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Amperometric Recording of the Vertical Distribution of Oxygen and Hydrogen Sulfide in Sea Water.

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Summary: The possibilities of the electrochemical oxygen determination in sea water are discussed in short. The principles of the polarographic (amperometric) oxygen reduction at a plane platinum cathode which is covered with a cellophane and a plastic foil are described. Precise construction details of a high pressure stable electrode for recording oxygen tension down to 350 m are given. The diffusion current, the temperature coefficient, the relaxation time of the electrode, the constancy and the reproducibility of the measurements have been studied by laboratory and field experiments. The minimum lowering velocity is about 2m/min. The apparatus is also highly sensible to hydrogen sulfide. The change from the oxygen to the hydrogen sulfide diffusion current can be detected by the inversion of the current. Some examples of the first use of the oxygen recorder in the Baltic are given.

The chemical oceanography has been forced to stand behind in the development of the in situ measuring techniques because the change of analytical data to transmittable signals is naturally more difficult than in physical oceanography. To-day I should like to submit first results concerning continuous recording in situ for oxygen and hydrogen sulfide.

Basing on the amperometric method of CLARK (1953) for the determination of oxygen in blood we tried to work out an instrument which allows to record the distribution of dissolved oxygen in sea water even in greater depths. During the first tests of our oxygen sonde in the Baltic it appeared that the instrument is also suitable for recording dissolved hydrogen sulfide.

The fundamental method for the determination of oxygen in sea water is even today the classic procedure of WINKLER (1888) with slight modifications. It is based on the titration of iodine, which has been liberated proportionally to the content of dissolved oxygen. The procedure is simple but requires sampling and preparation of the samples. This, however, is time comsuming. To get reliable results special coated Nansen bottles must be used for sampling (COOPER (1961)). In highly heterogenous and laminated water it is difficult to place the Nansen bottle so that it will not close in a discontinuity. The precise observation of vertical profiles requires sampling just in the right but previously unknown depths and this is in the most cases impossible, especially in heavy weather.

It must be mentioned, that in consequence of the change in solubility of gas at different pressures and temperatures and especially at low oxygen contents systematic errors may occur when pouring the water from the Nansen bottle into the sample bottles, which cannot be taken into account. Very small differences in the oxygen content cannot be determined by the Winkler method without difficulties.

It has long been tried to estimate the dissolved oxygen in water by electrochemical analysis. But none of the proposed methods could be introduced in oceanography. The oxygen sonde of TÖDT (1933) and OHLE (1953) has proved to be useful in limnological research but has some disadvantage for use in oceanography. In sea water the current of the inner electrolysis, which should be proportional to the tension of the dissolved oxygen, is not stable. During measurement, trace metals, hydroxides, and cabonates plate at the precious metal cathode and reduce the reactive surface. A striking disadvantage of the oxygen sonde is the sensitivity to the movements of the surrounding water or to lowering of the sonde. The diffusion controlled reduction current is highly dependent on the diffusion layer at the electrode surface and therefore on the turbulence of the water passing the sonde.

The possibilities of the polarographic determination of dissolved oxygen with the dropping mercury electrode have been known since long. Several methods for the polarographic estimation of oxygen in sea water samples have been published, but they are all limited to the laboratory as the dropping mercury electrode is very sensitive to vibrations. To obtain reproducible results the drop frequency and the surfaces of the drops must be absolutely constant. This cannot be attained on board a sea going vessel.

FØYN (1955) combined the advantage of the inner electrolysis with that of the surface renewing mercury cathode. He proposed a method for the in situ determination of oxygen in sea water but in spite of the very simple construction of his apparatus it could not be introduced in all kinds of oceanographic oxygen determinations. The application of this amperometric method is limited to calm conditions at sea as for example in fjords.

The electrode arrangement of CLARK (1953) for the oxygen determination in blood and sera differs markedly from the known oxygen electrodes. KANWISHER (1959) introduced this electrode set up in the determination of dissolved oxygen in water. The electrode compartment is separated from the sample by a thin plastic foil which covers a blank platin cathode. A capillary layer of alkaline electrolyte is enclosed between the foil and the platinum surface to connect the silver anode with the cathode. Kanwisher describes a simple electrode arrangement, which is now commercially manufactured, suitable for laboratory experiments. The electrode has been used for the study of the photosynthetic processes and respiration rates. The author even describes the application in field experiments in shallow lake water.

For our oxygen sonde I accepted the measuring principle of CLARK because I think this to be the most promising one. In addition to CLARK and KANWINSHER four variations have been made:

1) The volume of electrolyte has been increased so that the changes of the alkaline electrolyte composition, caused by carbon dioxide passing the foil, may be neglected.

2) Every part of the sonde is made of plastic to make it unbreakable even under rough conditions.

3) A thin cellophane foil is situated between the plastic foil and the cathode surface to maintain a constant defined electrolyte leading layer at the cathode.

