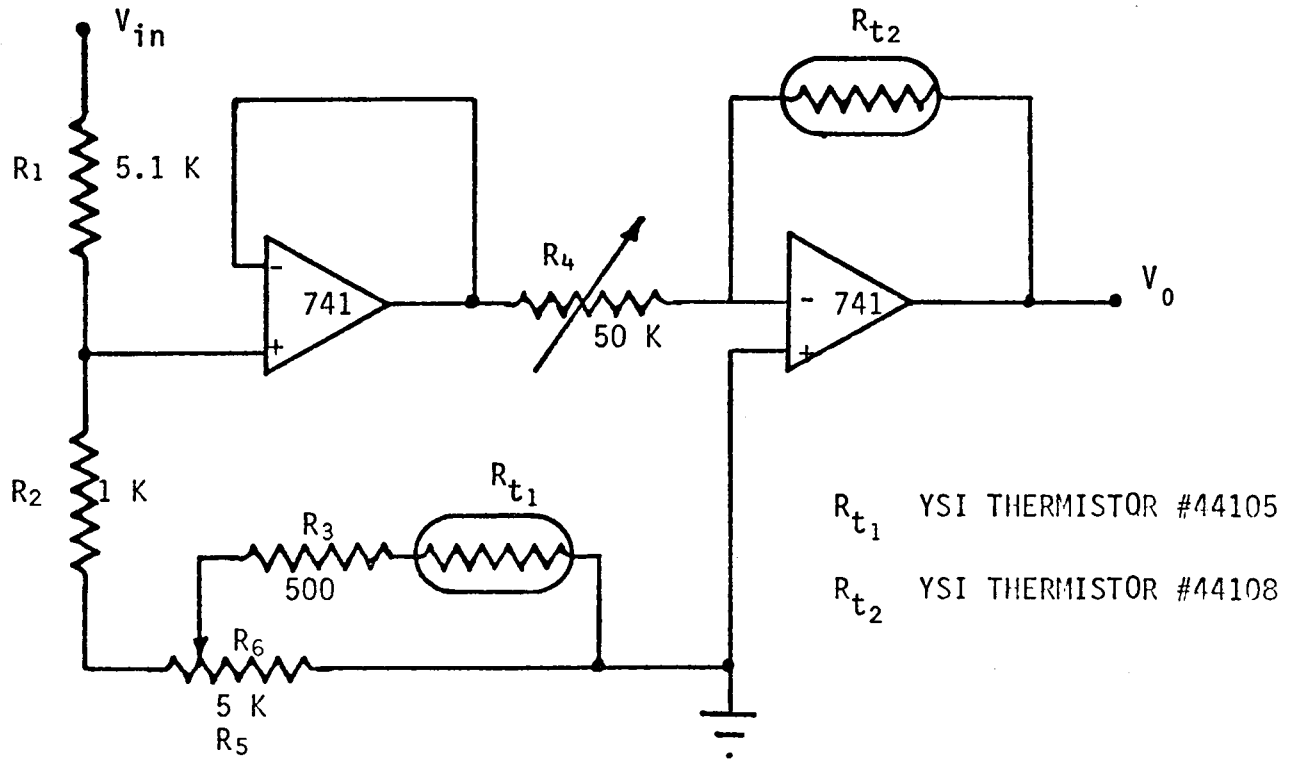


FIGURE 18

TEMPERATURE COMPENSATION CIRCUIT WITH COMPONENT VALUES

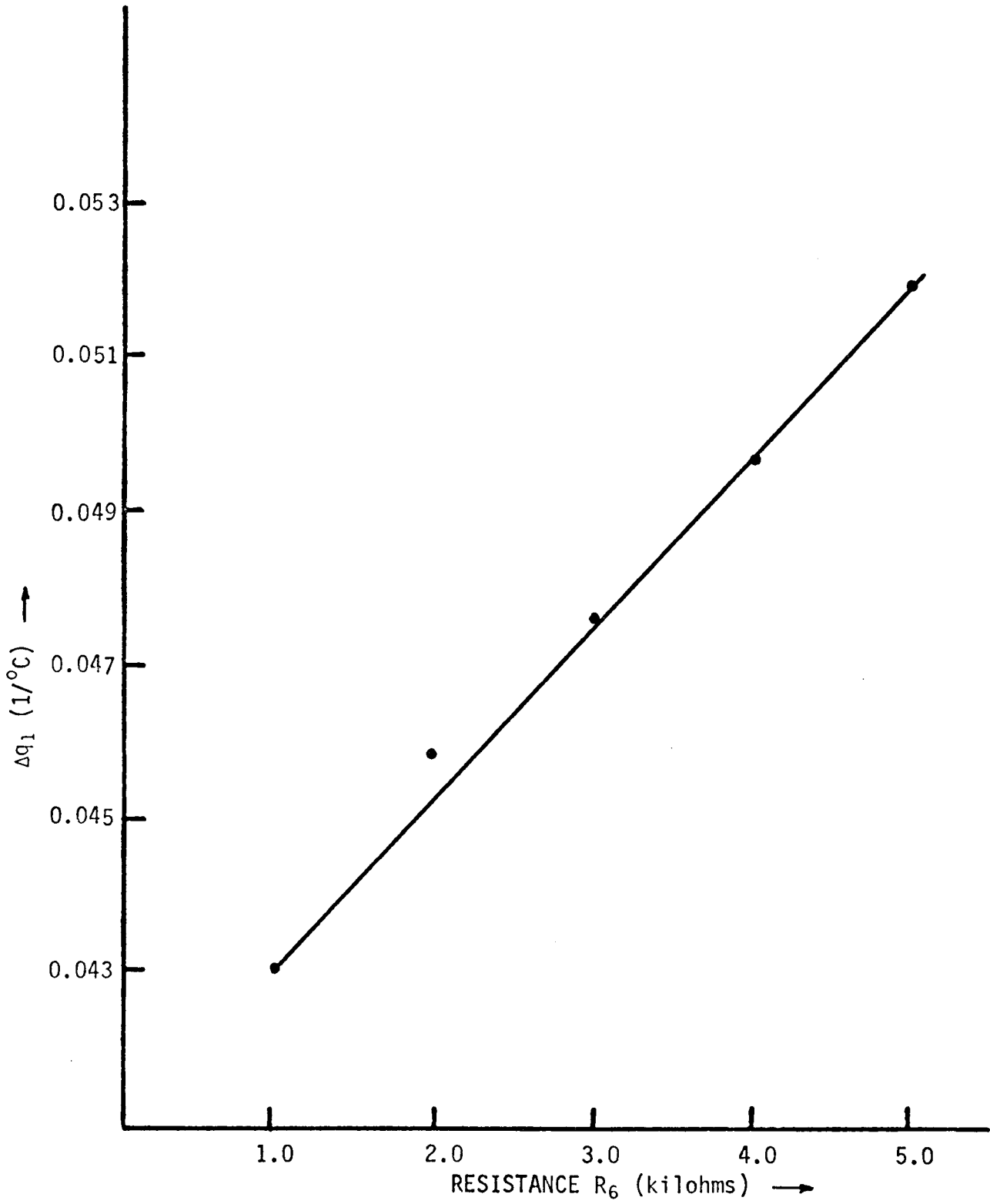


FIGURE 19

EXPONENT CORRECTION TERM VERSUS R_6

TABLE XV
VARIATION OF CONSTANT Δq_1 IN COMPENSATION
CIRCUIT WITH R_6

<u>Resistance R_6 Kilohms</u>	<u>Value of Δq_1</u>
1.0	0.0430
2.0	0.0457
3.0	0.0475
4.0	0.0495
5.0	0.0519

The second part of this work was to test the circuit for temperature compensation. For this work the complete circuit was assembled, including the measuring circuit and the compensating circuit. The complete circuit is shown in Figure 20.

The dissolved oxygen probe was placed in a water bath and the water bath was sealed off from the atmosphere. The water bath was kept at a constant temperature by circulating the cooling/heating media through a copper coil placed in the water bath. The temperature was maintained within $\pm 0.2^{\circ}\text{C}$ at any given temperature. It was possible to vary the temperature from 5° to 35°C and to maintain it at a given temperature. The oxygen concentration was varied by bubbling nitrogen and oxygen into the water. It was possible to vary the flow rates of nitrogen and oxygen and the oxygen concentration was proportional to the flow rates of the gases. After initial calibration of the mixing system, repeated series of runs at various known oxygen levels could be made without the necessity for Winkler calibration. This mixing system is described in Appendix I. The pump outlet was directed at the electrode membrane and provided more than enough flow to maintain the electrode well up on the current-flow plateau. The pump also provided good mixing action for the test chamber. The experimental arrangement is diagramed in Figure 21.

As a first step the constants of the probe were determined by measuring the probe output at different temperatures. Air instead of nitrogen and oxygen was bubbled through the water to provide air saturation. Sample data are given in Tables XVI and XVII. The probe constants Q and k were calculated from these data by substituting the values of probe output, V_t ; concentration, c ; and temperature, t in the equation

