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PROJECT TRIDENT
TECHNICAL REPORT

**THE EFFECT OF PRESSURE ON
THE ELECTRICAL CONDUCTIVITY
OF SEA WATER**

ARTHUR D. LITTLE, INC.

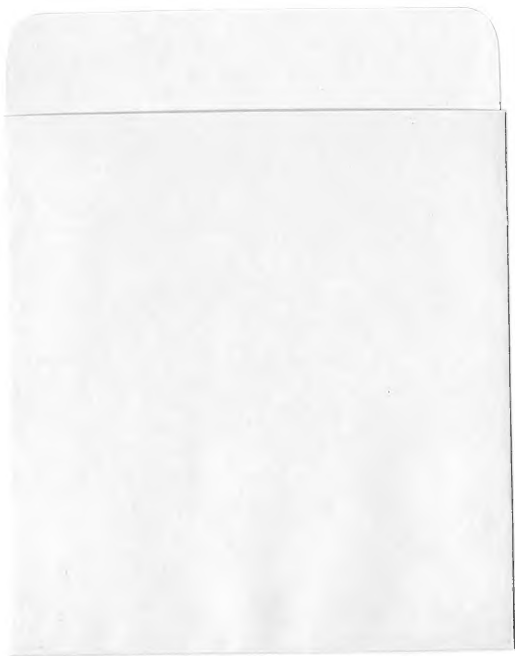
35 ACORN PARK CAMBRIDGE, MASSACHUSETTS

DEPARTMENT OF THE NAVY
BUREAU OF SHIPS

N0bsr-81564 S-7001-0307

AUGUST 1962

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I. SUMMARY

This report describes measurements made in the laboratories of Arthur D. Little, Inc., of the effect of pressure on the electrical conductivity of sea water of different salinities (and chlorinities) and at various temperatures. The first part of this report describes the design, construction, and calibration of the equipment, while the experimental data and the conclusions are presented in the second part. Over the range 0 to 25°C, 15 to 10,000 lb/in.², and 9.68 to 19.38 ‰ chlorinity the specific conductance at pressure P (in lb/in.²) can be approximated from the value at one atmosphere, $K_{1, T, Cl}$ using the simple empirical relation

$$K_{P, T, Cl} = K_{1, T, Cl} + 1.17 \times 10^{-8} Cl P$$

where Cl is the chlorinity in parts per thousand. If P is expressed in bars this relation becomes

$$K_{P, T, Cl} = K_{1, T, Cl} + 1.70 \times 10^{-7} Cl P$$

II. INTRODUCTION

In the past, studies of the variation of physical and chemical processes with environmental conditions have concentrated on that parameter which varies most widely in commonplace experience, namely, temperature. As our explorations move into the ocean depths, knowledge of additional environmental factors will have to increase. In underwater operations the temperature range of interest covers only a few degrees centigrade, whereas the pressure range covers 10,000 atmospheres. For undersea operations, our knowledge of the pressure dependence of physical and chemical processes should be ideally as complete as our present knowledge of the temperature dependence of these processes.

Relatively little experimental research has been conducted in the areas of moderately high and high pressure physics and chemistry. Much of the earlier work, it is worthy of note, was prompted by oceanographical and geological interests.

The importance of detailed knowledge concerning the electrical conductivity of the sea and of the variation of this parameter with concentration, temperature, and pressure is widely recognized. As a consequence of The Conference on Physical and Chemical Properties of Sea Water, held at Easton, Maryland, in September, 1958, (1) sponsored by the Office of Naval Research and the Committee on Oceanography of the National Academy of Sciences, the Committee on Chemical Properties recommended "that electrical conductivity be used as a sea-water characteristic," and the Committee on Physical Properties reported that knowledge of "the effect of pressure on the conductivity of sea water would be useful." In a paper given at this same conference, D. W. Pritchard of the Chesapeake Bay Institute of Johns Hopkins University noted that the "lack of certain basic information restricts the use of in situ conductivity measurements in deep water for the determination of salinity. There appears to have been no investigation of the effect of pressure on the conductivity of sea water. Thus it would seem very desirable to include a study of the pressure effect of conductivity in any program developed to improve our knowledge of the physical and chemical properties of sea water."(2, 3)

III. DESCRIPTION OF APPARATUS

A. HIGH-PRESSURE EQUIPMENT

1. Operation

The high-pressure equipment was designed and constructed by Harwood Engineering Company, Inc., Walpole, Massachusetts. The assembled equipment is shown in Figures 1, 2, and 3, and a schematic representation of it is given in Figure 4. We can best describe this equipment by describing its operation, which is as follows.

Close drain valve 4 (see Figure 4) and the valve on handpump 3. Open needle valve 5 and the valves on handpumps 1 and 2, and pump with handpump 3 until the hydraulic fluid begins to escape from release valve 7. This operation brings the piston of the intensifier to the bottom of its stroke and brings the pressure on the high-pressure side of the intensifier to 10,000 psi. Next, close the valves on handpumps 1 and 2, and open the valve on handpump 3. Raise the piston of the intensifier by pumping first handpump 1 until the desired pressure is obtained. (Release valve 6 releases at 10,000 psi.) If pressures higher than 10,000 psi are desired, handpump 2 is used. Handpump 1 was included in the system because of its greater effectiveness in the lower pressure range. Hydraulic fluid escapes from release valve 6 when the Bourdon-type gauge (10, Figure 4) on the low-pressure side of the intensifier reads approximately 10,000 psi. The pressure multiplication factor of the intensifier is 16. The pressure on the high-pressure side of the intensifier is measured by a manganin cell* and recorded on a Foxboro Dynalog recorder (11, Figure 4).

When the intensifier piston reaches the top of its stroke, the pressure on the high-pressure side will cease to increase as the pressure on the low-pressure side increases. In order to continue to increase the pressure on the high-pressure side of the intensifier, a second piston stroke is required. This stroke is accomplished by slowly opening the valve on handpump 2, opening the needle

*Manganin is a Cu-Mn-Ni alloy whose electrical resistivity is pressure-sensitive. The manganin element was calibrated by Harwood Engineering Company by a dead weight testing technique, and the pressure reading is accurate to within 0.5 to 1% (at full scale deflection). A novel feature of the present apparatus is the location of the manganin element in a fitting rather than in its own separate pressure vessel. This arrangement, while making the manganin element more vulnerable to damage, simplifies construction and appreciably reduces the expense of the equipment.

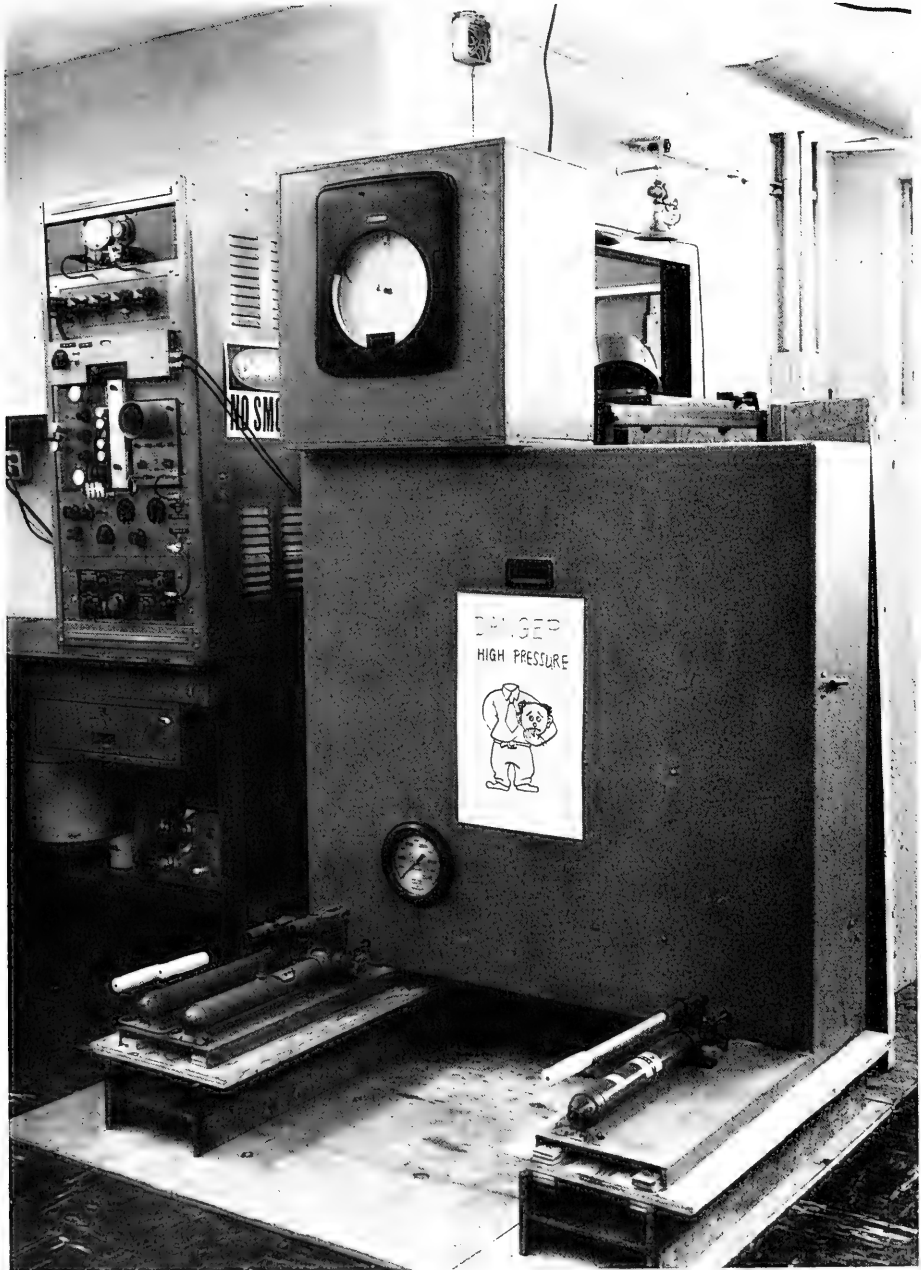


FIGURE 1 HIGH PRESSURE APPARATUS (FRONT VIEW)

The conductivity bridge is on the left with the bath thermoregulator beneath. The man-ganin cell recorder is set on top of the cabinet of the high pressure producing equipment. The three hand pumps are in the foreground.



FIGURE 2 HIGH PRESSURE APPARATUS (REAR VIEW)

The shielding has been moved aside to show the bath and the pressure producing equipment. The release valve 7 is just visible in the lower left corner. To the right is the intensifier and the high pressure check valve. The connection containing the manganin cell is partially hidden by the left hand support of the steel plate shielding on the bath. The top of the pressure vessel with its closure in and electrical leads attached is visible over the walls of the bath.

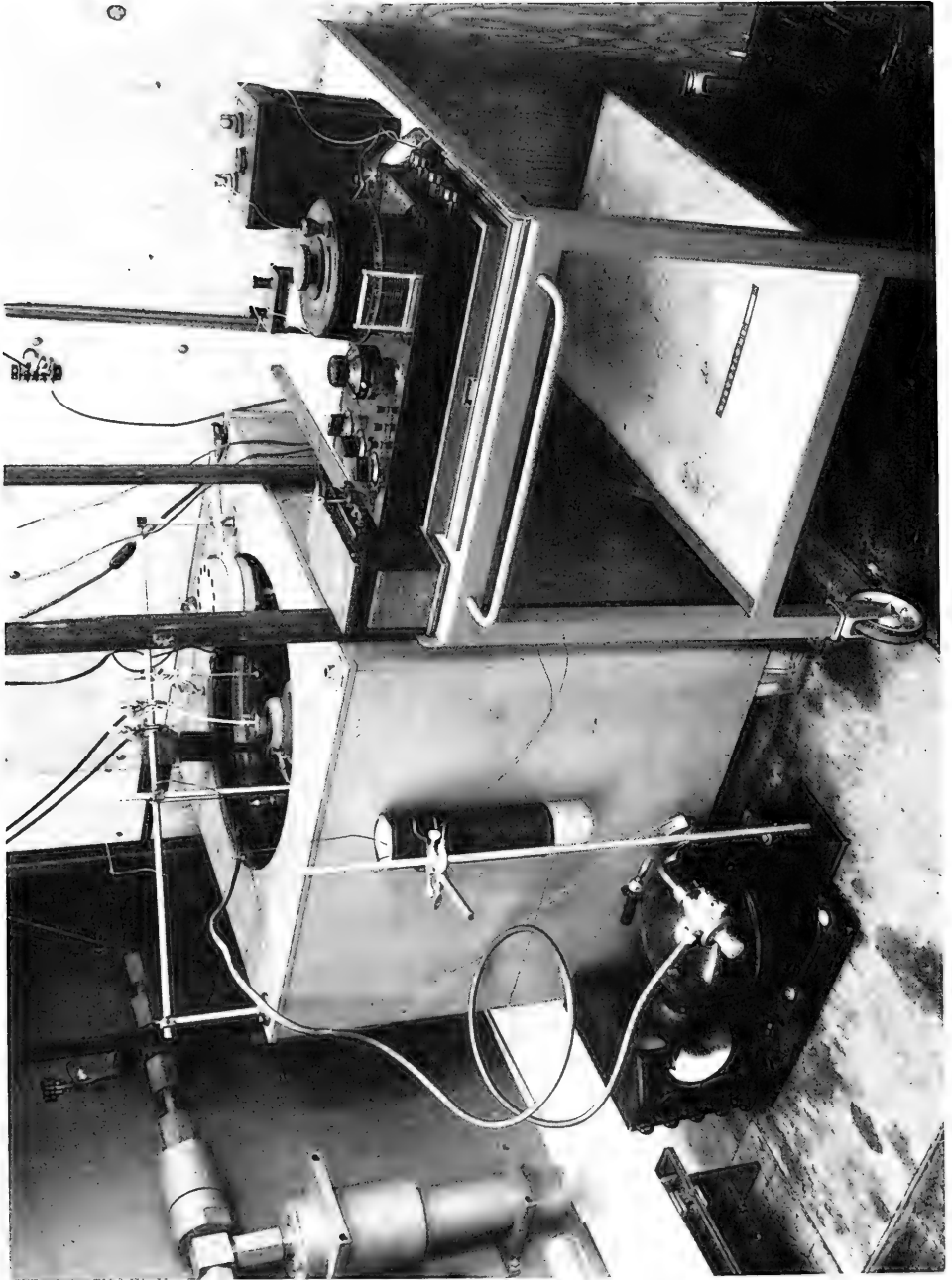


FIGURE 3 THERMOSTATIC BATH
Showing cooling unit and thermocouple potentiometer.

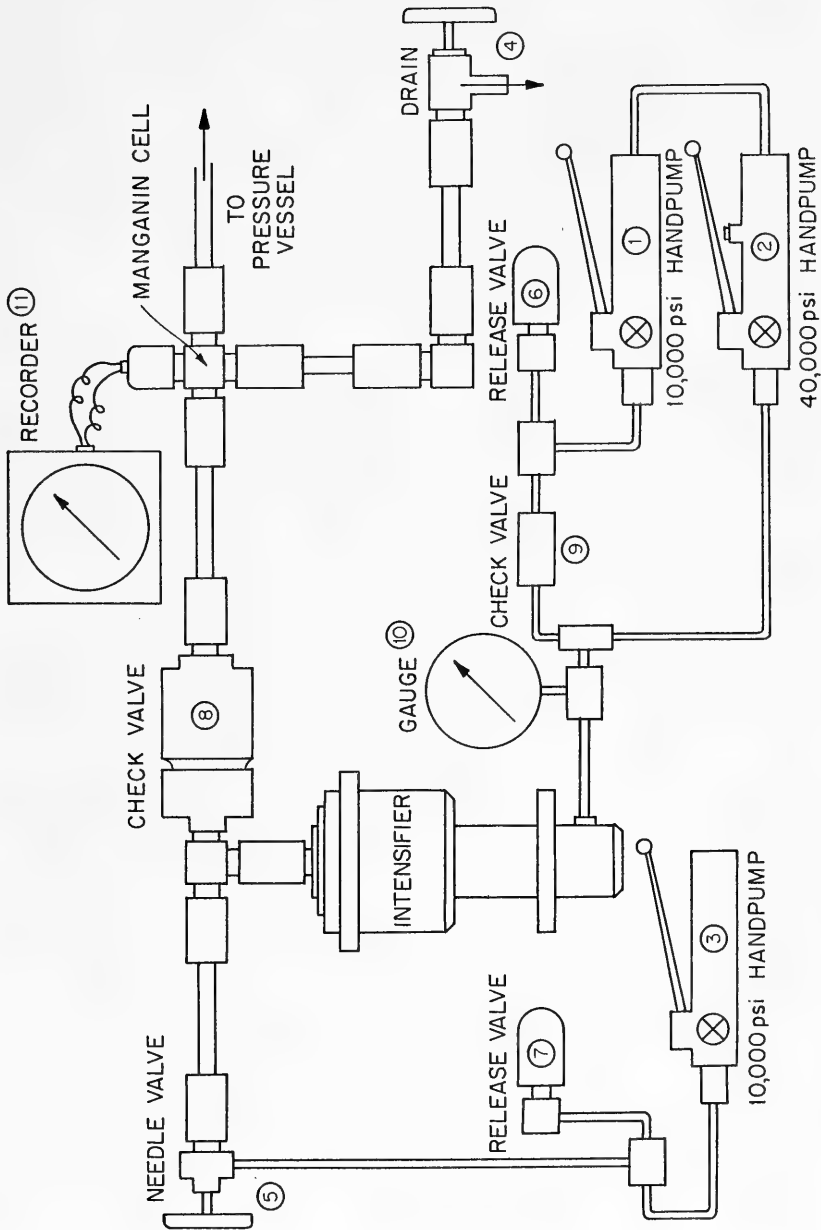


FIGURE 4 SCHEMATIC DIAGRAM OF 200,000 PSI PRESSURE-PRODUCING EQUIPMENT

valve 5, closing the valve on handpump 3, and then pumping on handpump 3 until the intensifier piston is returned to the bottom of its stroke, indicated by the release of hydraulic fluid from release valve 7. The second upward stroke is then accomplished by a repetition of the procedure for raising the piston, described above. The pressure can be reduced in a controlled manner by opening drain valve 4.