4) The pressure in the electrolyte compartment is completely balanced to the water pressure at the respective depths. In addition, a thermistor is built into the sonde to measure the temperature together with the oxygen.

We had the opportunity to get an expensive polarograph for all our investigations. It was the model SELECTOR D of the ATLAS GmbH, Bremen. But I think that it is worth while to know, that a cheaper arrangement may be used if only the determination of oxygen is wanted.

Figure 1 shows a schematic section through an oxygen sonde. The pressure balance is not plotted into this section. A record of the current voltage curve, as shown in figure 2, shows the function of the electrode best. Oxygen and all the other reducible gases diffuse from the surrounding medium through the thin plastic foil to the platinum cathode. With no voltage applied, the oxygen tension at the electrode surface is equal to that in the outer compartment. If a small negative voltage, say a little more than the decomposition voltage, is applied, the oxygen at the cathode surface is reduced to hydroxide ions according to equation:

$$O_2 + 2\,H_2O + 4\,e^- = 4\,OH^- \qquad (1)$$

As an intermediate reduction product hydrogen peroxide occurs. The anodic process is the solution of the anode metal:

$$4\,Ag + 4\,OH^- = 2\,Ag_2O + 2\,H_2O + 4\,e^- \qquad (2)$$

After FARADAY's law, the cathodic current is proportional to the quantity of reduced oxygen. With the beginning of the oxygen reduction, the oxygen tension immediately at the cathode surface decreases to a level which is balanced by the reduction and diffusion rate of oxygen. With increasing voltage the current increases according to the new balance tension of oxygen at the cathode surface. The lowest oxygen tension, which is possible at the lectrode, is zero. Now all the oxygen molecules are reduced at once when arriving at the cathode surface after diffusion through the foils. Thus the current is only diffusion controlled. It attains a maximum value, the so-called diffusion current. The current can only increase with increasing voltage, if the decomposition voltage of a new reducible component present at the electrode is reached.

To exclude the influence of small changes in the polarizing voltage on the diffusion current, the working voltage is adjusted in practical measurements to a value of about the half of the diffusion current plateau. The diffusion current is now described by the equation:

$$I_{d\ (T)} = n.F.s.D.\ dC/dx \qquad (3)$$

n: number of electrons per reduced molecule
F: Faraday constant
s: electrode surface
D: diffusion constant
dC/dx: concentration gradient

If the diffusion layer is limited to the thin foils it is allowed to use an approximated equation:

$$I_{d\ (T)} = n.F.s.D.\ C_o/d \qquad (4)$$

C_o: concentration of oxygen in the bulk of the solution
d: thickness of the foil.

This demand can easily be obtained by a minimum turbulence at the outside of the foil. Field experiments showed that a water stream of about 2m/minute is sufficient. Higher velocity is of no influence on the diffusion current. At constant temperature in the oxygen sonde all the other figures from equation (4) are constant - except the concentration of the oxygen in the solution surrounding the electrode. Thus, the diffusion current is directly proportional to the oxygen tension.

Diffusion takes time. Therefore it is quite clear, that due to a change of oxygen tension in the solution, a certain delay appears in the "answer" of the diffusion current. In our oxygen sonde we succeeded to cut down the delay to 4 seconds for a 90% response and 14 seconds for a 99% response to the change of the oxygen tension in the solution. This means a local delay of 23 cm for a 90% correct answer due to an abrupt change in the oxygen content with the slowest lowering velocity of the sonde. I think this is sufficient for most purposes, especially having in mind that very abrupt changes do not appear in nature.

As yet it has not been taken into consideration that every diffusion controlled reaction also depends on the temperature. It is striking, that the temperature coefficient is higher at a foil covered electrode than it is in normal polarography of oxygen. Therefore the temperature coefficient must be determined with high accuracy. The temperature relation of the diffusion current at constant oxygen content of the water is shown in figure 4. We made these measurements in a laboratory arrangement which is shown in figure 3. We tried to construct a direct electrical correction for the temperature coefficient, but unfortunately there is no sufficient NTC - resistance available. I hope that it will be possible to construct a built-in temperature compensation in future. In the same apparatus we made also the other laboratory investigations, as calibration, proof of linearity, drift of the electrode, determination of the delay time etc. The necessary turbulence at the surface of the foil is obtained by a small water stream blowing against the foil. The results of the laboratory studies are as follows: The reproducibility of the values is better than 0.3%. Sensitivity of the sonde to changes in the oxygen tension is much higher than it can be obtained by the WINKLER procedure. For a change of 0.1 ml O_2/l it is possible to get the full scale deflection of 20 cm. We found no deviation from linearity of all calibration curves, reduced to a standard temperature by the correction factor, which is given in table 1. The drift of the electrode within five days is below 0.75% as can be seen from table 2.