$$V_t = Qce^{kt}. \quad (30)$$

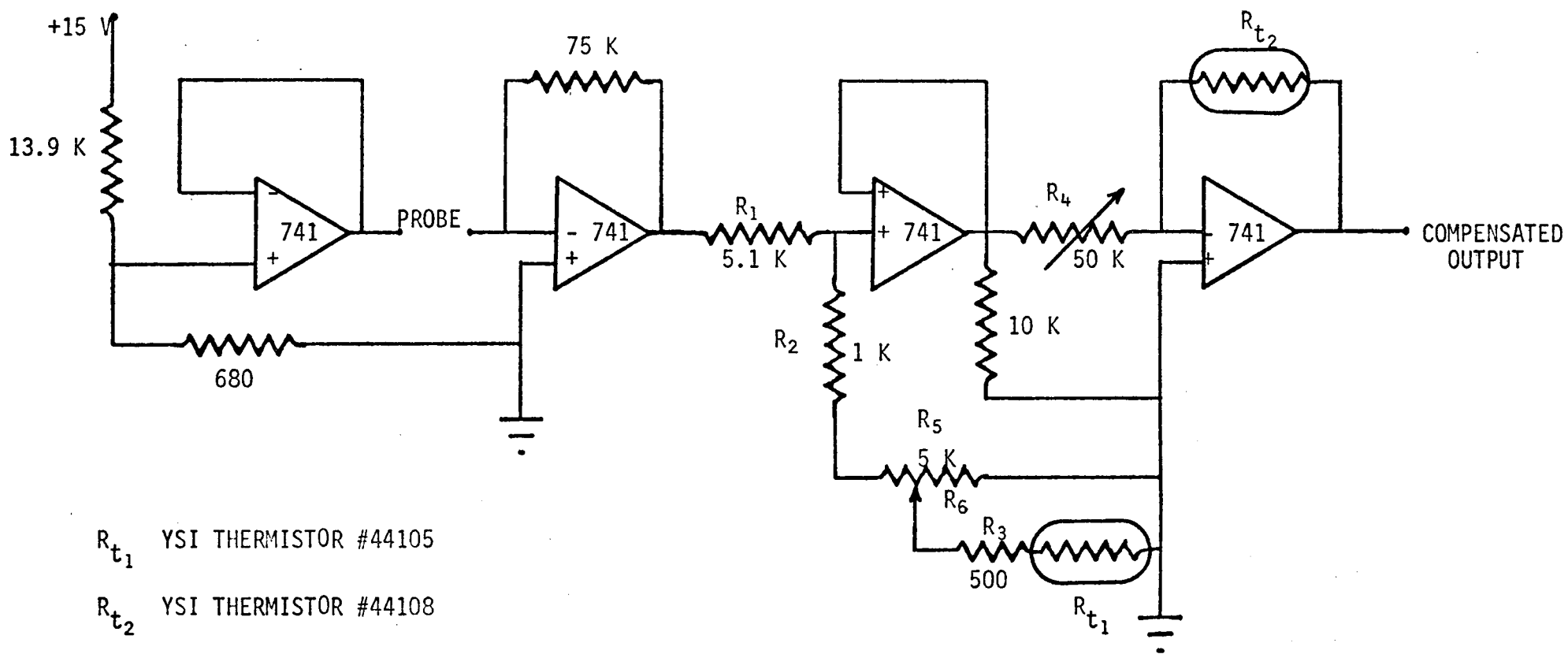


FIGURE 20

TEMPERATURE COMPENSATED D.O. PROBE MEASURING CIRCUIT

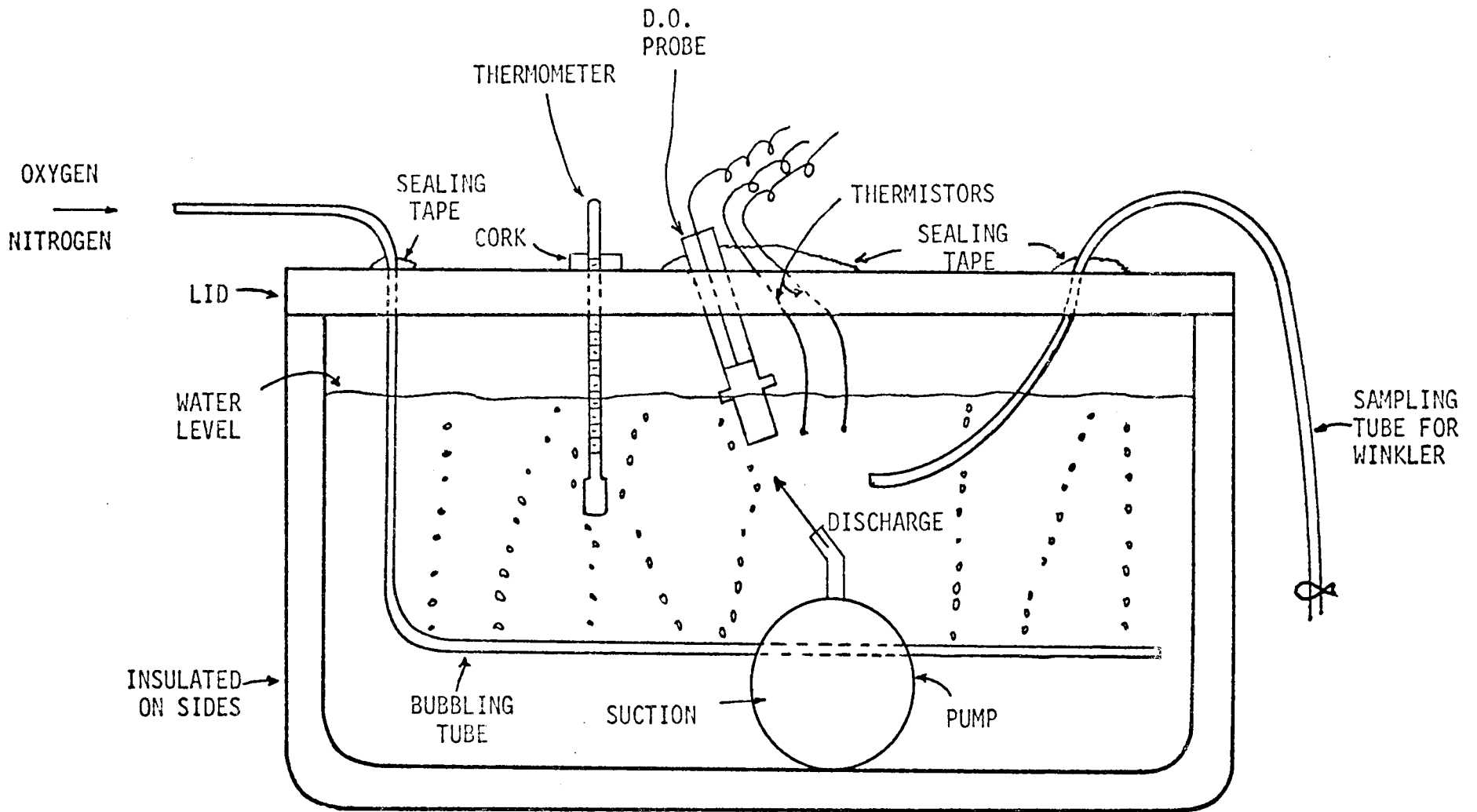


FIGURE 21

TEST SYSTEM FOR THE COMPENSATED D.O. PROBE

TABLE XVI
UNCOMPENSATED D.O. PROBE OUTPUT AT DIFFERENT TEMPERATURES
FIRST REJUVENATION

Temperature of Water °C	Probe Output (Uncompensated) volts	Concentration ppm
8.6	5.70	11.7
12.5	6.30	10.6
14.7	6.70	10.1
18.0	7.35	9.4
21.8	8.39	8.7
23.4	8.96	8.1
28.4	9.82	7.5
31.7	10.26	7.2
33.0	10.53	7.0