The high-pressure vessel is shown in Figure 5. It is a jacketed or compound cylinder of tapered shrink construction. Since in a vessel of this design the inner cylinder is in compression and the outer one in tension, very great strength results. Bridgman's "shrunk-on" method of supporting tapered vessels is based on the same mechanical principle.⁽⁴⁾ The hydraulic fluid is transmitted through the bottom of the pressure vessel. From the closure, the conductivity cell is suspended in the vessel's cavity, which is 9-3/8 inches in length and 1 inch in diameter. In order to reduce the total volume of fluid which must be compressed, the remainder of the vessel's cavity is filled with a loose-fitting filler-bar. This filler-bar must be crosscut in the bottom to prevent it from acting as a check valve.

Figure 6 shows an enlargement of the closure of the pressure vessel. At moderate pressures the mild steel ring and the lead back-up ring extrude and act as seals. One electrical lead is sealed with a cone and is insulated. The closure itself, which is in electrical contact with the remainder of the high-pressure equipment, acts as the second lead. The outside lead from the closure must be connected to the grounded terminal of the conductivity bridge.

2. Safety Precautions

On all sides of the high-pressure apparatus not protected by the equipment's steel-plate cabinet, a movable sectional shelf of a "Homosote"-plywood sandwich was erected. Personnel on the floor above were protected with a 1-inch steel plate mounted on a strong frame directly above the closure. A laboratory shower and additional dry-chemical fire extinguishers were installed, warning signs were posted, and face masks and gloves were provided. As an added safety precaution, a special, less flammable hydraulic fluid was obtained. (See below.)

3. Hydraulic Fluids

White gasoline is commonly used as the hydraulic fluid in high-pressure equipment. As a safety precaution, we used a less flammable fluid (Univis P-38) for runs at less than 100,000 psi. Univis P-38 (Humble Oil & Refining Co.) is an ester-type hydraulic fluid which was developed for military aircraft and large gun recoil mechanisms. Unfortunately, it becomes highly viscous and therefore unusable above 120,000 psi.

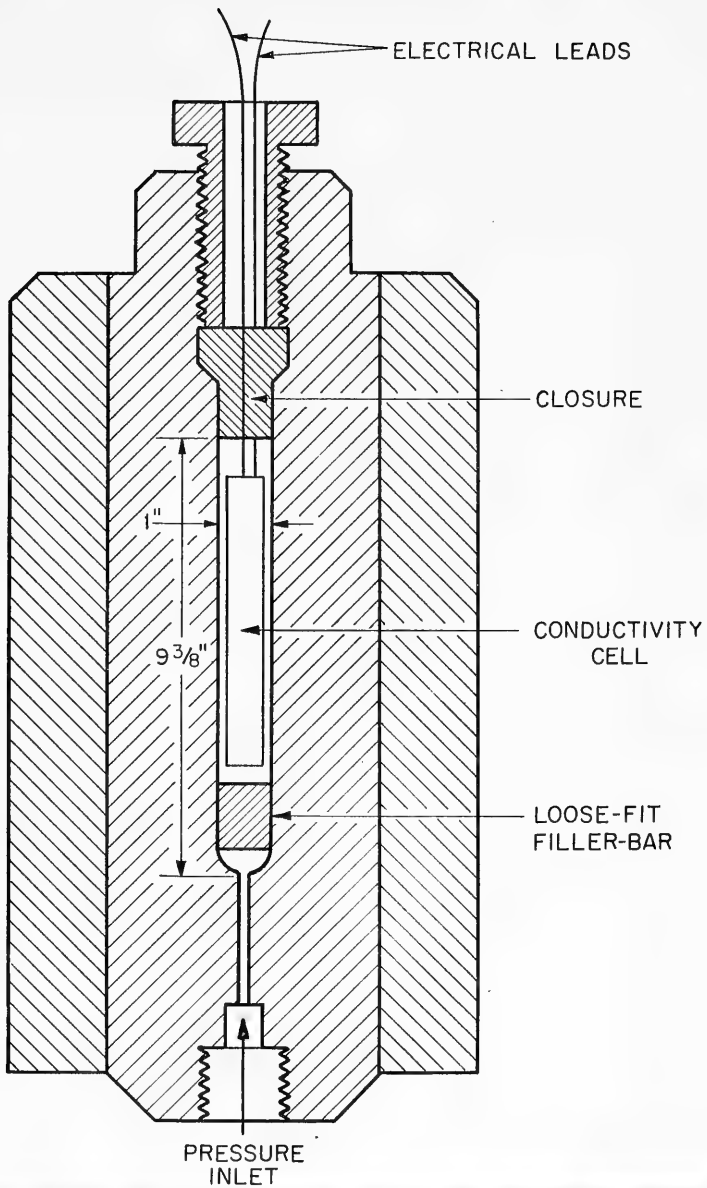


FIGURE 5 PRESSURE VESSEL

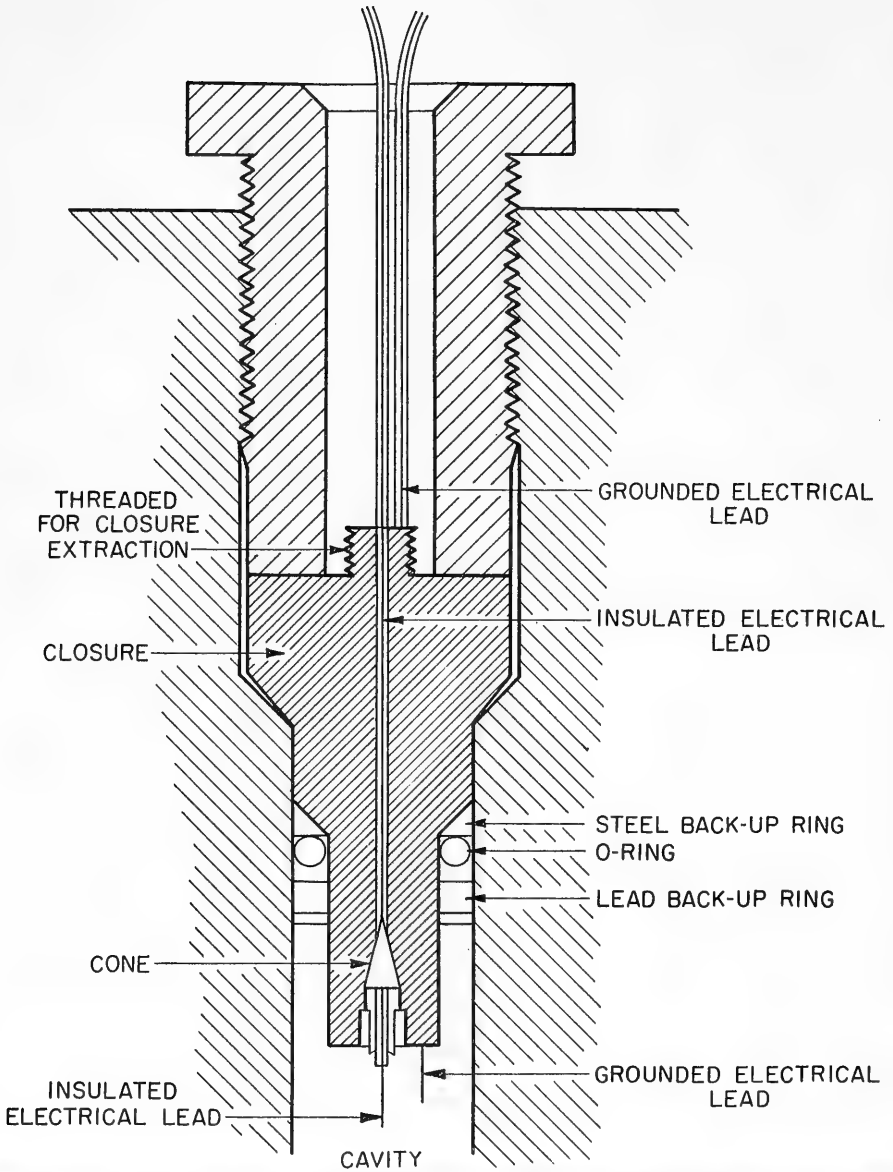


FIGURE 6 DETAILS OF PRESSURE VESSEL CLOSURE

Experiments showed that exposure to white gasoline and to Univis P-38 does not measurably alter the electrical conductivity of the aqueous electrolytic solutions under study.

B. TEMPERATURE CONTROL

The pressure vessel is submerged to within an inch of its upper shoulder in a 40-gallon thermostatic oil bath which is insulated with 2-5 inches of granular vermiculite. The temperature of the bath is controlled by a resistance heater and Fisher Model 44 thermoregulating unit with a thermistor probe. The manufacturer claims that this unit responds to temperature changes of $\pm 0.003^\circ\text{C}$ in the temperature range of interest. Initial temperature measurements were made with a National Bureau of Standards calibrated thermometer. A 10-junction, copper-constantan thermocouple was constructed and used in the data runs.

Deep-ocean temperatures correspond to a few degrees centigrade. A small compressor-type refrigeration unit for the thermostatic bath was designed and constructed by the Harris Manufacturing Co., Inc., to attain the low temperatures encountered in deep-ocean waters. This unit, in conjunction with the immersion heater, enables the bath to be operated over the range $0-50^\circ\text{C}$ (or a wider range if desired). This cooling unit and the thermocouple and potentiometer are shown installed in Figure 3.

C. CONDUCTIVITY CELLS

Two types of conductivity cells were constructed. The first of these was a Jamieson-type cell⁽⁵⁾ (see Figure 7) fabricated of Teflon, with parallel plate platinized platinum electrodes. Its cell constant is about 0.20. In this cell the hydrostatic pressure is transmitted to the electrolytic solution by a movable plug (see Figure 7). The plug is located some distance from the electrodes in order to minimize the effect of its position on the cell constant.

Since for more concentrated electrolyte solutions a cell with a larger cell constant is required, a special capillary cell (see Figure 8) with a cell constant of about 75 was designed, and a glass prototype was constructed. Due to differences in the compressibilities of glass and platinum, glass-platinum seals tend to fracture at high pressures; furthermore, a mercury contact sometimes contaminates the electrolyte.⁽⁶⁾ In order to avoid these difficulties, the special capillary-type cell (Figure 8) was designed with an electrolyte-hydraulic fluid boundary and with free platinum leads. Tests have shown that the hydraulic fluids used do not alter the resistivity of the electrolyte. The design of this cell was based on the thesis that the electrode snarls would behave as electrical volumes as far as ions in the capillary were concerned. Tests on a glass prototype cell do indeed indicate that the measured resistance of an electrolyte-filled cell

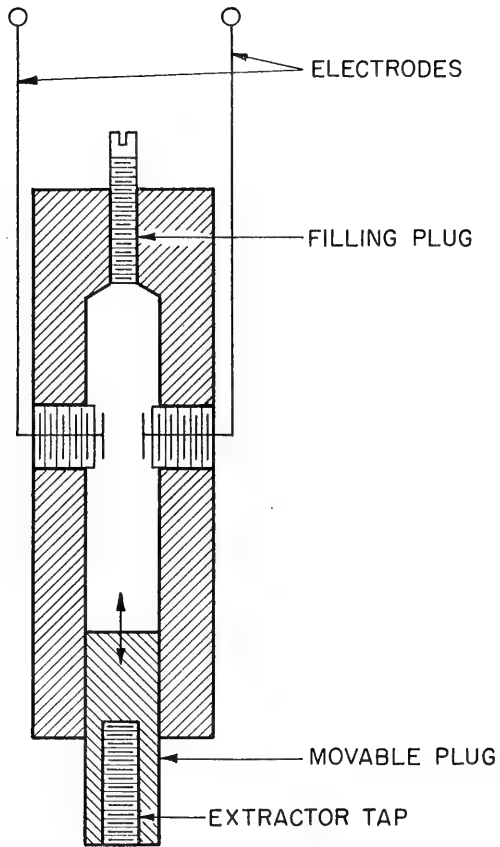


FIGURE 7 PARALLEL-PLATE-TYPE CONDUCTIVITY CELL

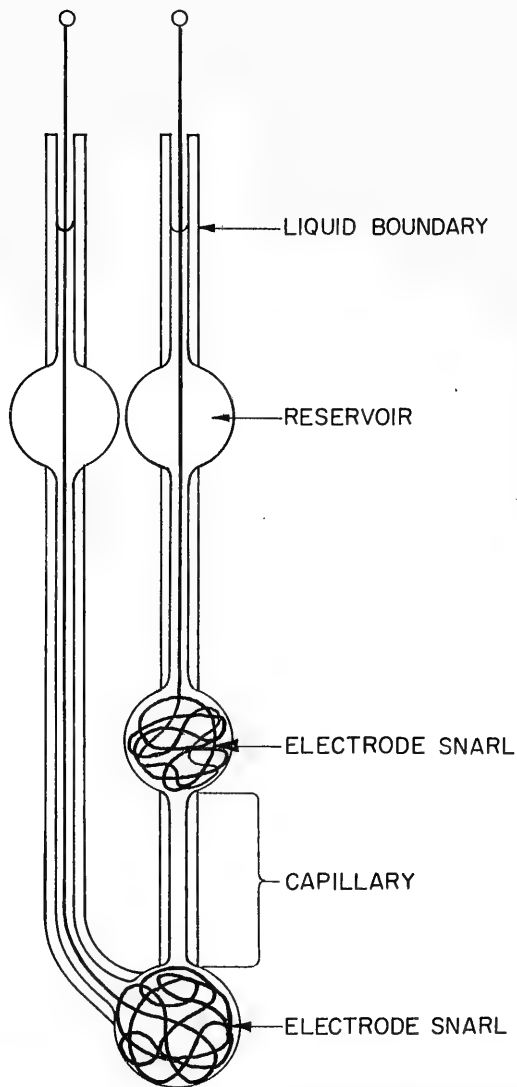


FIGURE 8 CAPILLARY-TYPE CONDUCTIVITY CELL (GCC-2)

is insensitive to the exact configuration of the electrode snarls. Another advantage of a capillary-type cell is that the correction of the cell constant for both changing temperature and pressure is relatively simple.

Since initial experiments suggested certain useful alterations in the design of the first glass capillary cell, GCC-1, a new cell, GCC-2, was constructed (Figure 9). The arms of this cell are bridged with a glass brace for added strength. Moreover, the volume of the reservoirs relative to that of the capillary and electrode compartments has been increased, in order to prevent the electrolyte level from falling below the upper electrode when high pressure is applied.

In order to reduce polarization, an aqueous chloroplatinic acid-lead acetate solution and procedure described by Creighton⁽⁷⁾ were used to platinize the platinum electrodes of both cells. We found that we could not platinize the electrodes of the capillary cell in the cell. Hence the platinum wires were platinized outside of the cell. The cell was then filled with solid NaCl up to the bottom of the upper electrode compartment. The platinized wire was fed into that arm of the cell through plastic "spaghetti," in order to avoid buckling in the reservoir, and was pushed into the solid NaCl to form the initial kink. Once the initial kink, which prevents the wire from entering the capillary, is formed, the rest of the electrode snarl can be formed without difficulty. The solid NaCl is next removed, and the electrode snarl in the lower electrode compartment formed by feeding the pre-platinized wire in through "spaghetti."

D. CONDUCTIVITY BRIDGE

A Shedlovsky conductivity bridge⁽⁸⁾ with a Wagner earth connection, based on the design of the bridge successfully used at the Sterling Chemistry Laboratory of Yale University for precision electrical conductivity measurements, has been constructed. The over-all arrangement of the principal components is shown in Figure 10, and the details of a Leeds & Northrup Campbell-Shackleton shielded ratio box are shown in Figure 11.