Calibration of the electrode can be made either by comparison with the oxygen value determinated by the WINKLER procedure or, if the sufficient function of the electrode has been established, by determination of the diffusion current of air saturated water. Only one accurate value is sufficient to get the slope of the calibration curve which normally goes through the zero point. The oxygen content can now be calculated from the equation:

$$C_o = (C_{sat.}/\ i_{sat.})\ i_d \qquad (5)$$

As mentioned above, the diffusion layer is a parameter in the equation for the diffusion current. Therefore it must not be influenced by the pressure in the surrounding solution. This demands the construction of a pressure balanced oxygen sonde, the section of which is shown in figure 5.

This pressure balance worked well down to 350 m. Records of oxygen polarograms at 200 m showed no difference to that obtained at the surface. In greater depths, the inlet of the cable became untight. In an improved construction of the sonde we shall eliminate this infirm detail by application of pressure prove underwater plugs. A normal 3-core lamp cable was taken to connect the sonde with the recorder. The sonde was lowered with the hydrographic winch.

All construction details, the description of preparation and calibration will be published in the next number of volume 18 of the "Kieler Meeresforschungen".

Field experiments with the oxygen sonde in the Baltic showed that it is possible to record hydrogen sulfide tension with very high sensitivity as well as oxygen. Hydrogen sulfide cannot be reduced but only oxidized. The hydrogen sulfide molecules which diffuse through the foil into the electrolyte dissociate into sulfide ions and hydrogen ions, which react with the alkaline electrolyte to water. Sulfide ions will possibly be oxidized to sulfate ions. The current record will pass the galvanometer zero line when the oxygen content in the water changes to hydrogen sulfide. Therefore a confusion between oxygen and hydrogen sulfide current is impossible.

The fact that it is possible now to determine and to record hydrogen sulfide in situ is very valuable because the estimation of small concentrations of hydrogen sulfide, as appear in the deep layers of the Baltic, is difficult not only with the sampling technique but even with the analytical procedure by the only possible methylene blue method.

What possibilities are there for application of an in situ record of dissolved oxygen in sea water for practical use in fishery research ? The complicated hydrographic situation in the Baltic leads to a large aperiodical change of the oxygen content of the deep water. Temporary hydrographic situations appear with nearly complete oxygen consumption in certain layers. This is for example the case in the most parts of the Baltic basins below 90-100 meters. At the moment we will find hydrogen sulfide in these regions. The only refreshing of the water which is poor in oxygen comes from the North Sea over the Darss Rise and from there over the following rise from the Arcona Basin into the Bornholm and Gotland Basins. In most cases the influx of the oxygen rich haline water is not sufficient to effect a sufficient renewal of the old deep water layers. It cannot be predicted over a long period how anoxic situations will develop. If anoxic conditions last over a long time this will have devastating consequences for all life in the water and on the bottom.

As shown by experience fish avoid water with an oxygen content of below 3 ml per liter. Therefore fishing in such areas will not be successful. On the other hand there are very good conditions for a growth of life according to the large offer of nutrients when the oxygen level rises. The use of the oxygen sonde makes it possible to locate oxygen poor water rapidly, to find its frontiers, to follow the refreshing process and by this to determine a striking factor for the migration of fish.

We used the oxygen sonde in the Skagerrak, Kattegat and the Inner Baltic. Two records, one from the Bornholm Basin (figure 6) the other from the Gotland Basin (figure 7) may show some of the results we got this summer. The small peaks on the records belong to the depth marks from a contact meter wheel. By this a resistance of 5 megohms is connected in series to the sonde every meter or, if wanted, every 5 or 10 meter. The Gotland record shows hydrogen sulfide below the 84 meter level.

In future we shall try to develop the first model of the oxygen sonde to get an automatic compensation of the temperature effect, and for application in oceanic depths.

Table 1: Determination of the Temperature Correction Factor

T (°C)	μ A/ml O_2	F_T (20°C)
0	0.760	3.96
1	0.823	3.65
2	0.892	3.32
3	0.970	3.09
4	1.043	2.88
5	1.115	2.73
6	1.198	2.50
7	1.273	2.33
8	1.377	2.18
9	1.475	2.03
10	1.578	1.900
11	1.682	1.785
12	1.800	1.666
13	1.931	1.555
14	2.070	1.450
15	2.212	1.385
16	2.350	1.276
17	2.498	1.200
18	2.658	1.127
19	2.825	1.061
20	3.000	1.000
21	3.185	0.943
22	3.393	0.885
23	3.620	0.829
24	3.850	0.779
25	4.805	0.734
26	4.320	0.694
27	4.565	0.658
28	4.810	0.623

Table 2: Determination of the Drift

T (h)	μ A (corr.)	Drift in %
0	14.67	± 0.00
1	14.68	+ 0.07
2	14.67	± 0.00
3	14.62	- 0.34
4	14.60	- 0.48
5	14.62	- 0.34
10	14.68	+ 0.07
24	14.72	+ 0.34
48	14.68	+ 0.07
72	14.72	+ 0.34
96	14.60	- 0.48
120	14.79	+ 0.75