Temperature range

8 to 22°C probe output = $0.32 \times c \times e^{0.0493t}$

21 to 33°C probe output = $0.41 \times c \times e^{0.0396t}$

8 to 33°C probe output = $0.34 \times c \times e^{0.0459t}$

TABLE XVII
UNCOMPENSATED D.O. PROBE OUTPUT AT DIFFERENT TEMPERATURES
SECOND REJUVENATION

Temperature of Water °C	Probe Output (Uncompensated) volts	Concentration ppm
5.5	3.63	12.6
7.6	3.81	11.9
9.7	4.04	11.4
13.2	4.43	10.5
16.2	4.80	9.7
20.0	5.41	9.1
24.2	6.01	8.3
26.4	6.30	8.0
29.8	6.70	7.5
31.7	7.00	7.3
33.3	7.20	7.0

Temperature range

$$\begin{aligned} 5 \text{ to } 20^{\circ}\text{C} & \text{ probe output} = 0.22 \times c \times e^{0.0504t} \\ 20 \text{ to } 33^{\circ}\text{C} & \text{ probe output} = 0.27 \times c \times e^{0.0403t} \\ 5 \text{ to } 33^{\circ}\text{C} & \text{ probe output} = 0.23 \times c \times e^{0.0464t} \end{aligned}$$

For temperature compensation the value of k is of importance. The value q of the compensation network should be equal to k . The value of R_6 was adjusted to obtain this value of q according to Figure 19.

With water temperature maintained at a constant value, the dissolved oxygen level was varied in increments of 1 ppm from 1 ppm to air saturation value at the measured temperature by bubbling nitrogen and oxygen into the system. Each time the concentration was changed the system was allowed two hours to equilibrate. The compensated output was noted and the oxygen concentration was determined. This procedure was repeated by increasing temperature in approximate increments of 5° up to 33°C . The data are reduced as indicated and actual concentrations as was done in the previous method. The difference between the indicated and actual concentration was the error due to imperfect temperature compensation. In the first run, the error was noted to be approximately 4 percent at an indication of 10 ppm.

The runs were repeated after rejuvenating the electrode to check for consistency in readings. It was possible to reproduce the readings within an accuracy of 4 percent at an indication of 10 ppm as compared against the standard winkler Test. The data are given in the Tables XVIII, XIX, and XX for various runs. The data from Table XX are plotted in Figure 22. Curve I is the actual concentration, based on Winkler analysis, while Curve II is the indicated concentration obtained from the compensated dissolved oxygen probe. The difference between the two curves is the error due to imperfect temperature compensation.

V. DISCUSSION

The results showed that dissolved oxygen electrode measurements can be temperature compensated with minimum operator attendance and simple

TABLE XVIII
 COMPENSATED PROBE OUTPUT AT DIFFERENT TEMPERATURES
 THIRD REJUVENATION, RUN 1

Indicated Concentration Obtained From Compensated Dissolved Oxygen Probe ppm	Actual Concentration ppm Based on Winkler Analysis					
	at <u>7.0°C</u>	at <u>12.1°C</u>	at <u>17.4°C</u>	at <u>22.8°C</u>	at <u>26.7°C</u>	at <u>33°C</u>
2.0	2.1	2.1	2.0	1.9	2.0	1.7
4.0	4.1	4.2	2.0	3.9	3.9	3.7
6.0	6.2	6.2	6.0	5.9	5.8	5.7
8.0	8.3	8.3	8.0	7.8	7.8	7.7
10.0	10.4	10.3	10.0	9.8	9.7	9.7

TABLE XIX

COMPENSATED PROBE OUTPUT AT DIFFERENT TEMPERATURES
 THIRD REJUVENATION, RUN 2

Indicated Concentration Obtained From Compensated Dissolved Oxygen Probe ppm	Actual Concentration ppm Based on Winkler Analysis					
	at <u>7.2°C</u>	at <u>15.3°C</u>	at <u>19.7°C</u>	at <u>23.7°C</u>	at <u>28.7°C</u>	at <u>33.4°C</u>
2.0	2.0	2.0	1.9	2.0	2.1	2.1
4.0	4.0	4.0	3.9	4.0	4.1	4.2
6.0	6.1	6.0	5.9	6.0	6.2	6.4
8.0	8.2	8.0	7.9	8.0	8.3	8.5
10.0	10.2	10.0	9.8	10.0	10.3	10.6

TABLE XX

COMPENSATED PROBE OUTPUT AT DIFFERENT TEMPERATURES
 THIRD REJUVENATION, RUN 3

Indicated Concentration Obtained From Compensated Dissolved Oxygen Probe ppm	Actual Concentration ppm Based on Winkler Analysis					
	at <u>7.2°C</u>	at <u>11.4°C</u>	at <u>15°C</u>	at <u>21.1°C</u>	at <u>29.5°C</u>	at <u>31.8°C</u>
2.0	1.9	2.0	2.0	2.0	2.0	2.0
4.0	3.9	3.9	4.0	3.9	4.1	4.1
6.0	5.9	5.9	6.0	5.9	6.2	6.2
8.0	7.9	7.9	8.0	7.9	8.3	8.4
10.0	9.9	9.8	10.0	9.9	10.4	10.5