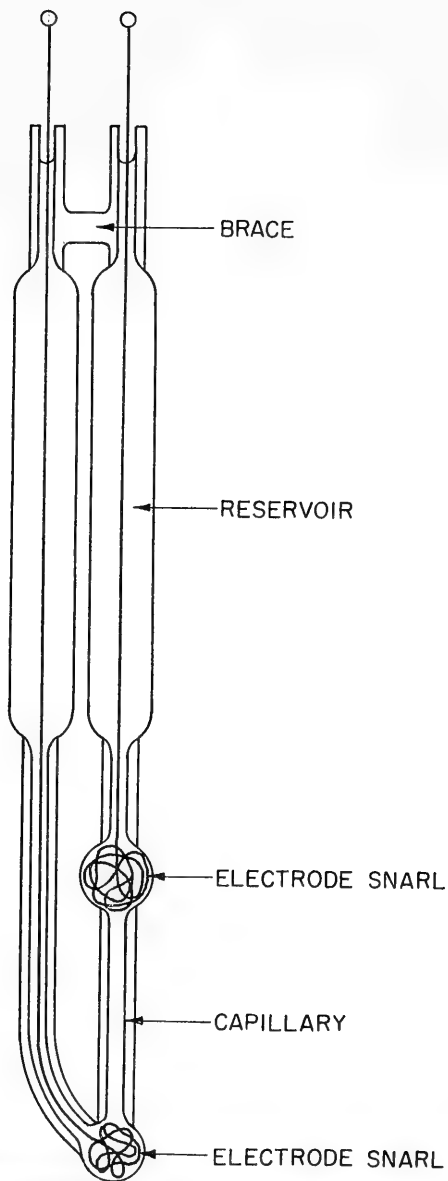


FIGURE 9 CAPILLARY-TYPE CONDUCTIVITY CELL (GCC-2)

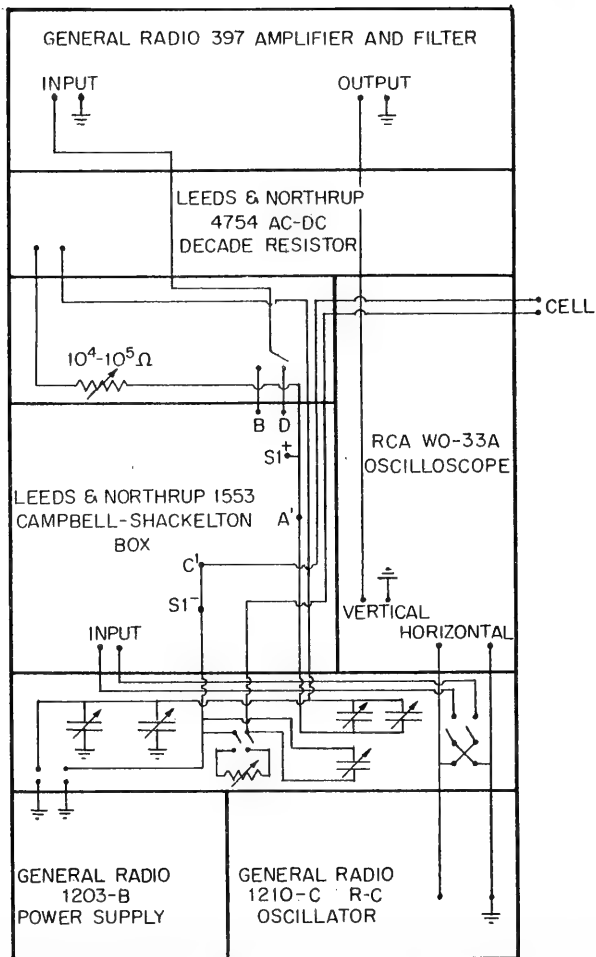


FIGURE 10 CONDUCTIVITY BRIDGE

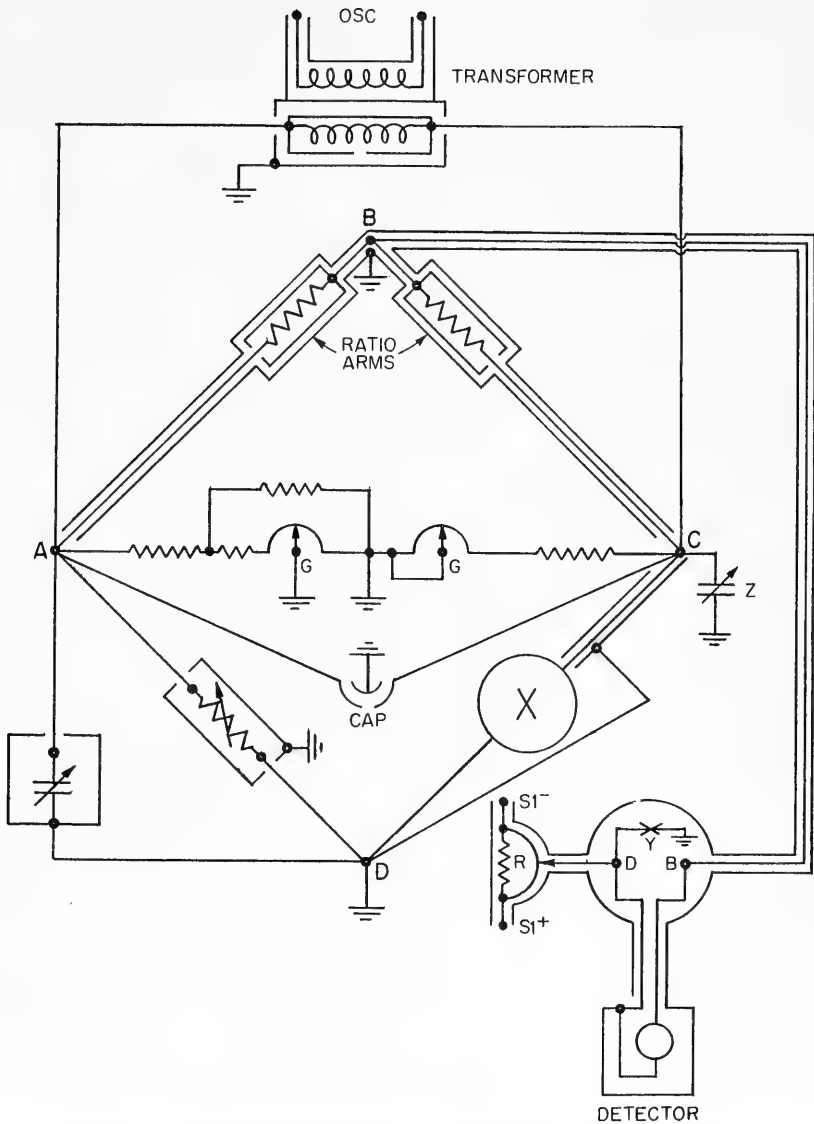


FIGURE 11 CONDUCTIVITY BRIDGE, SHIELDED RATIO BOX

IV. EQUIPMENT CALIBRATION

A. TEMPERATURE MEASUREMENT

In order to measure the thermostatic bath temperature to 0.005°C, a copper-constantan thermocouple was constructed. The emf's produced were measured with a Leeds & Northrup Model K-2 potentiometer, and the corresponding temperatures read from graphs that have been prepared.

Measurements comparing the temperature of the hydraulic fluid inside of the cavity of the pressure vessel with the temperature of the surrounding oil of the thermostatic bath were made. The results, given in Table I, show that, within the limits of experimental error, the temperature of the conductivity cell immersed in the hydraulic fluid inside the pressure vessel is the same as the bath temperature. Measurements were also made at 0 and 5°C. Within the deviation of the measurement, bath and cavity were at the same temperature. The temperature deviations within the bomb were significantly less than those in the bath, due to the thermal inertia of the massive pressure vessel. Measurements disclosed small (less than 0.5°C) temperature differences between the bottom and surface of the bath at different distances from the heating and cooling elements.

TABLE I

COMPARISON OF TEMPERATURE IN CAVITY AND BATH
(°C)

<u>Number of Measurements</u>	<u>In Bath</u>	<u>In Cavity</u>	
1st day			
6	24.533 ± 0.019		
6	24.170 ± 0.050		
10		24.405 ± 0.001	
8	24.453 ± 0.026		
	24.385	24.405	(ΔT = +0.020°C)
2nd day			
6	24.755 ± 0.001		
7		24.768 ± 0.011	
5	24.780 ± 0.001		
	24.767	24.768	(ΔT = +0.001°C)
3rd day			
10	24.787 ± 0.004		
8		24.790 ± 0.000	
5	24.790 ± 0.000		
	24.789	24.790	(ΔT = +0.001°C)
1	52.80	53.75	(ΔT = +0.95°C)
1	54.96	54.10	(ΔT = -0.86°C)
1	57.78	57.78	(ΔT = 0.00°C)

B. LEAD CORRECTIONS

The measured electrical resistance of the shielded leads from the conductivity bridge terminals of the closure is 0.46 ± 0.02 ohm. The resistance of the leads of the conductivity cells was calculated from their length and handbook values of the resistivity of No. 24 platinum wire. The lead corrections thus obtained for each cell are summarized in Table II. The dependence of the lead correction on temperature and pressure is negligible.

TABLE II

LEAD CORRECTIONS (25°C)

<u>Cell</u>	<u>Leads and Closure</u> (ohm)	<u>Length of Pt Leads</u> (inches)	<u>Pt Leads</u> (ohm)	<u>Total Correction</u> (ohm)
Teflon Jamieson (TJC-1)	0.54	10	0.12	0.66
Glass Capillary (GCC-1)	0.54	13	0.16	0.70
Glass Capillary (GCC-2)	0.54	11	0.14	0.68

The resistance of the solution-filled conductivity cell, R_c' , is given by

$$R_c' = R_m - L, \quad (1)$$

where R_m is the resistance as measured on the bridge, and L is the appropriate total basis correction from Table II.

C. CELL STABILITY

Considerable shielding and grounding difficulties were encountered, but have been for the most part removed. In particular, the conductivity bridge and the manganin cell recorder were interfering with one another. When the cell is in

the pressure vessel, interference pickup still restricts the number of obtainable significant figures, especially when the resistance is high. A filter was added to circumvent this difficulty but was not entirely effective.

Cell stability, i. e., invariance of resistance with time, is necessary in order to make precision conductivity measurements. Table III summarizes the results of measurements, at a frequency of 1000 cps, of total cell resistance, R_m , over extended time intervals. The several cells stabilize within approximately 20 minutes, and subsequent fluctuations are small and random. As mentioned above, the conductivity of the electrolytic solution is not altered by exposure to the hydraulic fluids.

TABLE III
CELL STABILITY

<u>Temperature</u> (°C)	<u>Solution</u> (M)	<u>Cell</u>	<u>Time</u> <u>Period</u> (hr)	<u>Deviation in</u> <u>the Measured</u> <u>Resistance, R_m</u> (%)
25.05 ± 0.03	0.020 KCl ^a	TJC-1	19	0.062
25.05 ± 0.04	1.00 KCl ^b	GCC-1	2.4	0.012
25.05 ± 0.03	0.20 KCl ^b	GCC-1	1.3	0.007
27.01 ± 0.04	0.20 KCl ^a	GCC-1	18	0.034
24.91 ± 0.01	0.10 KCl ^c	GCC-2	1	0.008

a. In contact with Univis P-38.

b. Open to the air.

c. In contact with white gasoline.

D. FREQUENCY DEPENDENCE

Cells for precision conductivity measurements should be so designed that electrical leads and any filling tubes are widely separated.⁽⁹⁾ However, since in the present experiments the entire cell must fit into a cavity approximately 9 inches long and 1 inch in diameter, such precautions are unfeasible. Improperly designed conductivity cells may exhibit a Parker effect.⁽¹⁰⁾ Jones

and Bollinger⁽¹¹⁾ have pointed out that this phenomenon is equivalent to a capacitor and a resistance in parallel with the resistance across the conductivity cell. The Parker effect becomes more pronounced with increasing frequency. A series of preliminary studies was conducted to detect any dependence of R_M on the frequency used for the measurement. The results, summarized in Table IV and in Figures 12 and 13, show that the measured resistance is not dependent upon the frequency of the measurement. Sodium bicarbonate was used in these studies, because the conductivity of solutions of this electrolyte is less likely to alter due to pickup of carbon dioxide from the air. A frequency of 1000 cps was chosen for all subsequent experiments.

E. WALL EFFECT

Although no frequency dependence was observed, the results in Table IV indicate that the measured resistance is somewhat less when the conductivity cell is inside of the pressure vessel than when it is outside immersed in the thermostatic bath. Table V presents further experiments designed to examine this effect. We performed all these experiments on cell TJC-1. The observed decreases in measured resistance when the cells are in the pressure vessel are summarized in Table VI. Although this effect is very small (less than 1%), we nevertheless applied a correction for it. The observed depression of measured resistance when the conductivity cells are within the pressure vessel was attributed to a resistance in parallel with that of the cell. The actual resistance of the conductivity cell, R_C , was calculated from the relation

$$\frac{1}{R_C} = \frac{1}{R_C'} - \frac{1}{R_S} \quad (2)$$

where R_C' is the measured resistance corrected by equation (1) for the resistance of the leads and closure, and R_S is spurious resistance in parallel with the cell. The resistivity of the hydraulic fluid is very large compared with that of the aqueous solutions in the cells; however, because one electrical lead is grounded to the pressure vessel, the cell is literally surrounded by a very large electrode. Although the scatter is large, Table VI shows that, roughly speaking, the percent reduction in measured resistance is independent of the value of the resistance being measured, that is to say

$$R_S \approx CR_C' \quad (3)$$

where C is a constant whose value, on the basis of the average reduction given in Table VI is about 240. The observation that C is roughly constant indicates that the spurious electrical path, at least in part, involves the electrolytic solution in the cell.

TABLE IV

FREQUENCY DEPENDENCE OVER THE RANGE 200 TO 20,000 cpsA. Total Resistance of the Teflon Jamieson Cell (TJC-1)

<u>Temperature</u> (°C)	<u>Electrolyte</u> (M NaHCO ₃)	<u>Total Electrical Resistance, ohms</u>	
		<u>Outside Bomb</u>	<u>Inside Bomb</u>
27.19 ± 0.08	0.10	43.98 ± 0.40	-
27.45 ± 0.04	0.10	-	43.56 ± 0.10
		(0.96% lower inside bomb) ₁	
26.10 ± 0.05	0.010	394.28 ± 0.21	-
26.18 ± 0.02	0.010	-	392.01 ± 0.16
		(0.55% lower inside bomb)	

B. Total Resistance of the Glass Capillary Cell (GCC-1)

27.01 ± 0.01	0.50	2360.18 ± 1.97	-
27.04 ± 0.01	0.50	-	2337.76 ± 2.12
		(0.95% lower inside bomb)	
27.00 ± 0.02	0.10	17,629 ± 25	-
27.01 ± 0.02	0.10	-	17,000 ± 10
		(0.42% lower inside bomb)	

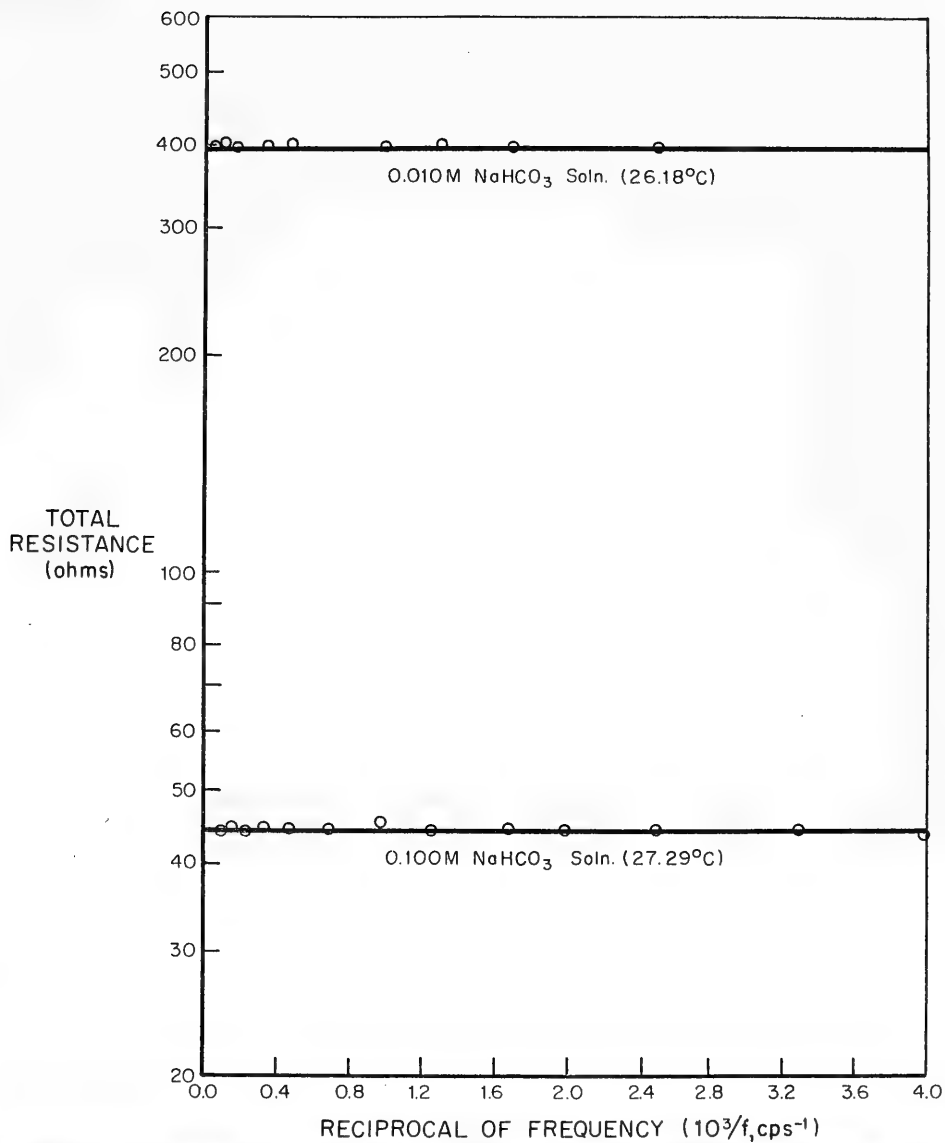


FIGURE 12 FREQUENCY DEPENDENCE OF THE
TEFLON JAMIESON-TYPE CELL (TJC-1)