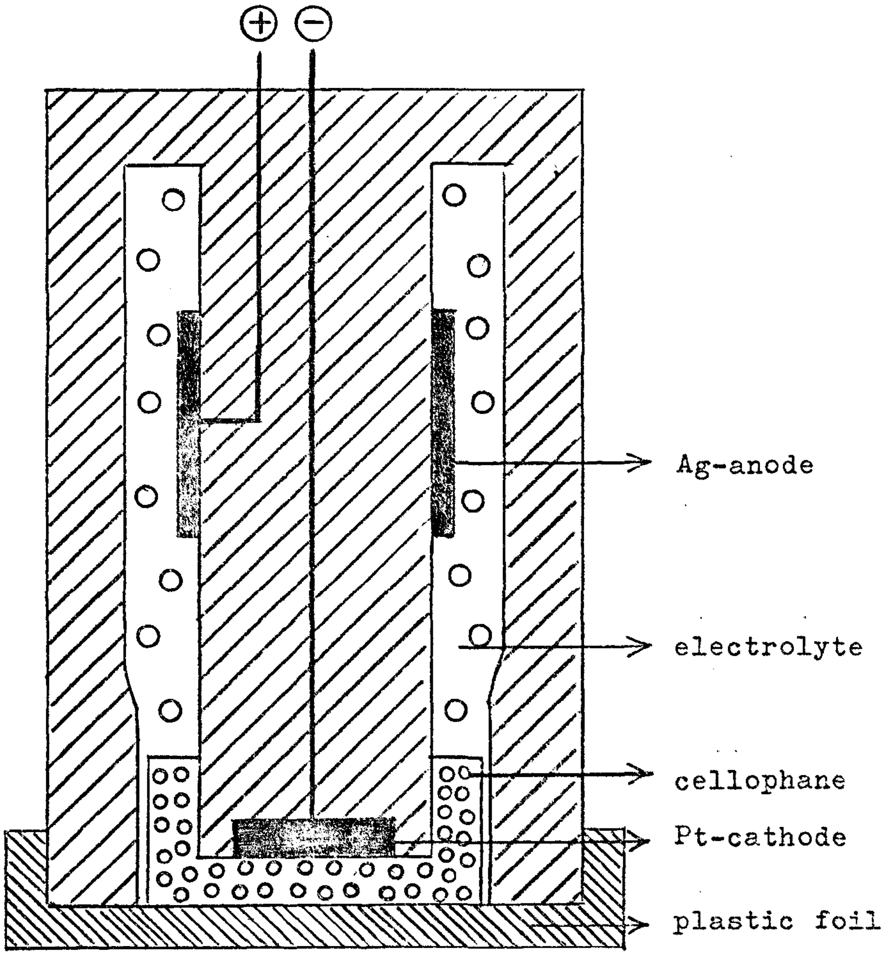


Figure 1: Schematic section of a polarographic cell for the determination of oxygen.

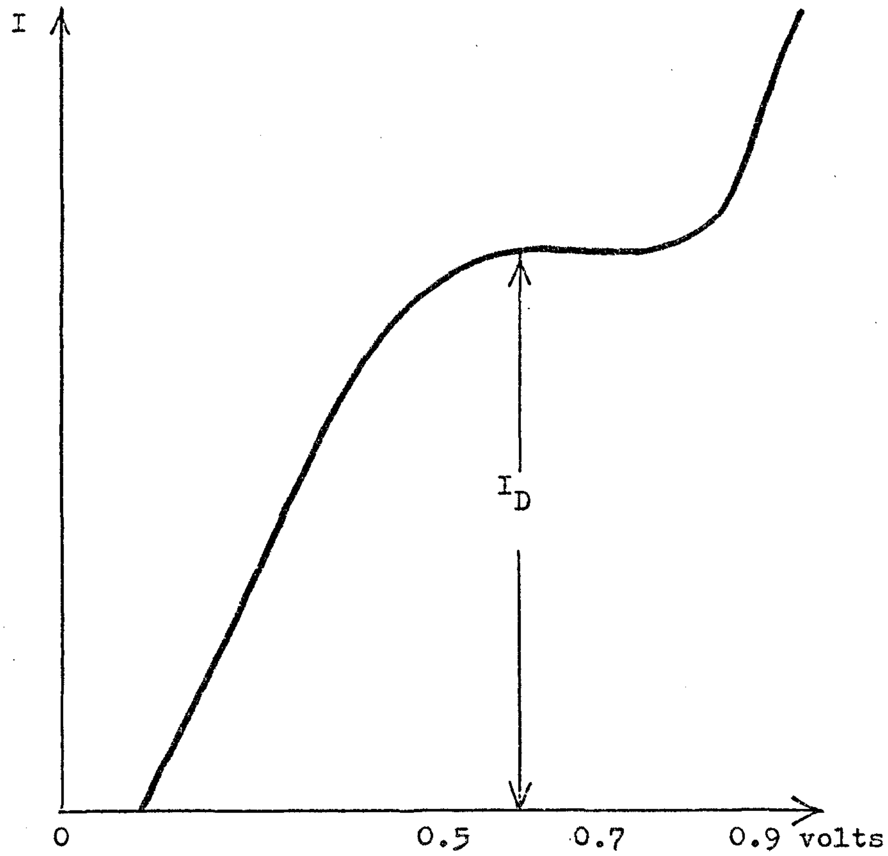


Figure 2: Polarogram of oxygen at a platinum cathode in KOH.