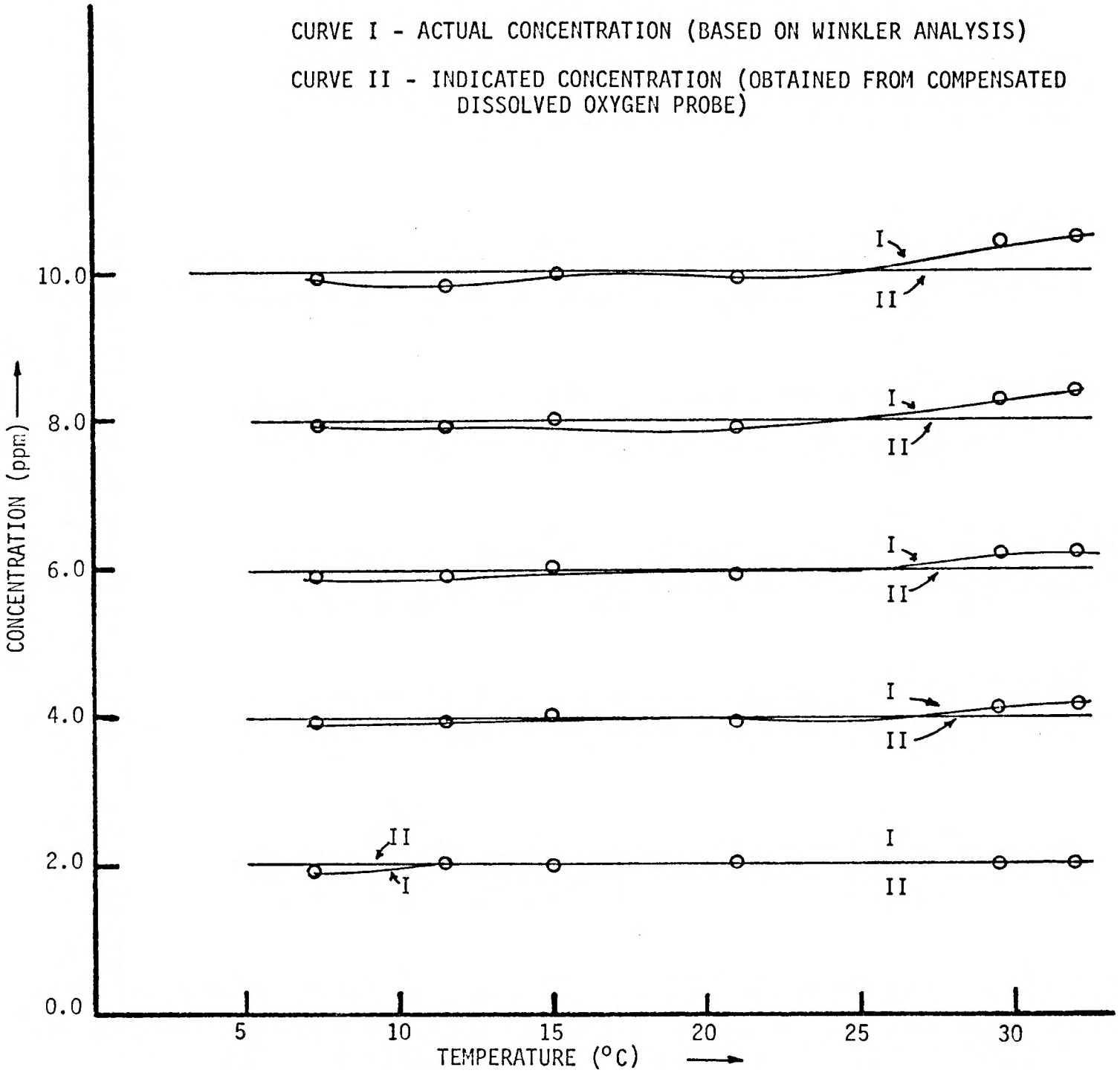


FIGURE 22

COMPENSATION USING FINAL CIRCUIT IN FIGURE 20

circuitry. The measuring and compensating circuit did not drift as did the logarithmic-antilogarithmic circuitry and multiplier circuitry. At the same time, this circuit was based on the same principle as in the other methods and hence the accuracy of measurement will be the same or even better.

The error noted between the actual (based on Winkler analysis) and the indicated values (obtained from compensated dissolved oxygen probe) was due to the fact that the probe output current does not follow the equation $V_t = Ace^{kt}$ exactly over the entire temperature and dissolved oxygen concentration range. The value of k showed variation in the third decimal place and this, on a percentage basis, introduced an error of only 2 percent.

Let us say, k varied from k to $k + 0.001$, then corresponding probe outputs were

$$\begin{aligned} V_t &= Ace^{kt} \\ V_{t_1} &= Ace^{k + 0.001t} \end{aligned}$$

and

$$\frac{V_{t_1} - V_t}{V_t} = \frac{e^{k + 0.001t} - e^{kt}}{e^{kt}} = e^{0.001t} \quad (31)$$

was the relative error due to the .001 increase in k . If $t = 20$ then the percentage error is $e^{0.02} \times 100$ or approximately 2 percent. The variation of k is shown in Tables XVI and XVII for different temperature ranges.

The thermistors were assumed to have a relationship of $R_t = R_0 e^{-\alpha t}$. The values of R_0 and α depended upon the range over which the calibration was made. This is shown in Table XXI and the values have been calculated using the manufacturer's data.