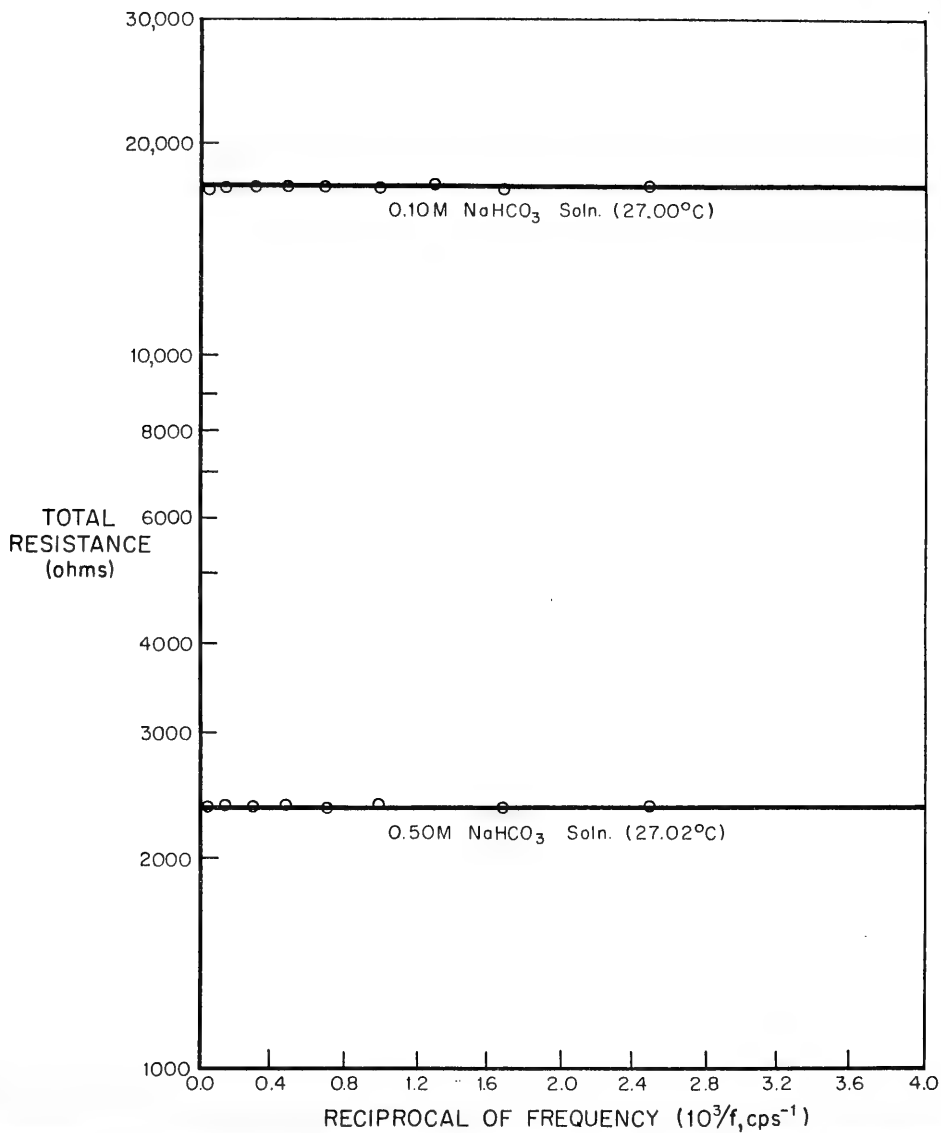


FIGURE 13 FREQUENCY DEPENDENCE OF THE GLASS CAPILLARY-TYPE CELL (GCC-1)

TABLE V

RESISTANCE INSIDE AND OUTSIDE THE BOMB

<u>Electrolyte</u> (M KCl)	<u>Temperature</u> (°C)	<u>Total Resistance, ohms</u>		<u>Number of</u> <u>Measurements</u>
		<u>In Bath</u>	<u>In Bomb</u>	
0.0100	25.05 ± 0.03		141.21 ± 0.08	4
0.0100	25.09 ± 0.03	141.02 ± 0.01		5
0.0100	25.04 ± 0.00		141.27 ± 0.02	5
0.0100	25.04 ± 0.01	141.28 ± 0.02		3
0.0100	25.02 ± 0.03		141.29 ± 0.01	6
0.0100	24.98 ± 0.08	141.28 ± 0.03		3
0.0100	24.91 ± 0.00	141.31 ± 0.02		2
	25.03 ± 0.04	141.22 ± 0.10	141.26 ± 0.03	
		(same in bomb and bath)		
0.0100	18.01 ± 0.05	159.94 ± 0.19		11
0.0100	18.02 ± 0.11		159.59 ± 0.05	8
0.0100	17.86 ± 0.00	159.86 ± 0.02		7
0.0100	18.09 ± 0.09		159.59 ± 0.03	8
0.0100	18.05 ± 0.06	159.88 ± 0.04		6
0.0100	17.90 ± 0.01		159.41 ± 0.18	5
	17.99 ± 0.07	159.89 ± 0.03	159.53 ± 0.08	
		(0.23% smaller in bomb than in bath)		
0.00100	18.08 ± 0.14	1480.14 ± 0.47		
0.00100	18.09 ± 0.01	1477.68 ± 0.09		
0.00100	17.99 ± 0.08		1479.53 ± 0.04	
	18.05 ± 0.04	1478.91 ± 1.23	1479.53	
		(same in bomb and bath)		
0.100	18.10 ± 0.23		17.81 ± 0.03	4
0.100	18.19 ± 0.09	17.89 ± 0.01		6
	18.14 ± 0.04	17.89	17.81	
		(0.45% smaller in bomb than in bath)		
0.00200	17.98 ± 0.01		728.46 ± 0.01	3
0.00200	17.90 ± 0.10	730.07 ± 0.37		8
	17.94 ± 0.04	730.07	728.46	
		(0.22% smaller in bomb than in bath)		

TABLE VIREDUCTION OF MEASURED RESISTANCE

<u>Electrolyte</u>	<u>Cell</u>	<u>Total Resistance in Bomb (ohms)</u>	<u>% Reduction in Bomb</u>
KCl	TJC-1	18	0.45
NaHCO ₃	TJC-1	44	0.96
KCl	TJC-1	141	0.00
KCl	TJC-1	160	0.23
NaHCO ₃	TJC-1	392	0.55
KCl	TJC-1	728	0.22
KCl	TJC-1	1,480	0.00
NaHCO ₃	GCC-2	2,337	0.95
NaHCO ₃	GCC-2	17,629	0.42
			<hr/> 0.42 ± 0.27

In order to measure R_S directly, the resistance of the cell (TJC-1 filled with 0.1 M KCl) in the pressure vessel was measured with an ohmmeter (the bridge could not be balanced) with the grounded lead between the closure and the cell electrode disconnected. The measured resistance was 5000 to 5700 ohms, corresponding to a value of C of 280 to 320. This was considered good agreement.

The variation of C with pressure cannot be measured, but is presumably negligible. In the pressure runs, the cell constant at 1 atmosphere is calculated directly from R_C and the value of C determined by measurements inside and outside the bath using the appropriate electrolyte (the manner of calculating cell constants is discussed in greater detail below). The cell constants at given pressures are then calculated on the basis of this cell constant. Thus C becomes absorbed in the cell constant, and the value of the specific conductance becomes very insensitive to the value of C. For example, for 19.376‰ chlorinity sea water at 4.82°C, with cell GCC-2, the measured value of C is 125, and at a pressure of 20,000 lb/in.² the corresponding value of the specific conductance is 0.03811 ohm⁻¹ cm⁻¹. If the value of C is increased fivefold to 600, the specific conductance becomes 0.03816 ohm⁻¹ cm⁻¹, a change of only 0.13%; and if C becomes infinite, the specific conductance becomes 0.03817 ohm⁻¹ cm⁻¹.

F. PLUG POSITION AND LIQUID LEVEL EFFECTS

Although the movable plug of the Teflon Jamieson cell (TJC-1) is located remotely from the electrodes (see Figure 7), there is a detectable influence of plug position on the measured resistance.⁽¹²⁾ This effect was measured at 25.2°C and 1 atmosphere, and the following relationship was found to obtain:

$$R_C'' = R_C / (1 + 0.00262 d) \quad (4)$$

where R_C'' is the resistance of TJC-1 when the lower end of the plug is flush with the lower end of the cell's wall, and d is the displacement (in inches) of the plug. As the pressure is increased, the electrolyte in the cell is compressed and the plug is displaced. Assuming that the variation in cross sectional area of the cell with pressure is negligible, equation (4) can be rewritten in terms of pressure as

$$R_C'' = R_C / (1 - 0.0105 k'P) \quad (5)$$

where the pressure, P, is in atm and k' is the mean compressibility of the electrolyte in atm⁻¹. When the electrolyte is water, at 20,000 lb/in.² the denominator on the right of equation (5) has the value 0.993.

At 25°C, and with 1.0 M KCl as electrolyte, the measured total resistance of the glass capillary cell GCC-2 varied by less than 0.003% as the electrolyte level in the cell was varied from the top to the bottom of the reservoir. Inasmuch as this error lies within the experimental deviation, the conclusion is drawn that the measured resistance is independent of the position of the hydraulic fluid-electrolyte interface in the capillary-type cell.

G. DETERMINATION OF CELL CONSTANTS

Cell constant measurements were made with the cells both in the bath and within the pressure vessel. Measurements and computations involving KCl were based on the procedures and results of Jones and Bradshaw, (13) while for NaCl and sea water the cell constants were computed from the specific conductances reported by Chambers, Stokes, and Stokes, (14) and Thomas, Thompson, and Utterback. (15) The results of these measurements are summarized in Table VII. In the case of the Jamieson cell (TJC-1), the measured cell constant was only in fair agreement with that calculated from cell dimensions, probably due to the nonparallelism of the electrodes; in the case of the glass capillary cells (GCC-1) and (GCC-2), the agreement was good.

The deviations in cell constant in Table VII are somewhat greater than is desirable in conductivity measurements of the highest precision. Also, for GCC-2, the values determined using KCl are about 8% greater than the values determined using sea water or 0.500 M NaCl. In the case of GCC-2, the large cell constant and the upper limit of the conductivity bridge's capacity prevents cell constant determinations using dilute KCl solutions. Because of these difficulties and the spurious parallel resistance effect discussed above, in order to get entirely self-consistent results and to make the present results compatible with the 1 atmosphere values now being used by oceanographers, we decided to base our calculations on cell constants as determined immediately before and after each pressure run and using the electrolyte of the run. In the case of the sea water run, this procedure makes the correctness of the specific conductances we report contingent upon the 1 atmosphere values reported by Thomas, Thompson, and Utterback. (15)

The accuracy of the results of Thomas, Thompson and Utterback has been questioned on several occasions. In particular, Pollak (16) has suggested that their results may be in error due to a Parker effect. In the event that more accurate values for the specific conductance of sea water become available, the values which we report for specific conductances can be readily corrected simply by multiplying by the factor K_n/K_{ttu} , where K_n is the new value of the specific conductance and K_{ttu} is the value reported by Thomas, Thompson, and Utterback at the same chlorinity and temperature. The values of the constants in the empirical equations which we will generate subsequently for expressing the specific conductance at elevated pressure in terms of the 1 atmosphere value will be unaffected, inasmuch as the above correction factors out.

TABLE VII

CELL CONSTANT DETERMINATIONS

<u>Cell</u>	<u>Temperature</u> (°C)	<u>Electrolyte</u>	<u>Cell Constant</u> (cm ⁻¹)	
TJC-1	0.93 ± 0.03	19.376 ^o /oo sea water	0.216	
	5.11 ± 0.12	19.376 ^o /oo sea water	0.227	
	15.20 ± 0.02	19.376 ^o /oo sea water	0.198	
	18.20 ± 0.10	0.001 M KCl	0.181	} 0.193 ± 0.0
	18.20 ± 0.05	0.002 M KCl	0.178	
	18.03 ± 0.07	0.010 M KCl	0.195	
	18.20 ± 0.10	0.100 M KCl	0.217	
	25.00 ± 0.02	19.376 ^o /oo sea water	0.194	} 0.196 ± 0.004
	25.00 ± 0.00	0.010 M KCl	0.200	
	25.02 ± 0.03	0.010 M KCl	0.200	
	25.03 ± 0.06	0.010 M KCl	0.192	
	25.08 ± 0.10	0.010 M KCl	0.185	
	25.40 ± 0.05	0.010 M KCl	0.195	
	25.06 ± 0.02	0.020 M KCl	0.195	
	25.00 ± 0.01	0.100 M KCl	0.195	
	25.02 ± 0.02	0.200 M KCl	0.193	
	25.13 ± 0.09	0.200 M KCl	0.199	
	25.40 ± 0.05	1.00 M KCl	0.205	
	25.00 ± 0.05	1.00 M KCl	0.203	
	35.20 ± 0.11	0.010 M KCl	0.187	
44.98 ± 0.03	0.010 M KCl	0.184		
GCC-1	25.25 ± 0.04	0.010 M KCl	79.88	
	25.25 ± 0.04	0.100 M KCl	75.90	
	25.60 ± 0.00	1.00 M KCl	79.45	
	25.00 ± 0.08	1.00 M KCl	79.43	

TABLE VII (Continued)

<u>Cell</u>	<u>Temperature</u> (°C)	<u>Electrolyte</u>	<u>Cell Constant</u> (cm ⁻¹)
GCC-2	0.18 ± 0.05	19.376 ^o /oo sea water	164.0
	0.27 ± 0.10	19.376 ^o /oo sea water	164.66
	0.08 ± 0.07	17.61 ^o /oo sea water	165.01
	0.00 ± 0.00	9.68 ^o /oo sea water	163.9
	0.00 ± 0.02	1.00 M KCl	177.0
	4.82 ± 0.06	19.376 ^o /oo sea water	165.1
	5.01 ± 0.20	17.61 ^o /oo sea water	165.9
	4.94 ± 0.14	9.68 ^o /oo sea water	164.9
	15.01 ± 0.02	17.61 ^o /oo sea water	162.1
	14.83 ± 0.15	9.68 ^o /oo sea water	165.2
	18.05 ± 0.10	0.100 M KCl	180
	25.00 ± 0.02	19.376 ^o /oo sea water	164.96
	24.91 ± 0.02	19.376 ^o /oo sea water	167.1
	24.83 ± 0.07	17.61 ^o /oo sea water	168.0
	25.06 ± 0.02	9.68 ^o /oo sea water	166.6
	25.20 ± 0.05	0.100 M KCl	179
	25.10 ± 0.08	1.00 M KCl	175.6
	24.95 ± 0.01	0.400 M NaCl	166.62

164.4 ± 0.5

165.0 ± 0.4

163.6 ± 1.5

166.7 ± 0.9

Due to limitations of time, we were unable to perform a complete check on the work of Thomas, Thompson, and Utterback, although there appears to exist enough question concerning their work to warrant its repetition with carefully designed conductivity cells.

H. PRESSURE DEPENDENCE OF CELL CONSTANTS

The geometrical dimensions of the conductivity cells and hence their cell constants will vary as the hydrostatic pressure exerted on the cells is varied, due to the compressibility of the materials of which the cells are constructed.

The electrodes in the Jamieson cell are remote from the ends of the cylindrical cell, and, as a consequence (except for the effect of the position of the movable plug, discussed above), will have a negligible influence upon the value of the cell constant. Figure 14 represents a cross section of this cell in the region of the electrodes. The inside radius of the cell is r , the distance between the parallel plate electrodes is d , the surface area of the electrodes is A ($A = 2r^2$, where S is the length of the edge of the square electrode surfaces), and e is the length of the leads from the electrodes to the cell walls. Now

$$d = 2r - 2e \quad (6)$$

The linear compressibility, $\Delta l/l$, of platinum at 30°C given by the International Critical Tables⁽¹⁷⁾ is

$$\Delta l/l = 0.124 \times 10^{-6} P - 0.63 \times 10^{-12} P^2, \quad (7)$$

where P is the pressure in atmospheres. The linear compressibility of Teflon may be approximated by 1/3 of the volume compressibility, $(\Delta V/V)$. Thus (6) becomes

$$d_p = 2r_1 (1 - 1/3 (\Delta V/V)) - 2e_1 (1 - 0.124 \times 10^{-6} P + 0.63 \times 10^{-12} P^2) \quad (8)$$

and the cell constant becomes

$$k_p = \frac{d_p}{A_p} = \frac{2r_1 \left[1 - 1/3 (\Delta V/V) \right] - 2e_1 (1 - 0.124 \times 10^{-6} P + 0.63 \times 10^{-12} P^2)}{\left[S_p (1 - 0.124 \times 10^{-6} P + 0.63 \times 10^{-12} P^2) \right]^2} \quad (9)$$

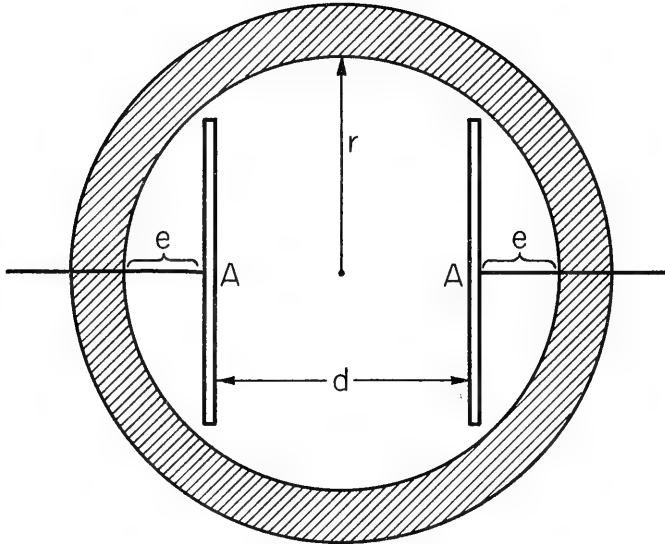


FIGURE 14 JAMIESON CELL, CROSS SECTION

The elastic properties of platinum change by less than 0.01% per degree centigrade; therefore, the temperature dependence of $\Delta l/l$ has been ignored. Unfortunately, the behavior of Teflon under compression appears to be complex, involving a 2.3% contraction in volume at 5000 atm at room temperature. (17, 18, 19, 20) The proposed phase diagram for Teflon is shown in Figure 15. Values of $\Delta V/V$ for Teflon at the appropriate pressures and temperatures were read from a plot of the data of Weir⁽²¹⁾ (Figure 16). Over the pressure range of our experiments, changes due to change in the dimensions of platinum parts were relatively small, so when S and r are expressed in cm, equation (9) becomes

$$k_P = 2r_1 \left[1 - 1/3 (\Delta V/V) \right] - 1.077. \quad (10)$$

As mentioned above, r_1 was determined from conductivity measurements immediately prior to the application of pressure.

Examination of the results summarized in Tables IX to XI (see Section VI) shows that the variation with pressure of the constant of TJC-1 is quite appreciable and represents about a 6% decrease at 30,000 lb/in.².