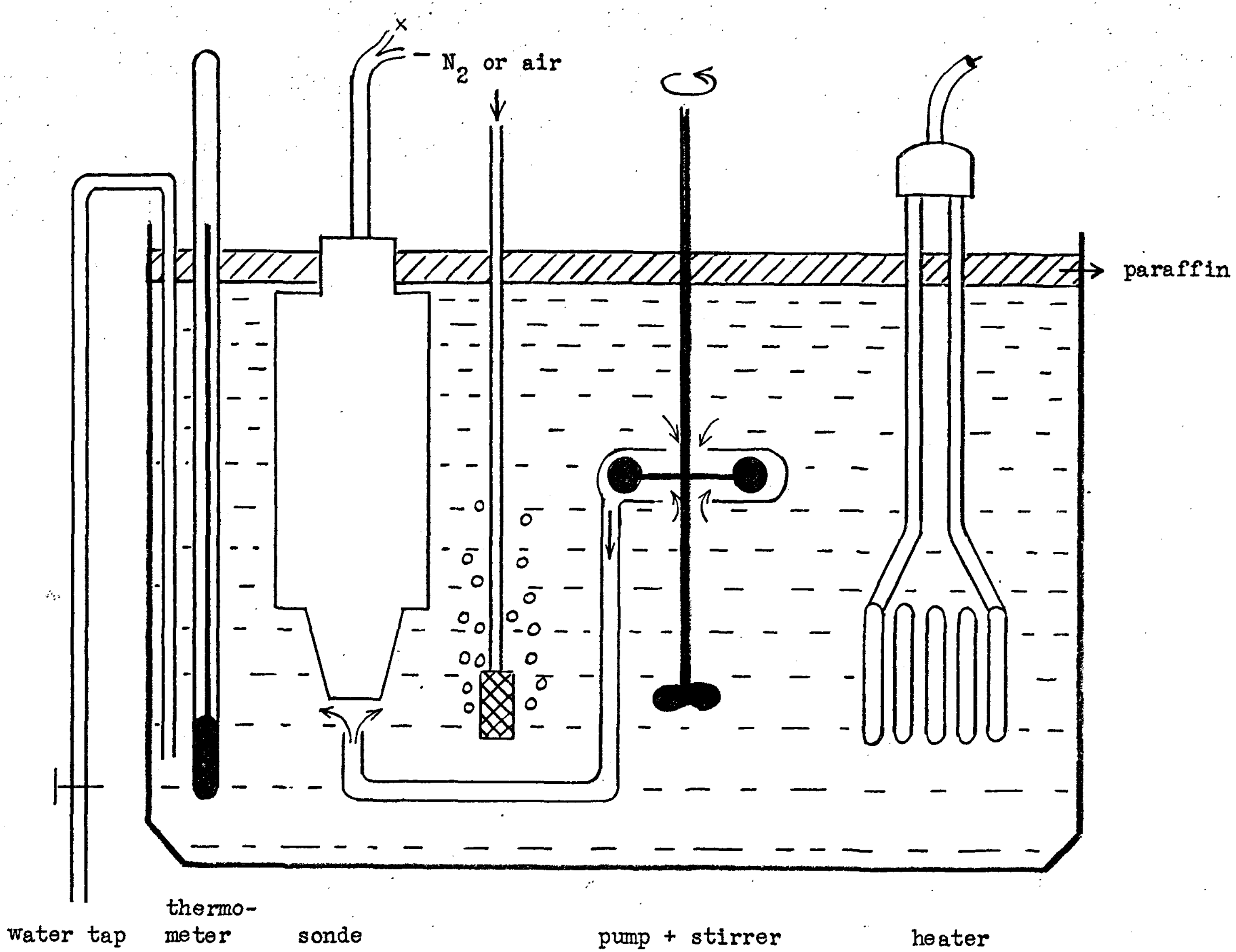


Figure 3. Apparatus for laboratory investigations with