Similar variation existed for the constants H and q in the equation for the compensation circuit

$$V_2 = Ne^{-qt} \quad (32)$$

TABLE XXI

VALUES OF THERMISTOR CONSTANTS

General Equation $R_t = R_0 e^{-\alpha t}$ Temperature in °C

(1) Thermistor YSI no. 44105 (3K at 25°C)

Temperature Range °C	R_0	α
5 - 20	9615	0.0473
20 - 35	8873	0.0432
5 - 35	9390	0.0452

(2) Thermistor YSI No. 44108 (30K at 25°C)

Temperature Range °C	R_0	α
5 - 20	92871	0.0457
20 - 35	86883	0.0424
5 - 35	91449	0.0442

The variation is shown in Table XXII. Two independent sets of thermistors, all manufactured by YSI, were used to obtain the data and the thermistors were labeled as Set I and Set II.

Thus it can be seen that variation of k and q exists over the temperature range. This, in addition to any error in not exactly matching the compensating network with the probe, introduced an error of 2 to 5 percent.

Even though the percentage error seemed to be high, it should be remembered that performing the Winkler Test with commercially available standard kits has its own limitations. Assuming that an error of 0.1 cc in 5 cc was made while titrating P.A.O. against the test solution, the error introduced in determining oxygen concentration would be 2 percent. That is, the standard against which the system was checked may introduce an error of 2 percent. An error of 0.1 cc is a common occurrence with the Winkler Test, particularly so for field use.

The incorporation of more complex circuits could have reduced the remaining error. However, it was thought that such additional complexity was not justified because the present compensation is very good for air saturated water and is even better at low values of dissolved oxygen concentration in water where readings are of major importance. For low values of dissolved oxygen concentration where critical situations might be encountered, the compensation is much better and the readings obtained will be better than most single Winkler readings. This instrument is quite convenient since it requires minimum operator attendance and shows no drift problems.

TABLE XXII
VARIATION OF TEMPERATURE COMPENSATION CIRCUIT CONSTANTS

R ₆ Kilohms	Temperature Range C	Set I		Set II	
		N	q	N	q
3.0	8 - 20	3.55	0.0494	2.58	0.0501
3.0	20 - 34	3.28	0.0456	2.35	0.0454
3.0	8 - 34	3.45	0.0474	2.48	0.0473
3.5	8 - 20	3.49	0.0510	2.50	0.0506
3.5	20 - 34	3.18	0.0465	2.29	0.0465
3.5	8 - 34	3.38	0.0487	2.42	0.0484
4.0	8 - 20	3.39	0.0519	2.47	0.0529
4.0	20 - 34	3.17	0.0486	2.27	0.0487
4.0	8 - 34	3.31	0.0502	2.39	0.0505

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3. Advance Characterization Data, AD530J and AD530K Self-contained Integrated Circuit, Analog Devices, Norwood, Mass. (12-70).
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APPENDIX I

GAS MIXING SYSTEM

In the course of making a large number of runs of dissolved oxygen concentrations at a variety of temperatures, it was found desirable to devise a method whereby precisely known gas mixtures could be produced so that repeated runs could be made without the necessity for a large number of Winkler tests. It was also found that the variation in the Winkler tests from one run to another and from one operator to another was producing errors larger at times than those variations which were being examined with the dissolved oxygen electrodes. To eliminate the necessity for statistical treatment of repeated Winkler tests in order to strike a value with high confidence level, the gas mixing system to be described proved to be most useful.

The gas mixing system uses a pair of well regulated supplies at relatively high pressure in conjunction with a pair of capillary tubes which produce a constant volumetric flow rate. The amount of flow rate can be adjusted by adjusting separately the pressures of each of the two gases. The gas pressures are measured using a pair of 0-100 PSI Gauges having 0 - 1% accuracy. An initial calibration run is made for each of the pressurized supplies and its associated capillary using a bubble meter to measure the flow. A calibration curve is constructed relating back pressure to volumetric flow rate. Following this, one can combine the flow of the two outputs, and knowing the individual

flow rates, the percent composition of the mixture is precisely determined. Repeated tests made with the mixing system and checked with multiple Winkler tests proved that mixtures could be made and the same values repeated much more precisely than readings given by a single Winkler measurement. Because the bubble meter uses water together with a small amount of soap solution to measure the volumetric flow rate, it is necessary to make a water vapor correction as well as a barometric correction in order to obtain absolute values. The corrections to be applied follow:

$$\frac{P_S V_S}{T_S} = \frac{P_B V_A}{T_A}$$

$$V_S = V_A \left(\frac{P_B}{P_S} \right) \left(\frac{T_S}{T_A} \right)$$

$$V_S = (\text{Burette Volume}) \left(\frac{P_B - P_{wv}}{760} \right) \left(\frac{273}{T_A} \right)$$

$$f_{\text{corr}} = \frac{V_S}{t} = \frac{(50)(273)}{760} \left(\frac{P_B - P_{wv}}{T_A t} \right)$$

where P_S , V_S , and T_S are the pressure, volume and temperature at standard conditions.

P_B is the barometric pressure in the room where the measurement is made

V_A is the measured volume, i. e., the uncorrected burette volume

T_A is the temperature of the gas in the bubble meter,

P_{wv} is the vapor pressure of the water in the burette at room temperature,

t is the time for the soap bubble to traverse the length of the

burette volume (i. e. 50 ml), and
 f_{corr} is the corrected flow volume of the gas being measured.

Precautions should be taken to insure that any mixer or sparger used should not produce any appreciable back pressure at the capillary outlets. A simple water manometer may be used to check for outlet back pressure.

Typical calibration curves are shown in Figures 1 and 2 for the system shown in Figure 3.