In the case of the glass capillary cell, the pressure dependence of the cell constant takes a very simple form

$$k_P = k_1 / (1 - 1.08 \times 10^{-7} P), \quad (11)$$

Q (too high by about 50%)

where P is now in lb/in.². When P is expressed in bars the constant becomes 1.57×10^{-6} . In contrast with the pronounced pressure dependence of the Teflon cell constant, the constants for the glass cells increase only a few tenths of a percent at 20,000 lb/in.².

Although the Teflon and glass cells have entirely different pressure dependencies of their cell constants, results obtained with these two types of cells were in surprisingly good agreement (see Figure 22).

I. EQUILIBRATION

In our first experiment the electrical resistance of a 0.010 M KCl solution was measured as the pressure was continuously varied from 15 to 100,000 lb/in.² and back to 15 lb/in.². The pressure was varied rapidly, and the run was completed in about two hours. Serious hysteresis was observed (Figure 17); that is, the curve did not retrace itself as the pressure was decreased. This hysteresis was attributed to failure of the system to thermally equilibrate. This possibility was experimentally checked and confirmed.

The heat of compression of a fluid

$$\left(\frac{dQ}{dP} \right)_T = T \left(\frac{dv}{dT} \right)_P \quad (12)$$

is usually positive; thus, heat is released when a fluid is compressed and absorbed when the fluid is allowed to expand. If compression or expansion is rapid, and heat conduction into the surroundings is slow, then the process will be an adiabatic one, and the temperature will increase or decrease, respectively.⁽²²⁾ In the present experiments, rapid compression will result in a momentary increase of temperature and a corresponding transient decrease of measured electrical resistance (see Figure 18); rapid decompression will give rise to a transient increase of resistance (see Figure 19). These experiments indicated that re-establishment of thermal equilibrium requires about 20 minutes. In all subsequent experiments, resistance readings were made following each pressure change until a constant was obtained.

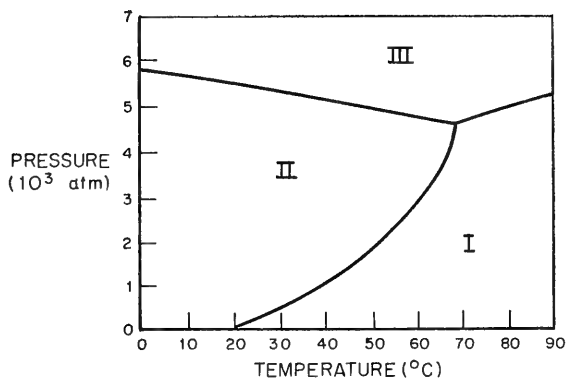


FIGURE 15 PROPOSED PHASE DIAGRAM OF TEFLON
(C. E. Weir, J. Research Nat. Bur.
Standards, 50, 95 (1953))

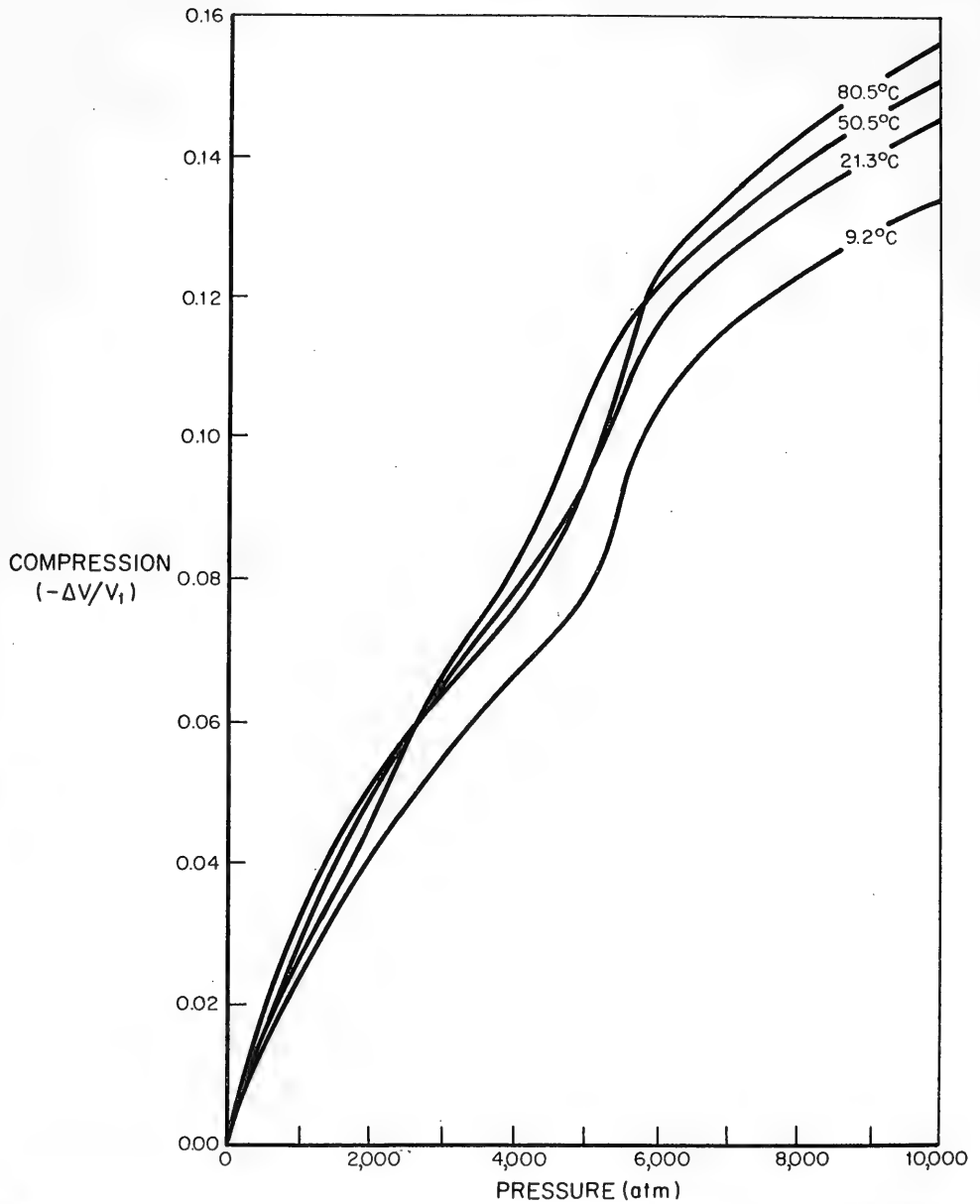


FIGURE 16 RELATIVE VOLUME CHANGES FOR TEFLON
(C. E. Weir, J. Research Nat. Bur. Standards,
53, 245 (1954))

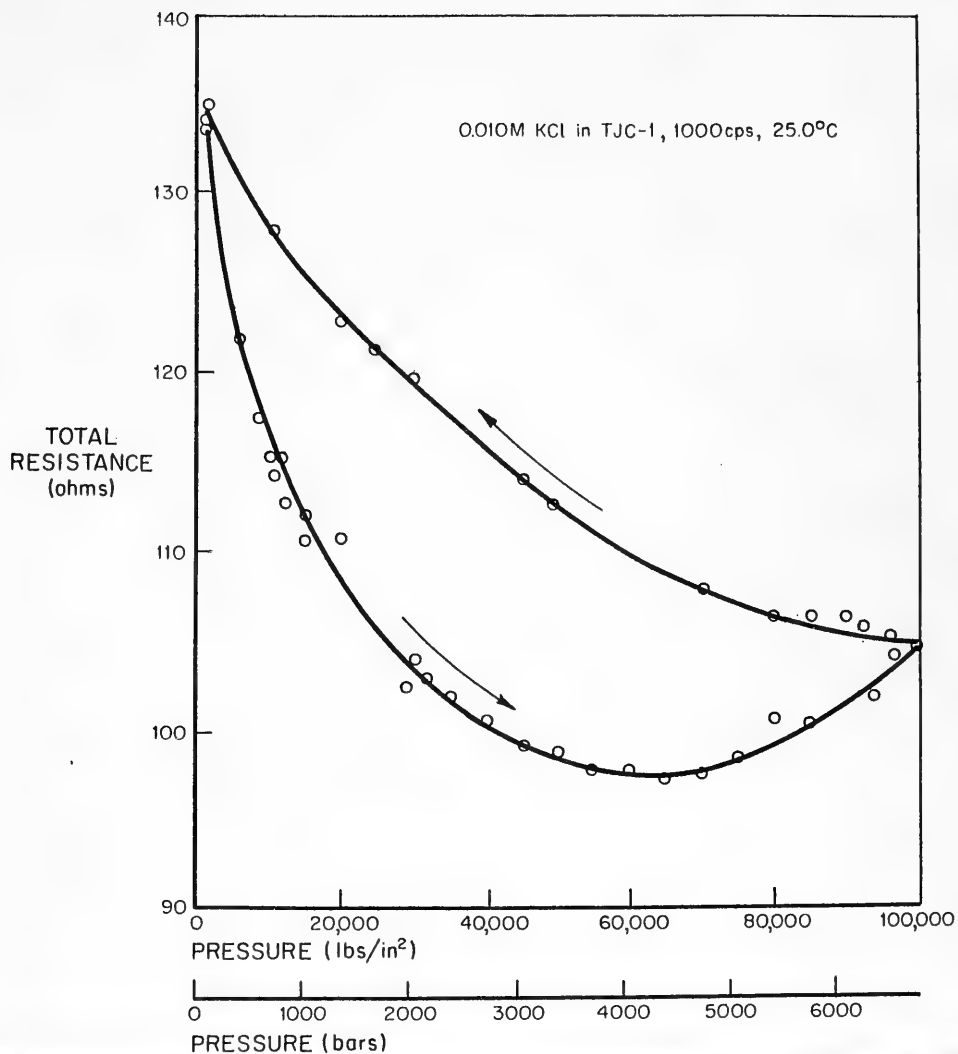


FIGURE 17 HYSTERESIS DUE TO FAILURE OF SYSTEM
TO THERMALLY EQUILIBRATE

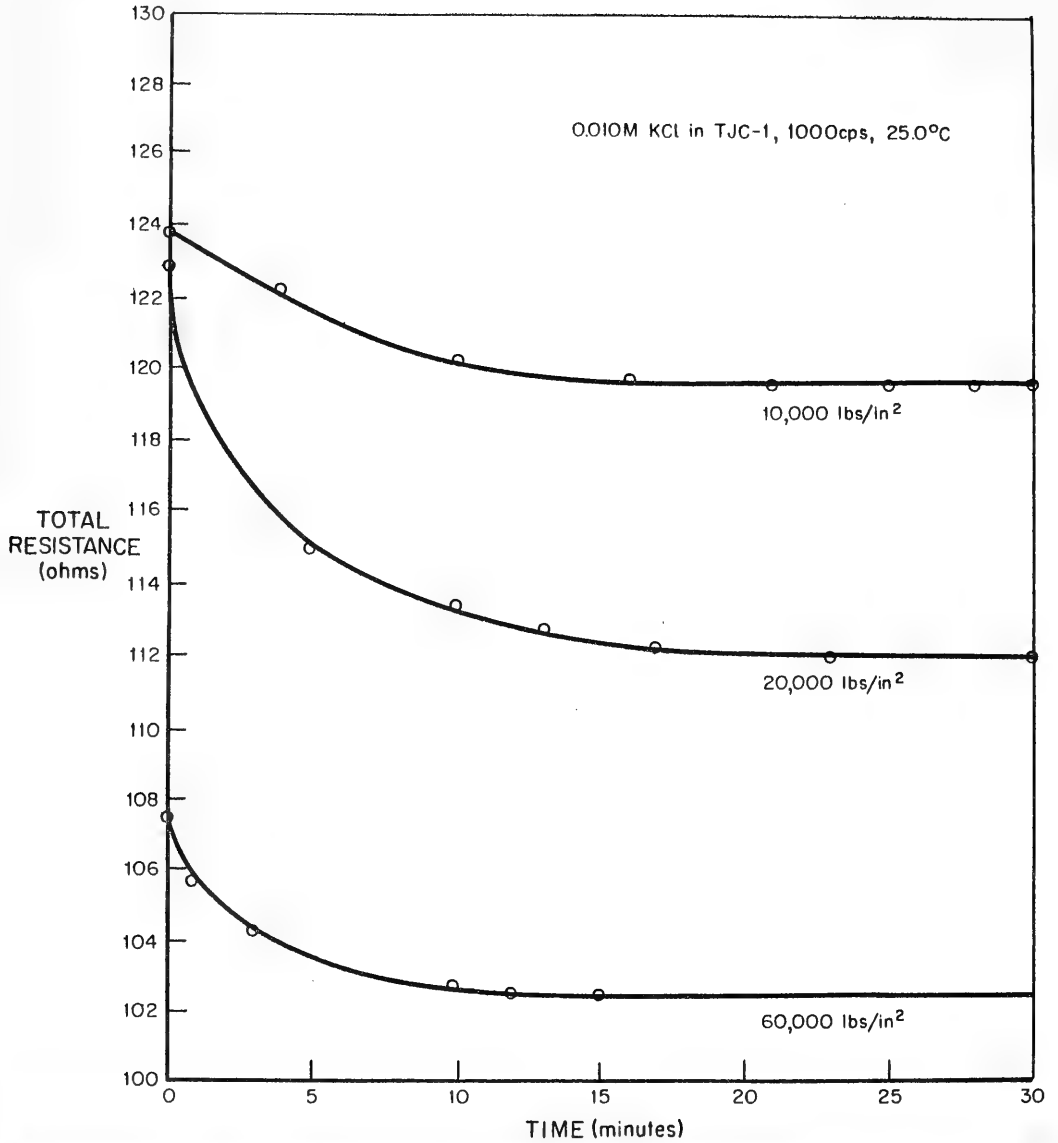


FIGURE 18 EQUILIBRATION TIME AT PRESSURE - PRESSURE APPROACHED FROM ABOVE

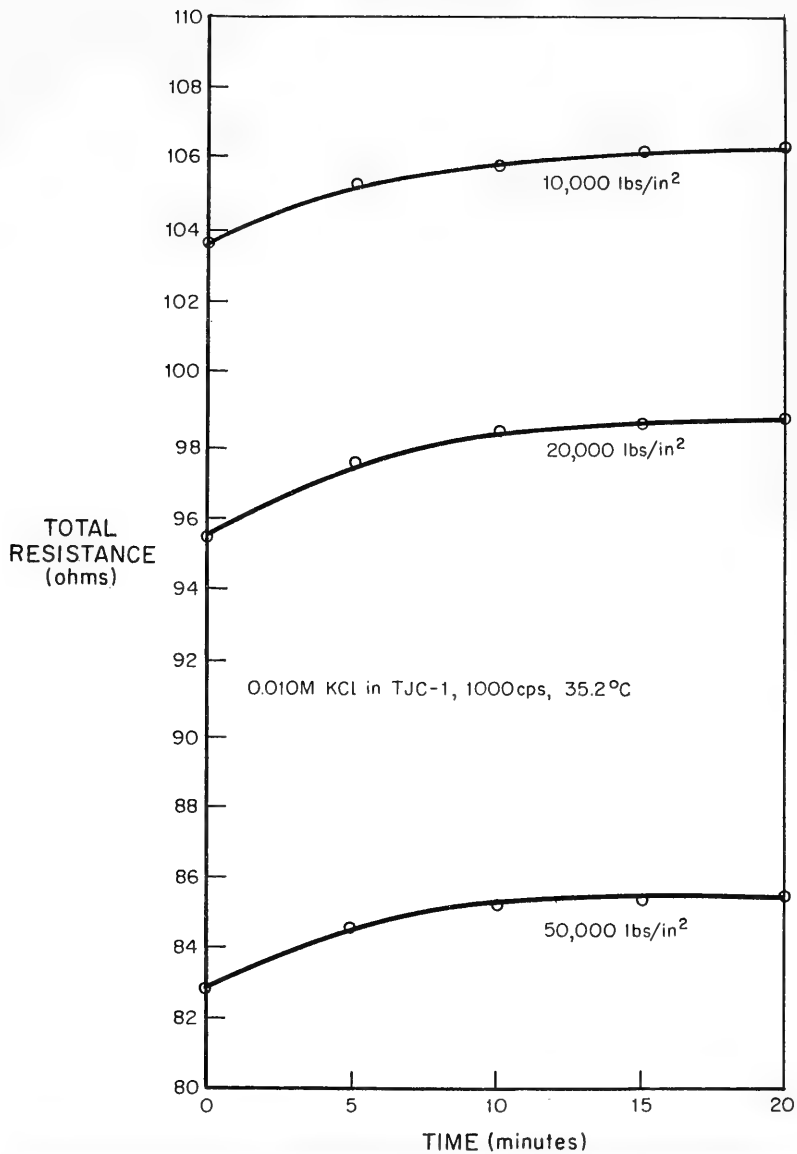


FIGURE 19 EQUILIBRATION TIME AT PRESSURE - PRESSURE APPROACHED FROM BELOW

V. THE EFFECT OF PRESSURE ON THE ELECTRICAL CONDUCTIVITY OF AQUEOUS POTASSIUM CHLORIDE SOLUTIONS

The molal conductance of an aqueous solution 0.010 m in KCl was measured at 25, 35, and 45°C over the pressure range 15 to 100,000 lb/in.² in TJC-1 at a frequency of 1000 cps. In each experiment the cell constant at 1 atmosphere was calculated on the basis of the measured corrected resistance, and the values of the molal conductance were calculated at the corresponding temperatures (see Figure 20). The results are summarized in Table VIII and Figure 21.

At 45°C and at pressures below 60,000 lb/in.² the present results are in satisfactory agreement with the results reported earlier by Hamann and Strauss.⁽²³⁾ Discrepancies in the two sets of data appear above 60,000 lb/in.². There are so many uncertainties involved in calculating the constant of the Teflon cell at higher pressures that it remains problematic how much significance can be assigned to these discrepancies.