the oxygen sonde

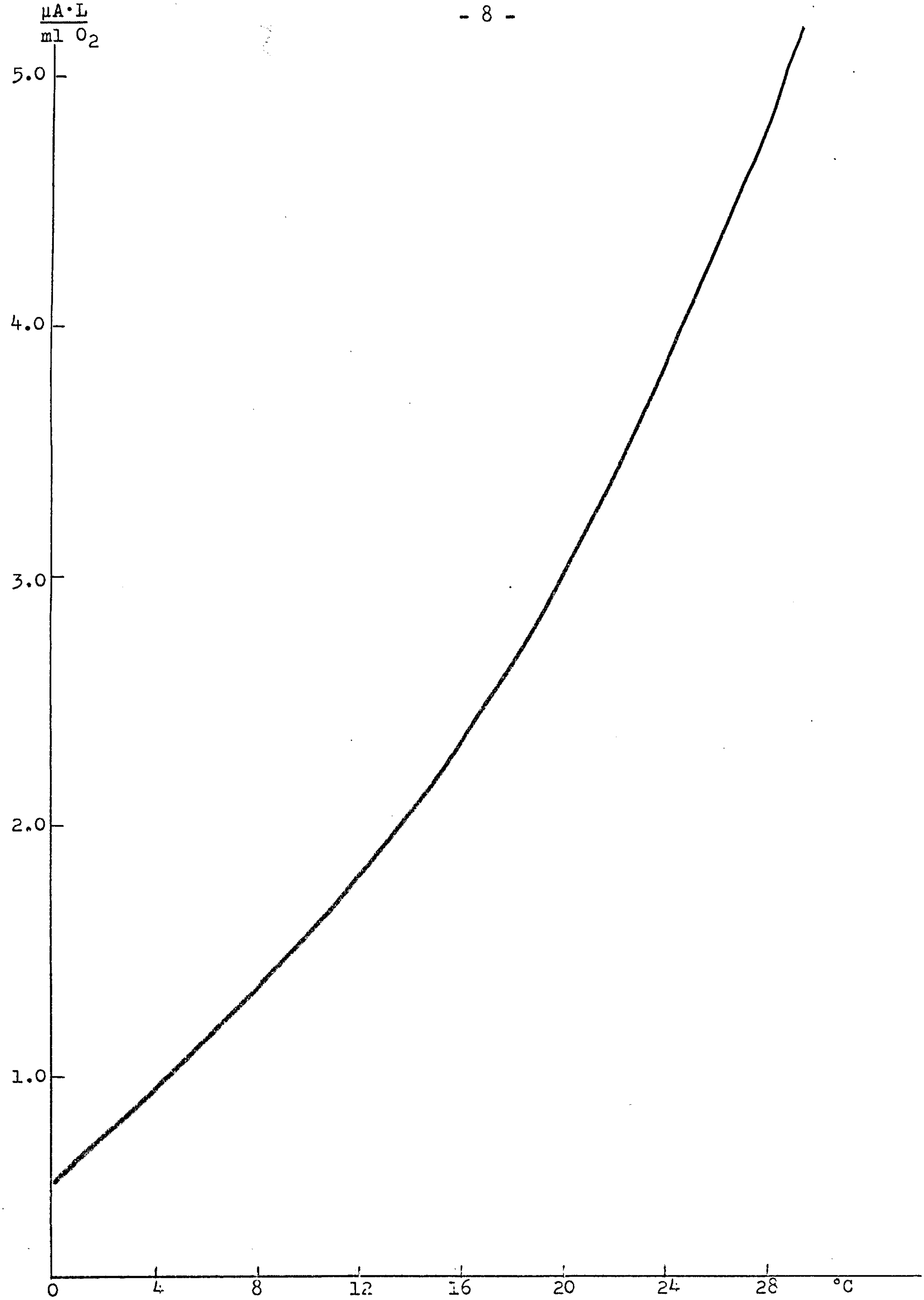
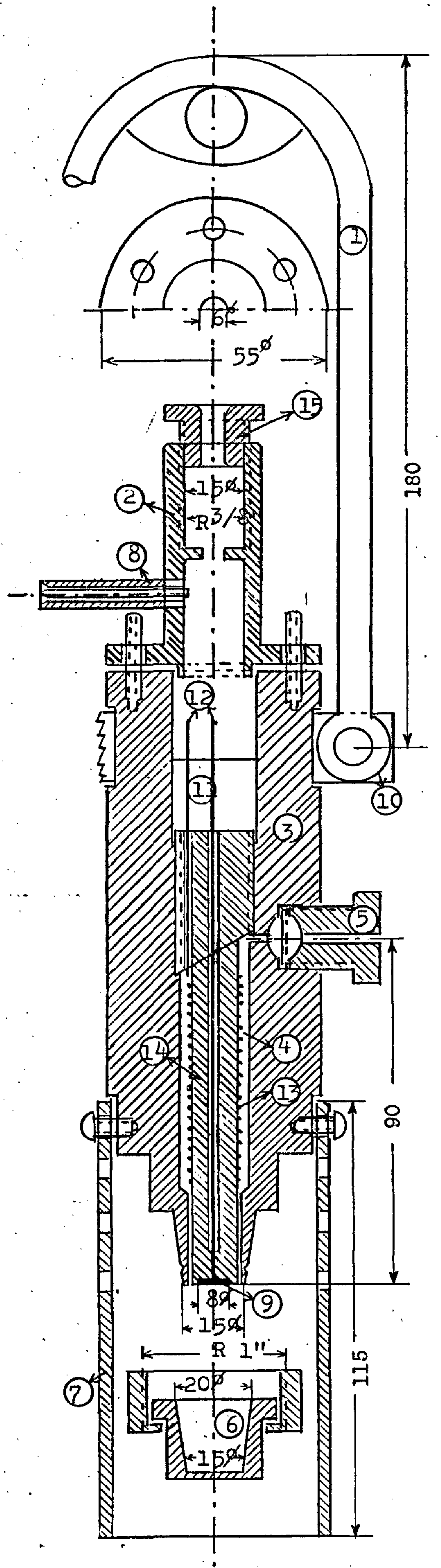