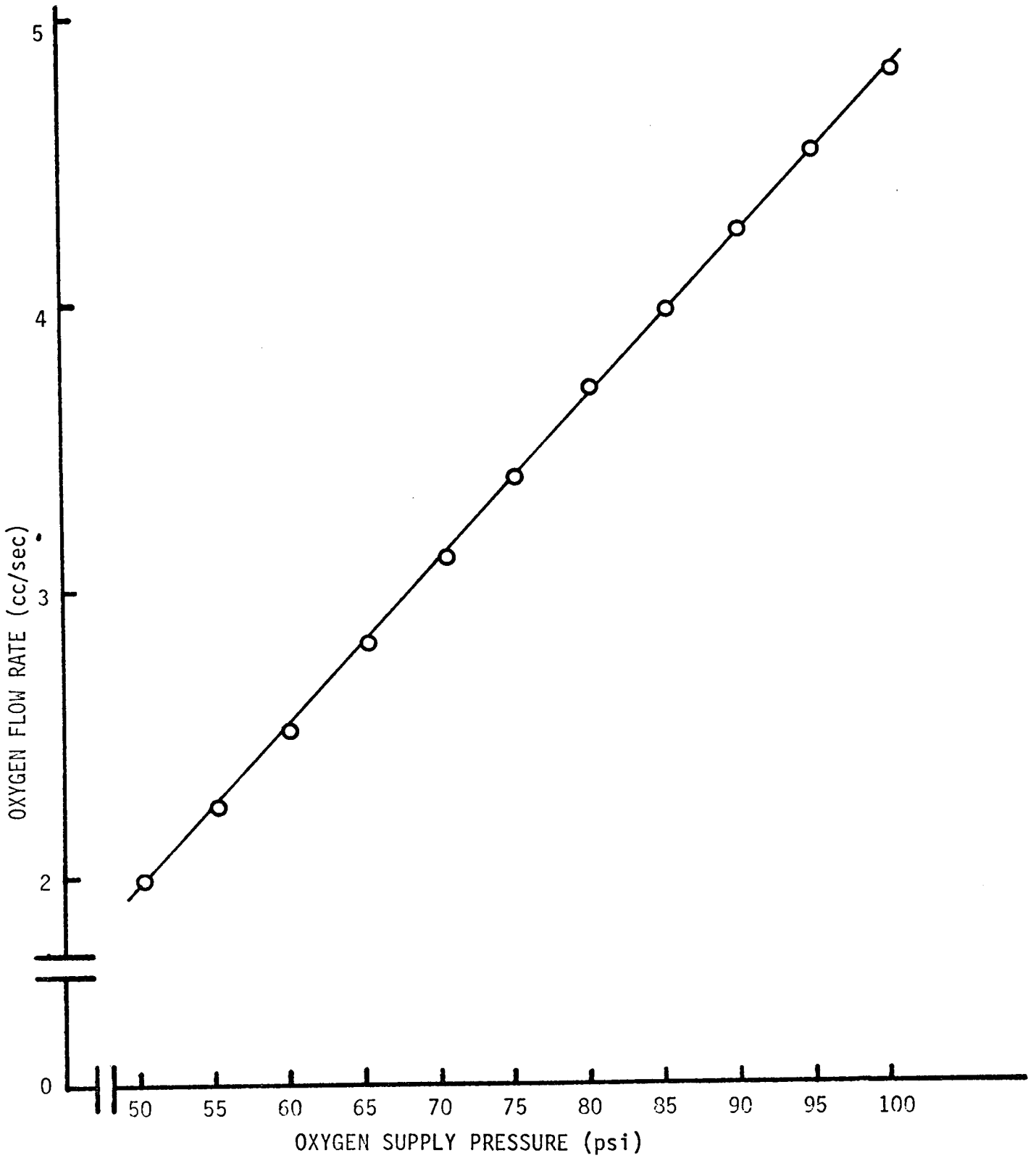


FIGURE 1
OXYGEN FLOW RATE CALIBRATION

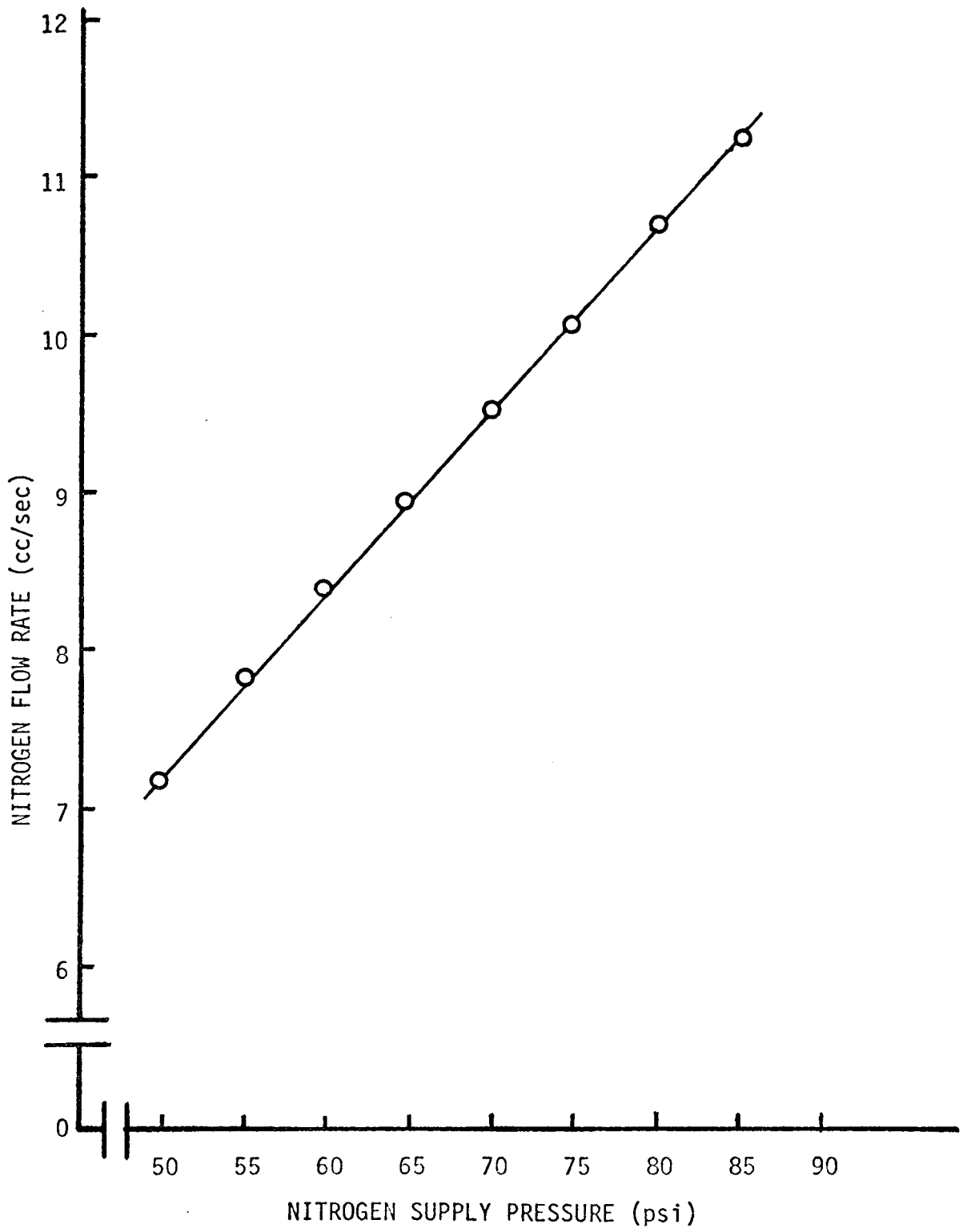