At 25°C the present results and those of Hamann and Strauss are in poor agreement. The causes of this discrepancy are not clear. We place the greater confidence in our own results for the following reasons:

1. Our 25°C curve more closely parallels the 35°C curve than does their curve.
2. The Teflon cell results were in agreement with our glass cell results.
3. There appears to be less scatter in our results.
4. Our change in the relative molal conductance of KCl with pressure is initially in agreement with the relative change in resistance measured by Adams and Hall.⁽²⁴⁾

With respect to the latter consideration, Adams and Hall, using a glass conductivity cell made very careful measurements of the relative resistance, R_p/R_1 , of a fairly concentrated (0.3730 weight %) KCl solution over the pressure range 15 to 26,800 lb/in.². They did not attempt to estimate cell constants and thereby obtain conductances. It can be shown that R_p/R_1 should vary with pressure in the same way as does the reciprocal of the relative conductance ($1/(\Lambda_p/\Lambda_1)$). Until the variation of the cell constant with pressure becomes significant, the initial slopes of R_p/R_1 and Λ_1/Λ_p should be the same. Up to 5000 lb/in.² a plot of the present values of Λ_1/Λ_p versus P has the same slope as the plot of Adams' and Hall's value of R_p/R_1 versus P. However, a plot of Hamann's and Strauss'

values of Λ_1 / Λ_p versus P has a slope whose absolute value is one half the value of the other two plots. Hamann and Strauss mention that their results also differ (by several percent at 10,000 atm) from those of Zisman,⁽²⁵⁾ and they attribute this discrepancy to contamination of Zisman's solutions by direct contact with his kerosene pressure fluid.

The conductance of KCl first increases with increasing pressure, goes through a maximum at about 30,000 lb/in.², and then decreases (see Figure 21). Solutions of other strong salts show similar behavior.⁽²⁵⁾ Hamann attributes the initial increase to the increase in the number of ions per unit volume as the solution is compressed, and the subsequent decline to decreasing ionic mobility with increasing viscosity of the solvent.^(12, 23) We shall see subsequently that this explanation is probably an oversimplification.

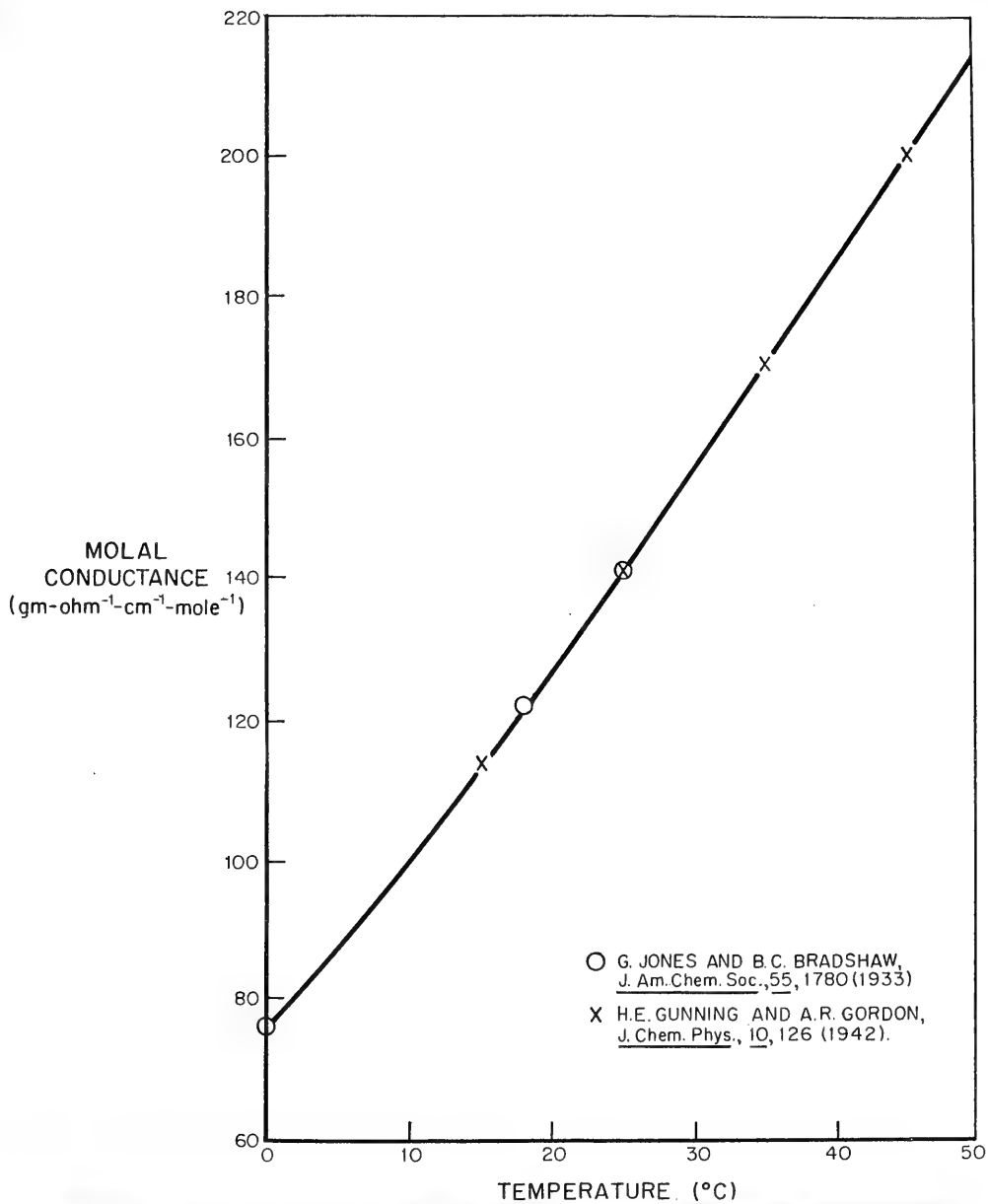


FIGURE 20 MOLAL CONDUCTANCE OF AQUEOUS 0.010 m KCl SOLUTIONS

TABLE VIII

MOLAL CONDUCTANCE OF 0.010 m KCl SOLUTIONS*

	Pressure		Molal Conductance in $\text{gm-ohm}^{-1}\text{-cm}^{-1}\text{-mole}^{-1}$		
	(lb/in. ²)	(bars)	(atm)	(25°C)	(35°C)
15	1.03	1	141	170	199
5,000	344	340	145	-	-
10,000	689	680	150	178	205
15,000	1030	1020	155	-	-
20,000	1380	1360	157	184	-
30,000	2070	2040	158	187	215
40,000	2760	2730	157	185	-
50,000	3440	3400	155	182	211
60,000	4140	4080	152	179	208
70,000	4820	4770	147	174	201
80,000	5510	5440	-	166	196
90,000	6200	6130	-	158	-
100,000	6890	6800	-	-	183

*For dilute solutions, molality and molarity are approximately equal.

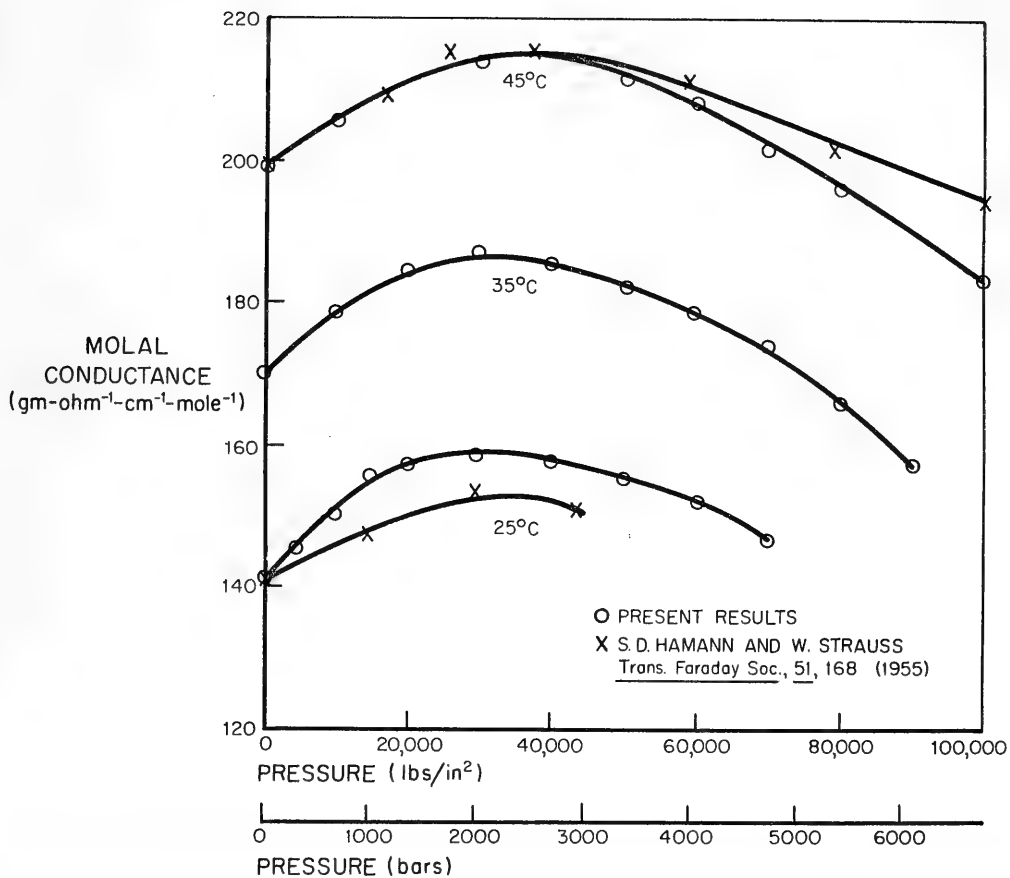


FIGURE 21 MOLAL CONDUCTANCE OF 0.010 m KCl SOLUTIONS

VI. THE EFFECT OF PRESSURE ON THE ELECTRICAL
CONDUCTIVITY OF SEA WATER

The standard sea water used in the present experiments was P₃₂(8/1/61), obtained from the I.A.P.O. Standard Sea Water Service of Charlottenlund Slot, Denmark. Its chlorinity, Cl, was 19.376 ‰; its salinity, S, calculated from the definition⁽²⁶⁾

$$S = 0.03 + (1.805) Cl, \quad (13)$$

was 35.00 ‰. In addition, sea water solutions of 17.61 ‰ and 9.68 ‰ chlorinity (31.81 ‰ and 17.50 ‰ salinity) were prepared by weight dilutions. Inasmuch as deionized water of specific conductance less than $1 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ was used for these dilutions, the contribution to the conductance from the water used for dilution is negligible (less than 0.05%).

The experimental results are summarized in Tables IX, X, and XI, and Figures 22, 23, and 24. The specific conductance, K, is given by

$$K = k/R, \quad (14)$$

where k is the cell constant and R the resistance.

The experimental results in Tables IX to XI and Figures 22 to 24 exhibit a number of interesting features. In the first place, it is important to notice that the pressure dependence of the specific conductance of sea water over the range of oceanographic interest (15,000 lb/in.²) is of comparable magnitude to the temperature dependence over the temperature range of interest (5°C). This finding emphasizes the importance of considering both pressure (or depth) and temperature when taking in situ conductivity measurements.

At a given salinity the plots of specific conductance versus pressure are nearly linear for most of the pressure range of interest (up to 10,000 lb/in.²), and, furthermore, the plots at different temperatures appear to have very nearly the same slopes, $\Delta K/\Delta P$.

Table XII summarizes the values of these slopes. Inasmuch as these values are ratios of differences, a great deal of the accuracy of the original data has been lost. But, although no temperature dependence of the values of $\Delta K/\Delta P$ is evident from Table XII, there does appear to be an increase in the value of $\Delta K/\Delta P$ with increasing chlorinity. This is shown more clearly in Figure 25.

TABLE IX

SPECIFIC CONDUCTANCE OF 19.376 ‰ CHLORINITY SEA WATER

<u>Pressure</u>		<u>Resistance</u>	<u>Cell</u>	<u>Specific</u>
<u>(lb/in.²)</u>	<u>(bars)</u>	<u>(ohms)</u>	<u>Constant, k</u>	<u>Conductance, K</u>
			<u>(cm⁻¹)</u>	<u>(ohm⁻¹cm⁻¹)</u>
Run No. 8, 0.93 ± 0.03°C, TJC-1				
15	1.03	7.18	0.216	0.0301
4,500	310	6.78	0.213	0.0314
8,000	550	6.52	0.209	0.0321
12,000	827	6.24	0.208	0.0332
15,000	1,030	6.12	0.207	0.0338
20,000	1,380	5.92	0.206	0.0349
Run No. 11, 0.18 ± 0.05°C, GCC-2				
15	1.03	5630	164.0	0.02913
5,000	344	5396	164.1	0.03034
10,000	689	5228	164.3	0.03143
15,000	1,030	5100	164.4	0.03224
20,000	1,380	5043	164.5	0.03268
25,000	1,720	4973	164.6	0.03310
Run No. 9, 5.11 ± 0.12°C, TJC-1				
15	1.03	6.77	0.227	0.0335
2,000	138	6.57	0.224	0.0341
4,000	276	6.36	0.222	0.0349
6,000	413	6.21	0.221	0.0356
8,000	551	6.08	0.219	0.0360
10,000	689	5.94	0.218	0.0367
12,000	827	5.82	0.217	0.0373
14,000	965	5.74	0.216	0.0377
16,000	1,100	5.67	0.216	0.0381
18,000	1,240	5.55	0.215	0.0388
20,000	1,380	5.50	0.214	0.0389
25,000	1,720	5.39	0.214	0.0397
30,000	2,070	5.28	0.213	0.0403
25,000	1,720	5.41	0.214	0.0396
22,500	1,550	5.43	0.214	0.0342
21,000	1,480	5.47	0.214	0.0389
19,000	1,310	5.55	0.214	0.0393
13,500	930	5.70	0.216	0.0379
15	1.03	6.77	0.227	0.0335

TABLE IX (Continued)

Run No.	Pressure		Resistance (ohms)	Cell Constant, k (cm ⁻¹)	Specific Conductance, K (ohm ⁻¹ cm ⁻¹)
	(lb/in. ²)	(bars)			
Run No. 12, 4.82 ± 0.06°C, GCC-2					
	15	1.03	4960	165.1	0.03329
	2,000	138	4870	165.2	0.03392
	4,000	276	4786	165.2	0.03452
	5,000	344	4738	165.2	0.03487
	6,000	413	4668	165.3	0.03541
	8,000	551	4631	165.3	0.03569
	9,500	654	4576	165.3	0.03612
	10,000	689	4580	165.4	0.03611
	12,000	827	4491	165.4	0.03683
	14,000	965	4444	165.4	0.03722
	16,000	1,100	4409	165.5	0.03754
	18,000	1,240	4380	165.5	0.03778
	20,000	1,380	4345	165.6	0.03811
	15	1.03	4958	165.1	0.03330
Run No. 7, 15.20 ± 0.02°C, TJC-1					
	15	1.03	4.59	0.198	0.0432
	3,000	207	4.46	0.194	0.0435
	6,000	413	4.32	0.192	0.0445
	9,000	620	4.22	0.190	0.0451
	12,000	827	4.11	0.188	0.0457
	15,000	1,030	4.03	0.186	0.0461
	18,000	1,240	3.96	0.185	0.0467
	20,000	1,380	3.91	0.185	0.0473
	40,500	2,790	3.77	0.184	0.0489
Run No. 13, 15.04 ± 0.01°C, GCC-2					
	15	1.03	3880	166.7	0.04300
	2,000	138	3805	166.7	0.04381
	4,000	276	3733	166.8	0.04468
	6,000	413	3685	166.8	0.04526
	8,000	551	3640	166.9	0.04585
	10,000	689	3604	166.9	0.04631
	12,000	827	3577	166.9	0.04666
	14,000	965	3545	167.0	0.04711
	16,000	1,100	3525	167.0	0.04738
	20,000	1,380	3492	167.1	0.04785

TABLE IX (Continued)

<u>Pressure</u>		<u>Resistance</u>	<u>Cell</u>	<u>Specific</u>
<u>(lb/in.²)</u>	<u>(bars)</u>	<u>(ohms)</u>	<u>Constant, k</u>	<u>Conductance, K</u>
			<u>(cm⁻¹)</u>	<u>(ohm⁻¹ cm⁻¹)</u>
Run No. 10, 24.91 ± 0.02°C, GCC-2				
15	1.03	3160	167.1	0.05288
2,000	138	3115	167.1	0.05364
5,000	344	3075	167.2	0.05437
6,000	413	3072	167.2	0.05443
7,500	517	3054	167.2	0.05475
9,000	620	3032	167.2	0.05515
10,000	689	3015	167.3	0.05549
12,000	827	3003	167.3	0.05571
14,000	965	2988	167.3	0.05599
16,000	1,100	2976	167.4	0.05625
18,000	1,240	2966	167.4	0.05644
20,000	1,380	2953	167.5	0.05672

TABLE X

SPECIFIC CONDUCTANCE OF 17.61 ‰ CHLORINITY SEA WATER

	Pressure		Resistance (ohms)	Cell Constant, k (cm ⁻¹)	Specific Conductance, K (ohm ⁻¹ cm ⁻¹)
	(lb/in. ²)	(bars)			
Run No. 21, 0.08 ± 0.07°C, GCC-2					
	15	1.03	6175	165.0	0.02672
	2,000	138	6080	165.0	0.02714
	4,000	276	5985	165.1	0.02759
	6,000	413	5885	165.1	0.02805
	8,000	551	5785	165.2	0.02856
	10,000	689	5695	165.2	0.02901
	12,000	827	5615	165.2	0.02942
	14,000	965	5545	165.3	0.02981
	16,000	1,100	5490	165.3	0.03011
	18,000	1,240	5440	165.4	0.03040
	20,000	1,380	5410	165.4	0.03057
Run No. 20, 5.01 ± 0.20°C, GCC-2					
	15	1.03	5420	165.9	0.03060
	2,000	138	5320	165.9	0.03118
	4,000	276	5222	166.0	0.03179
	6,000	413	5135	166.0	0.03233
	8,000	551	5060	166.1	0.03283
	10,000	689	4995	166.1	0.03325
	12,000	827	4952	166.1	0.03354
	14,000	965	4926	166.2	0.03374
	16,000	1,100	4875	166.2	0.03409
	18,000	1,240	4865	166.3	0.03418
	20,000	1,380	4825	166.3	0.03447
	25,000	1,720	4789	166.3	0.03473
	30,000	2,070	4775	166.5	0.03487
	40,000	2,760	4790	166.7	0.03480