Figure 4. Relation between diffusion current and temperature.



No. of pieces	Name	Part	Material
1	Aufhängung	1	Messing 8ø
1	Schelle	10	P.V.C.
1	Sondengehäuse	3	Nylon
1	Elektrolytraum	4	P.V.C.
1	Druckausgleich	5	Messingstopfen
1	Halterung f.Folie	6	Messing u.Nylon
1	Raum f.Vergussmasse	11	Araldit
1	Deckel mit Quetschverschluss	2	Messing
1	Schutzrohr	7	P.V.C.
1	Rohr f.Termistor	8	Messing
1	Anschluss Anode und Kadode	12	Feinsilber 1mmø
1	Anode	13	Platin 8o.1mmst.
1	Kadode	9	Feinsilber 1mmø
1	Einsatz	14	P.V.C.
1	Stopfen R 3/8"	15	Messing

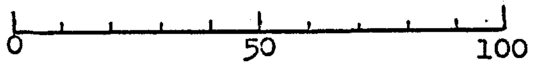


Figure 5: Oxygen-sonde. (Inst. f. Meereskunde d. Univ. Kiel)

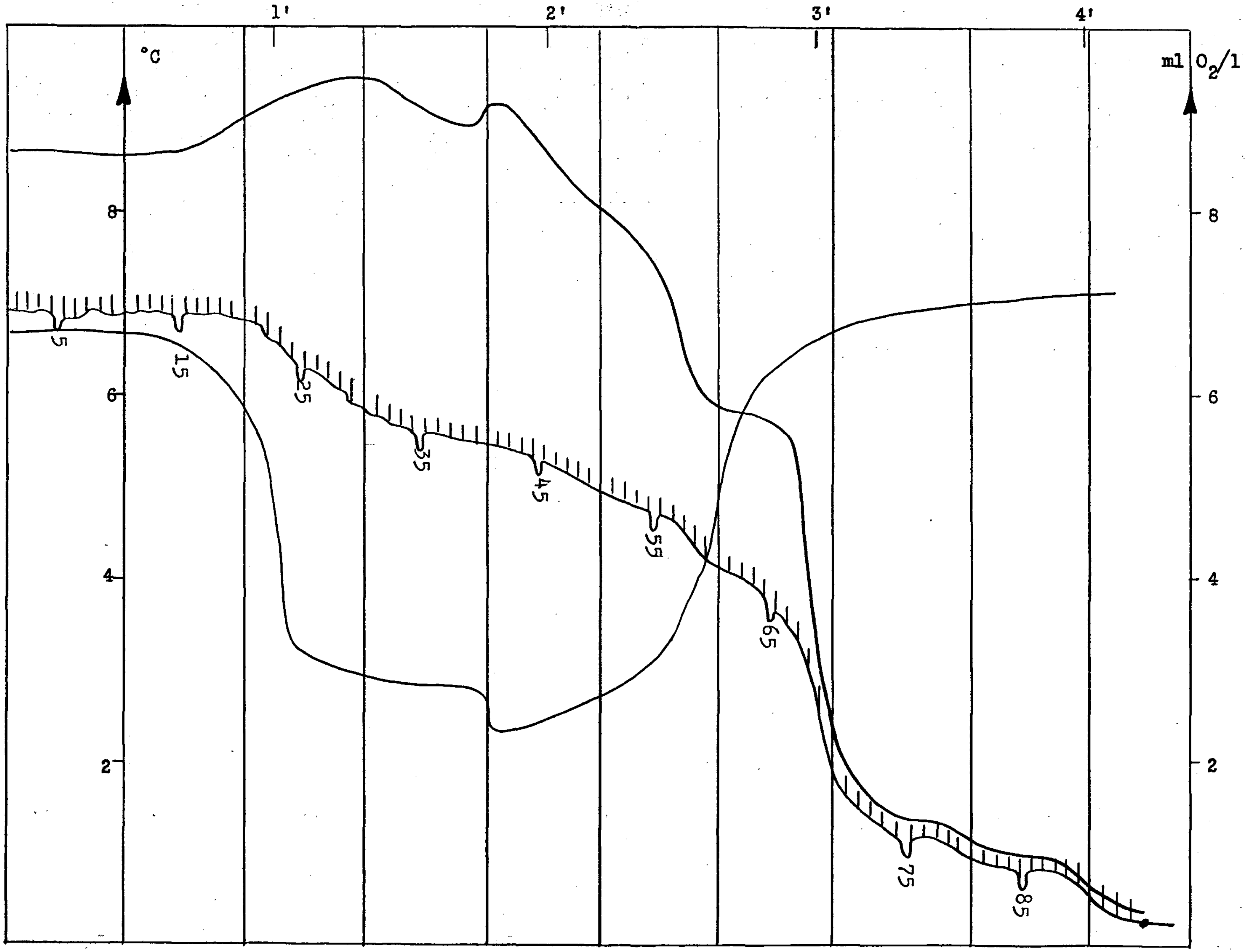


Figure 6. Oxygen record in the Bornholm Deep.

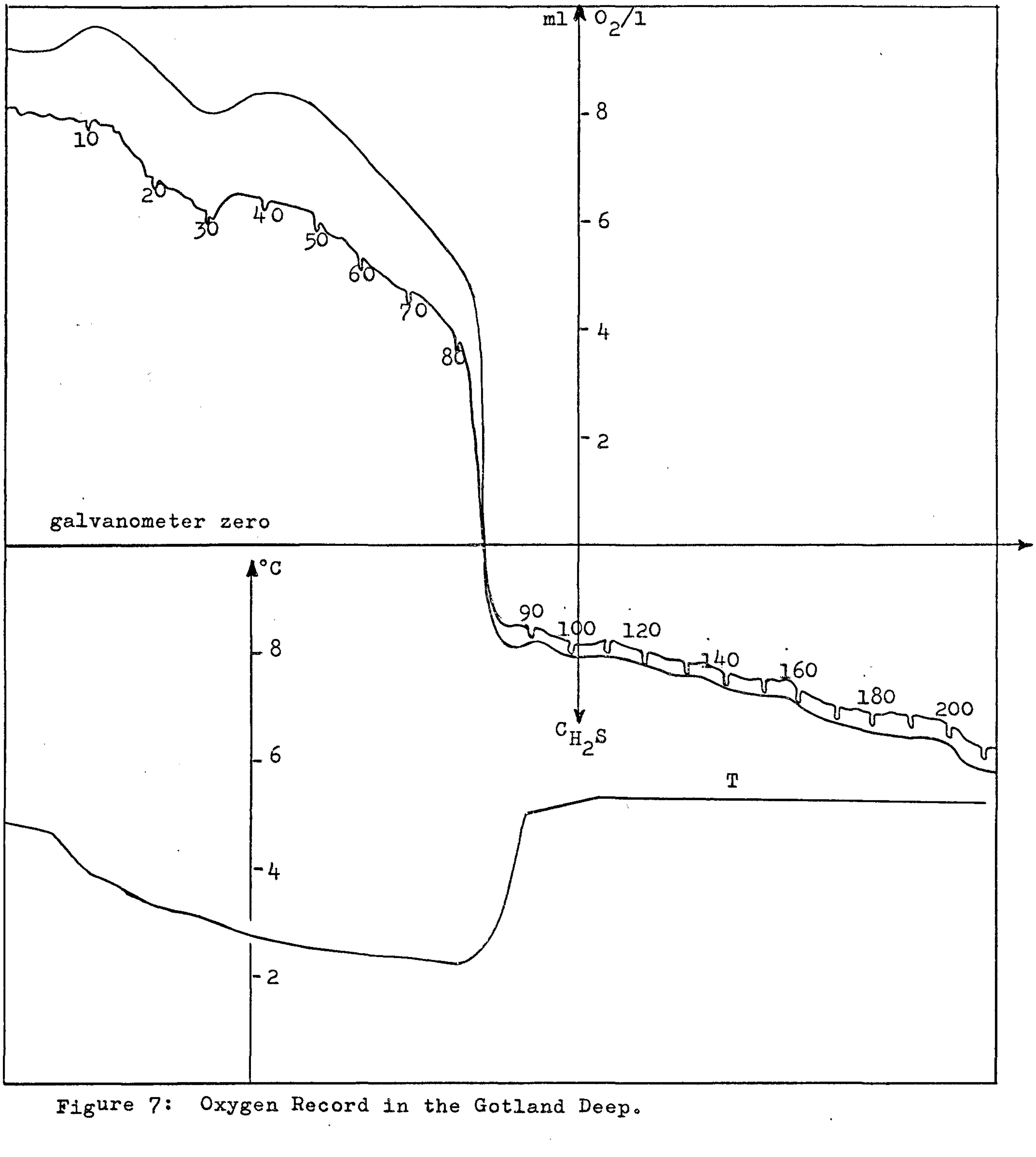


Figure 7: Oxygen Record in the Gotland Deep.