FIGURE 2

NITROGEN FLOW RATE CALIBRATION

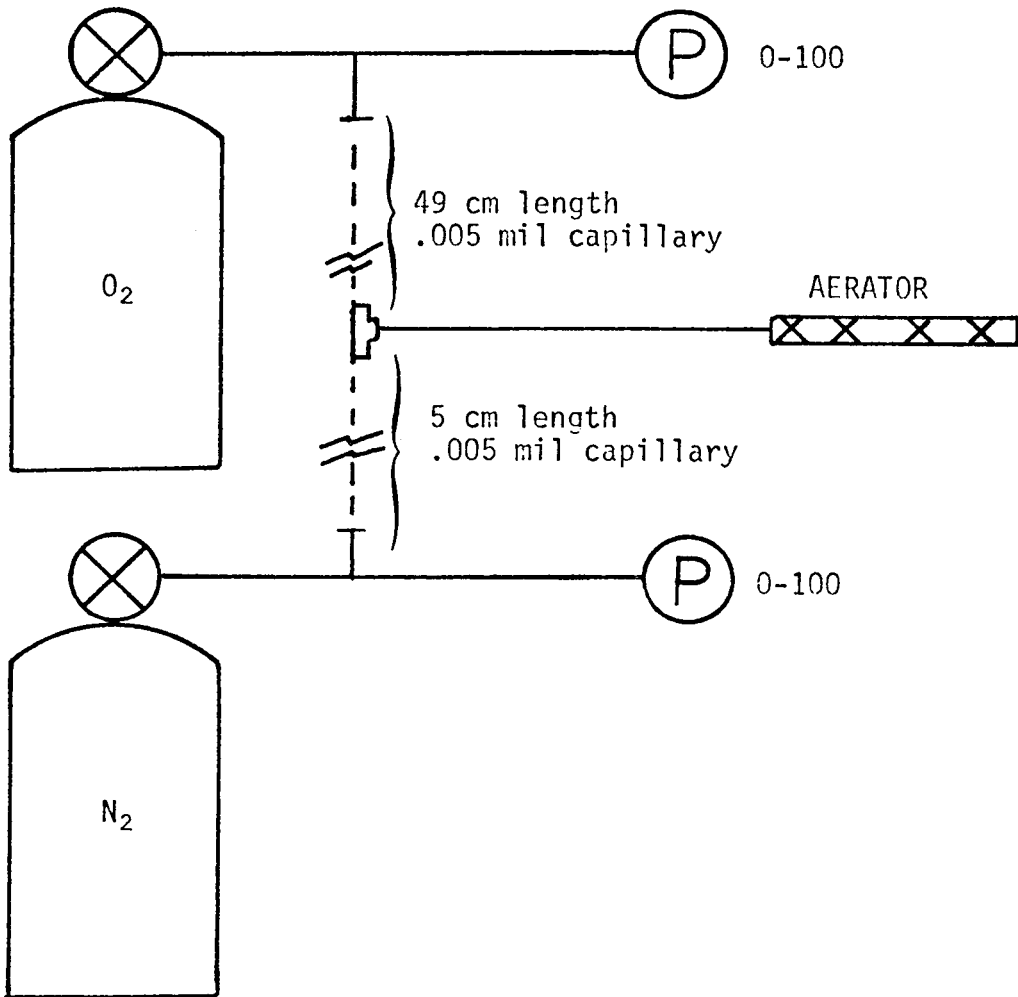


FIGURE 3
GAS MIXER