TABLE X (Continued)

	Pressure		Resistance (ohms)	Cell Constant, k (cm ⁻¹)	Specific Conductance, K (ohm ⁻¹ cm ⁻¹)
	(lb/in. ²)	(bars)			
Run No. 18, 15.01 ± 0.02°C, GCC-2					
	15	1.03	4246	162.8	0.03833
	2,000	138	4184	162.8	0.03891
	4,000	276	4134	162.9	0.03940
	6,000	413	4093	162.9	0.03980
	8,000	551	4063	163.0	0.04012
	10,000	689	4029	163.0	0.04046
	12,000	827	4002	163.0	0.04073
	14,000	965	3975	163.1	0.04103
	16,000	1,100	3951	163.1	0.04128
	18,000	1,240	3926	163.2	0.04157
	20,000	1,380	3902	163.2	0.04182

Run. No. 22, 24.83 ± 0.07°C, GCC-2

	15	1.03	3455	168.0	0.04963
	2,000	138	3422	168.0	0.04909
	4,000	276	3387	168.0	0.04965
	6,000	413	3356	168.1	0.05009
	8,000	551	3324	168.1	0.05057
	10,000	689	3297	168.2	0.05102
	12,000	827	3271	168.2	0.05144
	14,000	965	3249	168.3	0.05180
	16,000	1,100	3230	168.3	0.05211
	18,000	1,240	3217	168.4	0.05235
	20,000	1,380	3207	168.5	0.05254
	25,000	1,720	3187	168.5	0.05287
	30,000	2,070	3180	168.6	0.05302

TABLE XI

SPECIFIC CONDUCTANCE OF 9.68 ‰ CHLORINITY SEA WATER

	Pressure		Resistance (ohms)	Cell Constant, k (cm ⁻¹)	Specific Conductance, K (ohm ⁻¹ cm ⁻¹)
	(lb/in. ²)	(bars)			
Run No. 15, 0.00 ± 0.00°C, GCC-2					
	15	1.03	10653	163.9	0.01539
	2,000	138	10475	163.9	0.01565
	4,000	276	10275	164.0	0.01596
	6,000	413	10090	164.0	0.01625
	8,000	551	9925	164.1	0.01653
	9,000	620	9840	164.1	0.01668
	10,000	689	9760	164.1	0.01681
	12,000	827	9625	164.1	0.01705
	14,000	965	9510	164.2	0.01727
	16,000	1,100	9420	164.2	0.01743
	18,000	1,240	9340	164.3	0.01759
	20,000	1,380	9280	164.3	0.01771
Run No. 17, 4.94 ± 0.14°C, GCC-2					
	15	1.03	9272	164.9	0.01779
	2,000	138	9100	164.9	0.01812
	4,000	276	8950	165.0	0.01844
	6,000	413	8830	165.0	0.01869
	8,000	551	8700	165.1	0.01898
	10,000	689	8575	165.1	0.01925
	12,000	827	8470	165.1	0.01949
	15,000	965	8330	165.2	0.01983
	16,000	1,100	8300	165.2	0.01990
	18,000	1,240	8240	165.3	0.02006
	20,000	1,380	8200	165.3	0.02016

TABLE XI (Continued)

	Pressure		Resistance	Cell	Specific
	(lb/in. ²)	(bars)	(ohms)	Constant, k (cm ⁻¹)	Conductance, K (ohm ⁻¹ cm ⁻¹)
Run No. 16, 14.83 ± 0.15°C, GCC-2					
15		1.03	7217	165.2	0.02289
2,000		138	7124	165.2	0.02319
4,000		276	7038	165.3	0.02349
6,000		413	6960	165.3	0.02375
8,000		551	6875	165.4	0.02406
9,000		620	6845	165.4	0.02416
10,000		689	6810	165.4	0.02429
12,000		827	6735	165.4	0.02456
14,000		965	6675	165.5	0.02479
16,000	1,100		6620	165.5	0.02500
18,000	1,240		6575	165.6	0.02519
20,000	1,380		6530	165.6	0.02536

Run No. 14, 25.06 ± 0.02°C, GCC-2

15		1.03	5861	166.6	0.02843
2,000		138	5798	166.6	0.02873
4,000		276	5740	166.7	0.02904
6,000		413	5690	166.7	0.02930
8,000		551	5640	166.8	0.02957
10,000		689	5596	166.8	0.02981
12,000		827	5562	166.8	0.02999
14,000		965	5530	166.9	0.03018
16,000	1,100		5477	166.9	0.03036
18,000	1,240		5468	167.0	0.03054
20,000	1,380		5447	167.0	0.03066

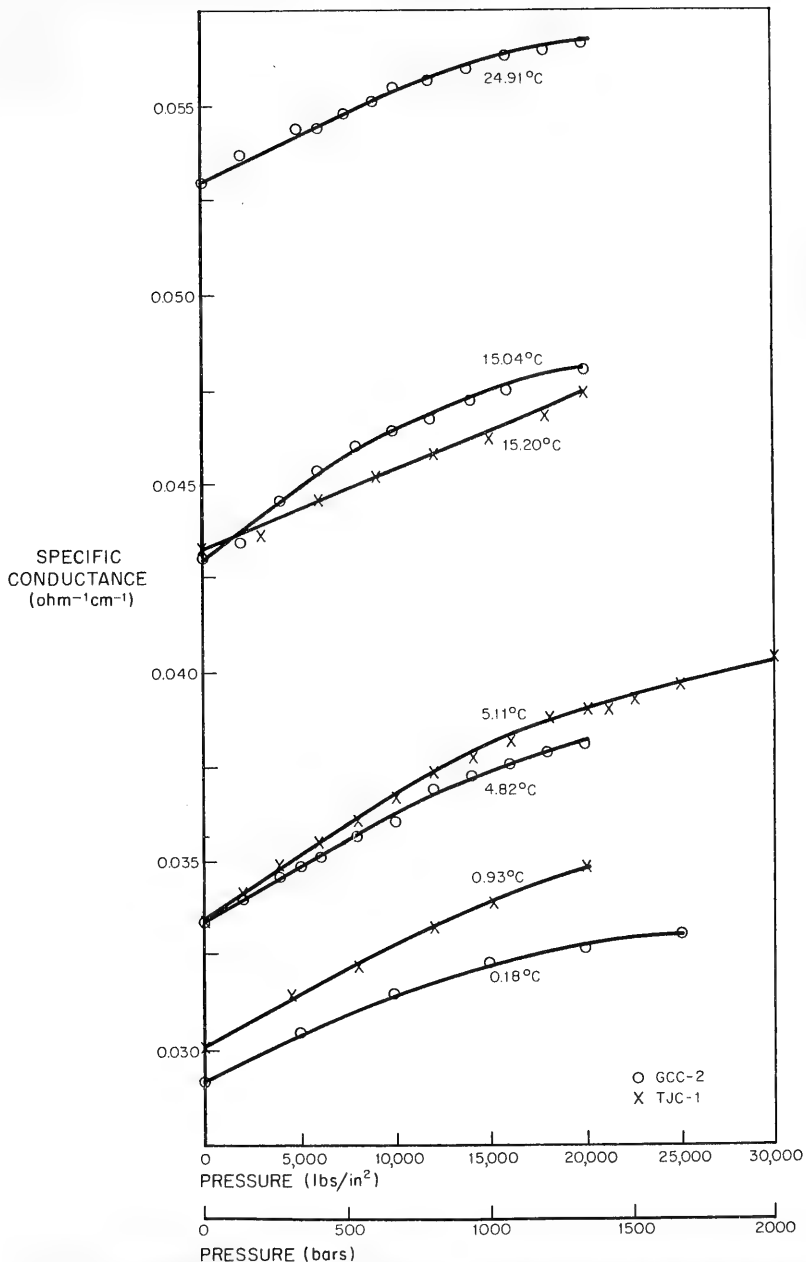


FIGURE 22 SPECIFIC CONDUCTANCE OF 19.376‰ CHLORINITY SEA WATER

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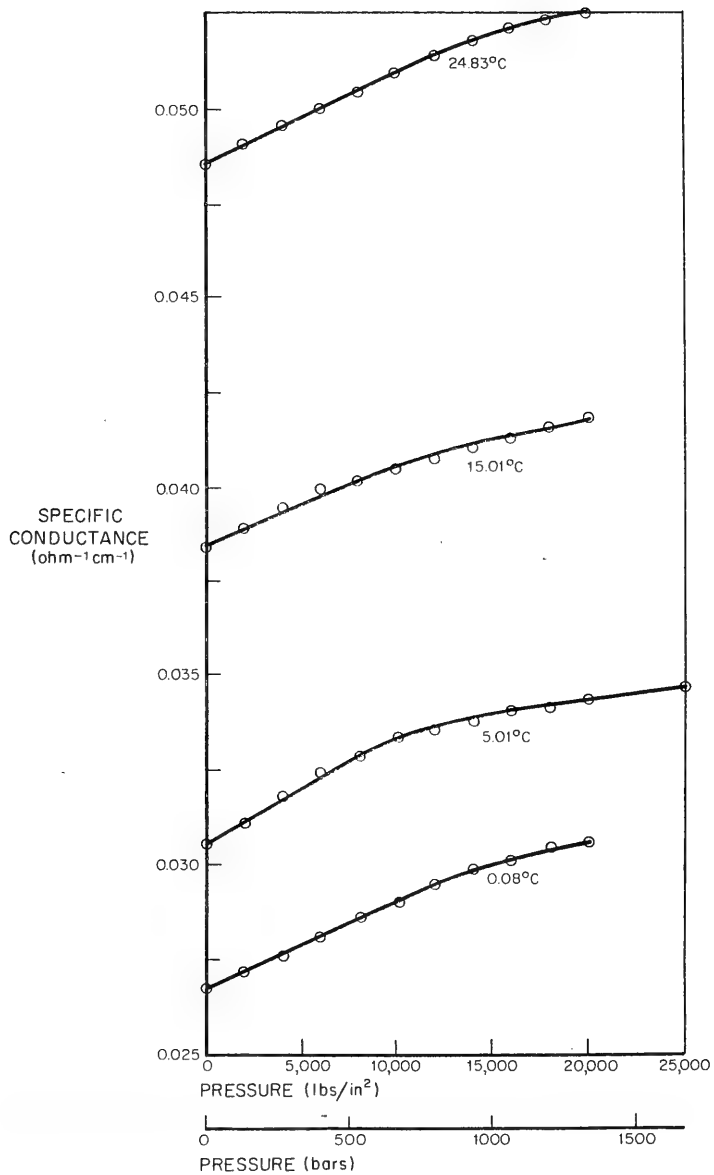


FIGURE 23 SPECIFIC CONDUCTANCE OF 17.6‰ CHLORINITY SEA WATER

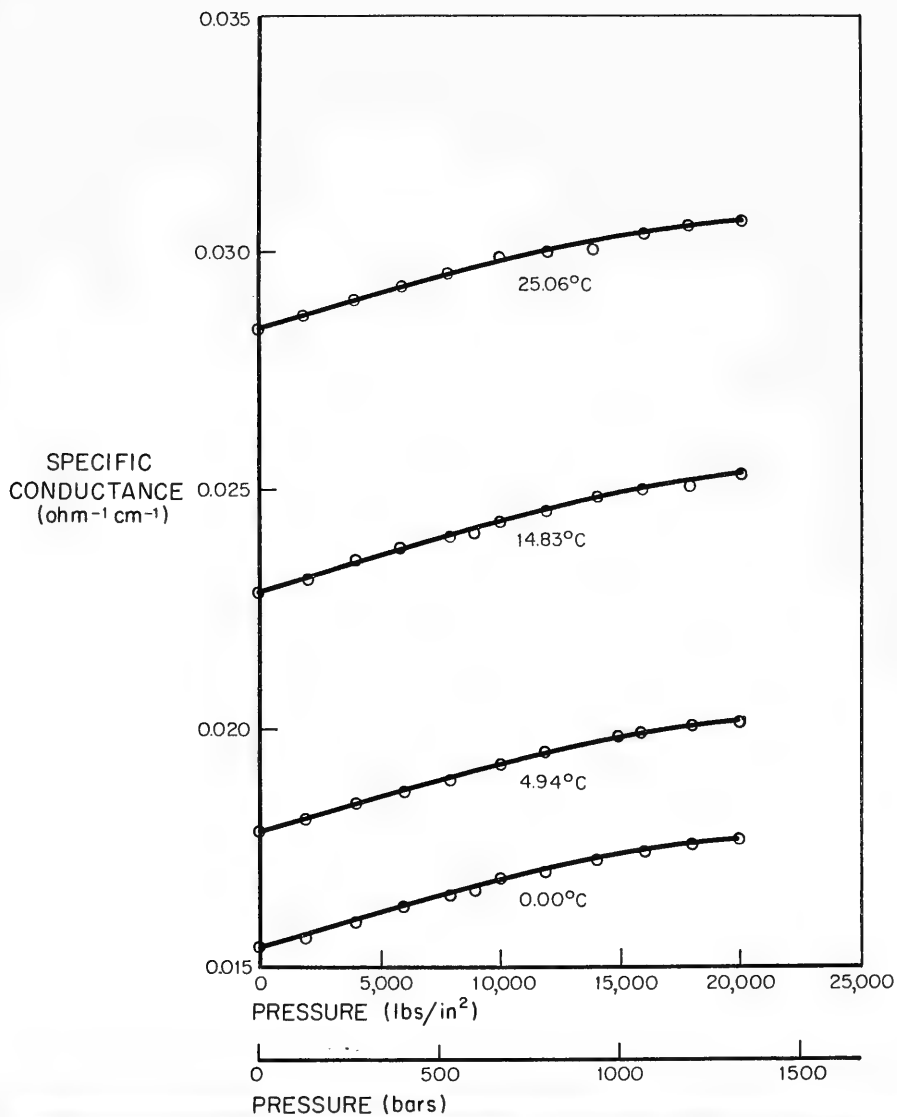


FIGURE 24 SPECIFIC CONDUCTANCE OF 9.6‰ CHLORINITY SEA WATER

TABLE XII

SLOPES OF SPECIFIC CONDUCTANCE VERSUS PRESSURE CURVES

<u>Run No.</u>	<u>Temperature</u> (°C)	$\frac{\Delta K/\Delta P}{(\text{ohm}^{-1}\text{cm}^{-1}\text{lb}^{-1}\text{in.}^2)}$
19.376 ‰ Chlorinity Sea Water		
8	0.93 ± 0.03	2.60 x 10 ⁻⁷
11	0.18 ± 0.05	2.36 x 10 ⁻⁷
9	5.11 ± 0.12	3.20 x 10 ⁻⁷
12	4.82 ± 0.06	2.98 x 10 ⁻⁷
7	15.20 ± 0.02	2.20 x 10 ⁻⁷
13	15.04 ± 0.01	3.50 x 10 ⁻⁷
10	24.91 ± 0.02	2.53 x 10 ⁻⁷
		<hr/>
		2.77 ± 0.41 x 10 ⁻⁷
17.61 ‰ Chlorinity Sea Water		
21	0.08 ± 0.07	2.28 x 10 ⁻⁷
20	5.01 ± 0.20	2.90 x 10 ⁻⁷
18	15.01 ± 0.02	2.17 x 10 ⁻⁷
22	24.83 ± 0.07	2.38 x 10 ⁻⁷
		<hr/>
		2.43 ± 0.23 x 10 ⁻⁷
9.68 ‰ Chlorinity Sea Water		
15	0.00 ± 0.00	1.41 x 10 ⁻⁷
17	4.94 ± 0.14	1.57 x 10 ⁻⁷
16	14.83 ± 0.15	1.44 x 10 ⁻⁷
14	25.06 ± 0.02	1.40 x 10 ⁻⁷
		<hr/>
		1.45 ± 0.06 x 10 ⁻⁷

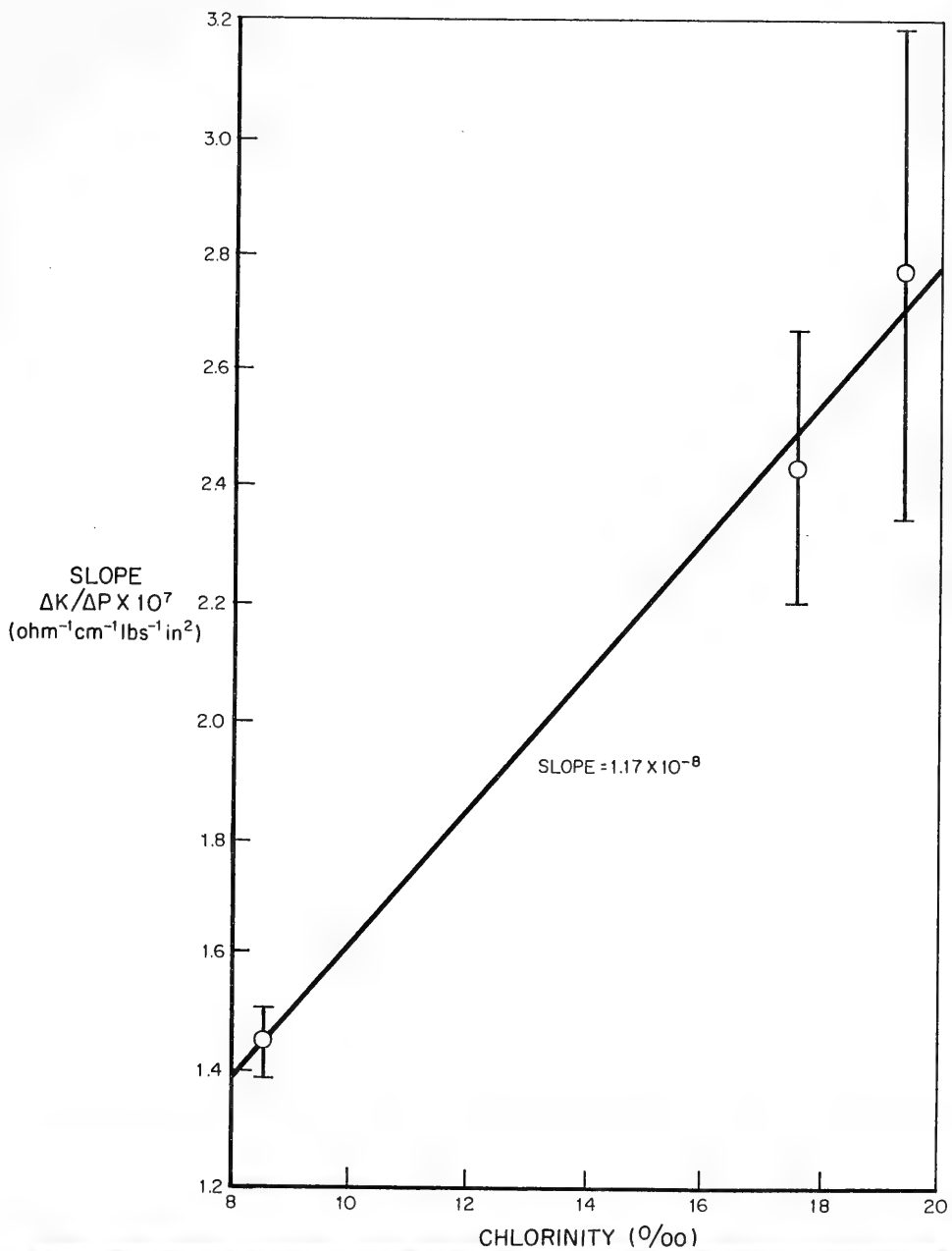


FIGURE 25 VARIATION OF SLOPE WITH CHLORINITY OF SEA WATER

Over the pressure range 15 to 10,000 lb/in.², the observed results can be represented by a simple empirical relation

$$K_{P, T, Cl} = K_{1, T, Cl} + C_{Cl} P, \quad (15)$$

that is to say, the specific conductance at any pressure in this range can be calculated from the value at 1 atmosphere and the same temperature and chlorinity and an additional term which is the product of a constant (for a given chlorinity) and the pressure. With a further sacrifice in accuracy but gain in generality, inasmuch as this constant, C_{Cl} or $\Delta K/\Delta P$, appears to be a linear function of chlorinity, equation (15) can be rewritten

$$K_{P, T, Cl} = K_{1, T, Cl} + 1.17 \times 10^{-8} Cl P \quad (16)$$

where P is the pressure expressed in lb/in.². Although it is less accurate than the original data, we believe that expression (16) will be of considerable practical use to oceanographers. Equation (16) probably can be extended within reasonable limits beyond the temperature (0 to 25°C) and chlorinity (9.68 to 19.376 ‰) ranges of the present experiments; however, it becomes increasingly inaccurate as the pressure is extended beyond 10,000 lb/in.².

As the sea water is subjected to pressure, due to its compressibility its volume will decrease, and thus the concentration of the electrolytes it contains will increase. The specific conductance of a solution increases with increasing concentration of electrolytic solute; however, as Table XIII and Figure 26 show, the observed increase in specific conductance with pressure is much greater than one would expect simply on the basis of the decreased volume of the solution.⁽²⁷⁾

TABLE XIII

COMPARISON OF CALCULATED AND OBSERVED SPECIFIC CONDUCTANCES
(19.376 chlorinity, 35.03 salinity sea water at 0°C)

Pressure		Observed ^a	From	%	From	%
(lb/in. ²)	(bars)		Empirical	Deviation	Compress-	Deviation
			Expression		ibility	
15	1	0.02906	0.02906	-	0.0291	-
5,000	340	0.03020	0.03038	0.6	0.0295	2.3
10,000	690	0.03125	0.03171	1.4	0.0297	5.1
15,000	1,000	0.03218	0.03303	2.6	0.0299	7.2
20,000	1,400	0.03325	0.03436	4.5	0.0301	9.6

a. Observed data extrapolated to 0.0°C.

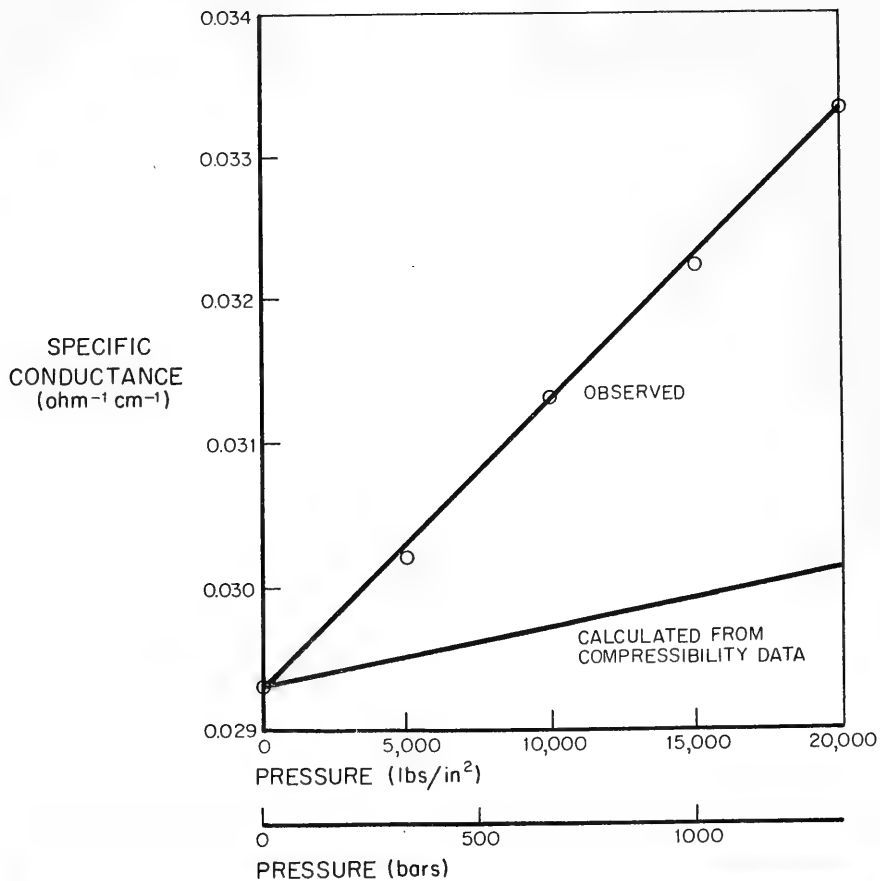


FIGURE 26 OBSERVED AND CALCULATED SPECIFIC CONDUCTANCES OF 35‰ SALINITY SEA WATER AT 0°C

In Table XIII the fourth column contains specific conductances calculated from the empirically determined equation (15), which takes the form

$$K_P = 0.02906 + 2.65 \times 10^{-7} P \quad (17)$$

When P is expressed in bars, K_P becomes equal to $0.02906 + 3.84 \times 10^{-6} P$. The values in column six of Table XIII were obtained by interpolation of chlorinity-specific conductance data of Thomas, Thompson, and Utterback.(15) The chlorinities were calculated from salinities using equation (13), and the salinities in turn were computed from the relation

$$(\text{Salinity})_P = (\text{Salinity})_{1 \text{ atm}} / V_R \quad (18)$$

where V_R is the relative volume of the sea water at pressure P compared with its volume at 1 atmosphere.(28) The relative volumes were obtained from the relation

$$V_R = V_P / V_{1 \text{ atm}} = 1 - \beta P \quad (19)$$

where the values of β used are those of 35⁰/oo salinity sea water at 0°C, as given by the International Critical Tables.(29)

In addition to NaCl, sea water contains other species (see Table XIV), and some of these may form weak electrolytes. In general, the ionization of weak electrolytes and hence their contribution to electrical conductivity increases with increasing pressure.(30)

TABLE XIV
COMPOSITION OF SEA WATER⁽³¹⁾

<u>Ion</u>	<u>Concentration</u> (gm/kgm)
Na+	10.556
Mg ⁺⁺	1.272
Ca ⁺⁺	0.400
K+	0.380
Sr ⁺⁺	0.013
Cl ⁻	18.980
SO ₄ ⁼	2.649
HCO ₃ ⁻	0.140
Br ⁻	0.065

The weak electrolyte present in largest amounts in sea water is MgSO_4 , whose dissociation constant has a value of 4.4×10^{-3} at 25°C .⁽³²⁾



In order to test the hypothesis that the unexpectedly great increase in the conductance of sea water with pressure might be due to a conductive contribution from the enhanced ionization of weak electrolytes such as MgSO_4 , the specific conductance of an 0.50 M NaCl solution, containing no other added electrolytes, was measured as a function of pressure. The results are shown in Figure 27. In the 15 to 10,000 lb/in.² pressure range, the curve is nearly linear and has a slope of $2.03 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1} \text{ lb}^{-1} \text{ in.}^2$. The slope calculated from equation (16) using the chlorinity corresponding to 0.50 M NaCl is $2.08 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1} \text{ lb}^{-1} \text{ in.}^2$. Inasmuch as these two slopes are in agreement well within experimental error, the unexpectedly rapid increase in the specific conductance of sea water with pressure evidently cannot be attributed to a conductive contribution from the ionization of a weak electrolyte such as MgSO_4 .

The conductance of electrolytic solutions depends on the viscosity of the medium. As viscosity increases, the mobility of the charge-carrying ionic species decreases, and the observed decrease in specific conductance at the higher pressure is undoubtedly due to the increase in the viscosity of water under high compression.⁽³³⁾ Water and dilute aqueous solutions are anomalous inasmuch as their viscosity versus pressure curves initially exhibit a shallow minimum.⁽³⁴⁾ This viscosity anomaly has been attributed to the breaking up of the residual ice structure of liquid water. An increase in the temperature or the addition of electrolytes tend to remove the anomaly. The observed conductance anomaly might be attributable to this viscosity anomaly. Adams and Hall⁽²⁴⁾ discuss the pressure dependence of the relative resistance of NaCl solutions, and, in addition to the viscosity effect just mentioned, suggest that the degree of dissociation of strong electrolytes such as NaCl, as in the case of weak electrolytes, may also increase with increasing pressure. Inasmuch as dilute NaCl solutions are supposed to be 100% dissociated at 1 atmosphere, the meaning of this suggestion is not entirely clear unless one evokes the concept of a weak ion pair.

Because of difficulties involved in determining the variation of their cell constant with pressure, Adams and Hall⁽²⁴⁾ reported only relative resistances, i. e., the ratio of the resistance at pressure P to the resistance at 1 atmosphere. When the present results (Figure 27) are expressed in terms of relative resistances, they are seen to be in good agreement with the results of Adams and Hall (Figure 28); and their results in turn are in agreement with the earlier findings of Körber.⁽³⁵⁾ This agreement is reassuring, especially in view of the less than satisfactory agreement in the case of KCl at 25°C (Figure 21).

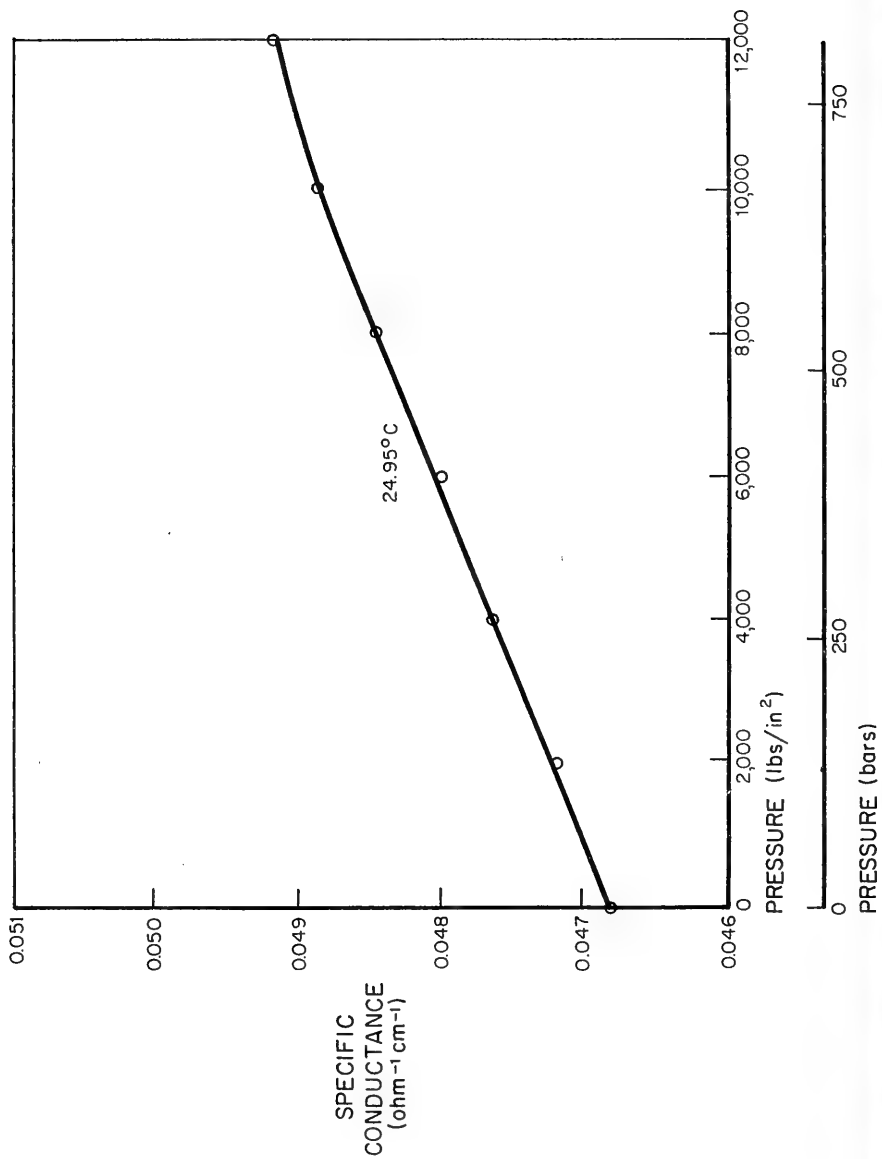


FIGURE 27 SPECIFIC CONDUCTANCE OF 0.50 m NaCl

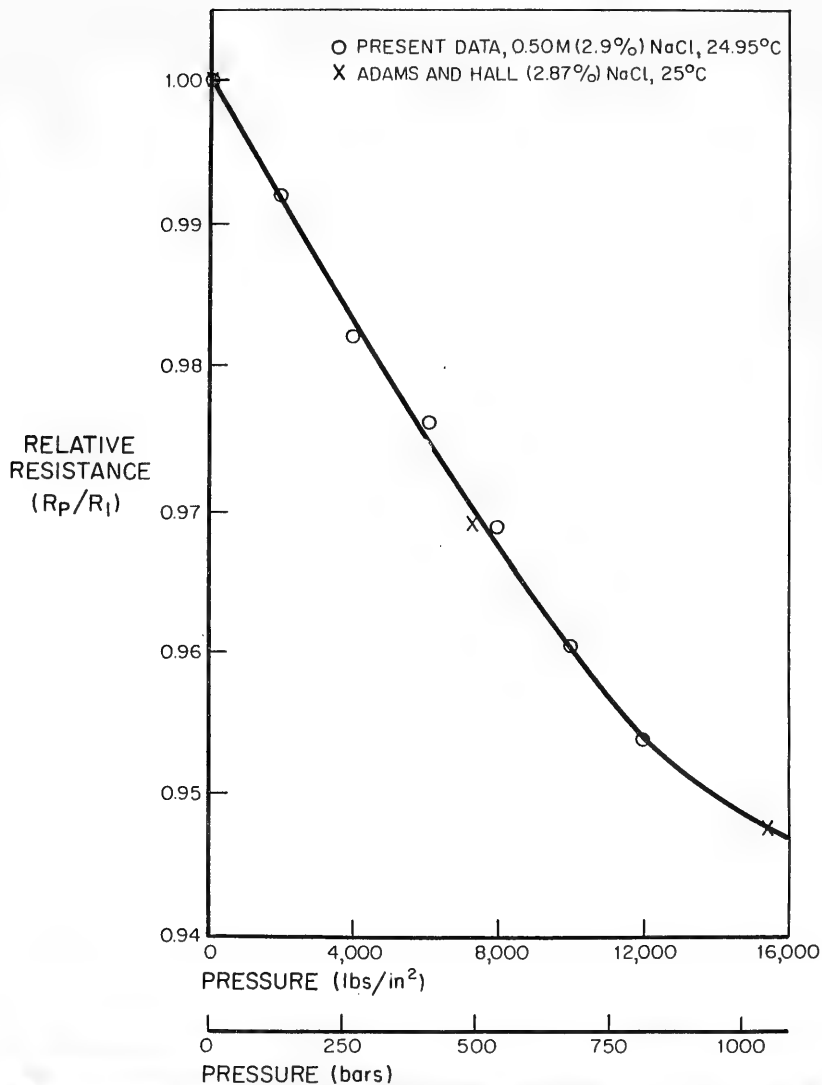


FIGURE 28 RELATIVE RESISTANCE OF NaCl SOLUTIONS

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