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THE EFFECT OF PRESSURE ON THE IONIC CONDUCTANCE THROUGH THE UPPER 2000 METERS OF THE OCEAN'S WATER COLUMN

by

Michael Everett Mays

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THESIS

THE EFFECT OF PRESSURE ON THE IONIC
CONDUCTANCE THROUGH THE UPPER 2000 METERS
OF THE OCEAN'S WATER COLUMN

by

Michael Everett Mays

December 1968

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THE EFFECT OF PRESSURE ON THE IONIC CONDUCTANCE THROUGH THE UPPER 2000 METERS OF THE OCEAN'S WATER COLUMN

by

Michael Everett Mays
Lieutenant, United States Navy
B.S., Naval Academy, 1963

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN OCEANOGRAPHY

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ABSTRACT

The specific conductivity of 5 different electrolytic solutions over a pressure range of 1 to 200 bars has been measured. The solutions were 0.01N, 0.10N and 1.00N KCl and 2 solutions of sea water. One sea water solution was real sea water, the other artificial. Each solution was tested at 4 temperatures, ranging from 4°C to 18°C. The pressure caused the specific conductivity of all solutions to increase in a non-linear fashion. First, second and third degree least square curves have been fitted to the data for comparisons. The specific conductivity caused by solution concentration changes during compression has been determined and found to be a significant error source. Explanations are offered to account for the conductivity changes considering the manner in which pressure alters the chemical structure of the solution. The areas discussed are solution concentration, applied voltage, inter-ionic reactions and viscosity.

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CHAPTER I

THE PROBLEM INVESTIGATED

During the 1950's the development instruments to measure, *In situ*, properties of the ocean became predominant. Among these devices was the *In situ* salinometer, which relied upon an ionic conductivity measurement. The instrument was limited in its application to depths of less than 1000 meters because there was a lack of knowledge concerning the effect of pressure on the electrical conductivity of sea water.[1]

I. THE PROBLEM

The practical range of *In situ* measurements of salinity in the ocean is the upper 2000 meters. Previous investigators have examined the effect of pressure on the specific conductivity of sea water up to pressures equivalent to depths of 13,000 meters. These investigations are characterized by an almost complete lack of conductivity measurements at pressures less than 2000 decibars. The investigators also believe the relationship between conductivity and pressure to be linear in the ocean over this range of pressures.

This research is an investigation of the effect on electrical conductivity of pressures encountered in the upper 2000 meters of the ocean's water column. Different electrolytic solutions have been tested over a realistic range of temperatures. Among these are artificial and real sea water. Several data points were collected

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[1] D. W. Pritchard, "The *In situ* Measurement of Salinity with the Inductive Conductivity Indicator," *Conference on Physical Properties of Sea Water*, (September 1958), p. 148.

and analyzed. There is evidence that the relationship between the two variables, pressure and specific conductivity, may be non-linear.

The experimental error of solution concentration changes due to compressibility has been examined and evaluated. Previous investigations either neglected this source of error or felt it to be insignificant. This study raises a serious doubt concerning the wisdom of doing so.

An explanation for the conductivity response to pressure has been offered in terms of what, chemically, is occurring to cause the observed conductivity changes of the solutions.

Due to the nature of the study and approach to the problem analysis, several terms are used which may be unfamiliar to the reader. A glossary of terms has been included in Appendix A which should be of assistance in better understanding the results of the investigation.

CHAPTER II

PREVIOUS INVESTIGATIONS OF THE PROBLEM

Several studies on the conductivity of aqueous solutions have been conducted over the past seventy years, but serious research with sea water solutions has only been carried out for the past thirty years. The majority of the investigations have been concerned with temperature effects only, with studies of the pressure influence becoming prominent during the past ten years.

Temperature effect at atmospheric pressure. As early as 1933, fairly reliable information about the conductivity of sea water at atmospheric pressure was available. Thomas, Thompson, and Utterback carried out extensive research on the subject and published values for the conductivities of sea water ranging in chlorinity from 1 PPT to 22 PPT at temperatures of $0^{o}C$, $5^{o}C$, $10^{o}C$, $15^{o}C$, $20^{o}C$ and $25^{o}C$.[1] This information has been valuable in establishing cell constants for followers as well as the calibration of salinity - temperature - depth measuring instruments. Their results have been recently shown to be slightly in error by M. J. Pollak and P. Weyle.[2]

---

[1] B. D. Thomas, T. G. Thompson, and C. L. Utterback, "The Electrical Conductivity of Sea Water," Journal of the Council for the International Exploration of the Seas, IX (March, 1934), pp. 28-35.

[2] J. J. Pollak, "The Use of Electrical Conductivity Measurements for Chlorinity Determination," Journal of Marine Research, XIII (November, 1954), pp. 228-231; P. K. Weyle, "On the Change of Electrical Conductivity of Sea Water with Temperature," Limnology and Oceanography, IX (August, 1964), pp. 75-78.

Pressure effect. The first investigation of the pressure effect upon electrical conductivity of sea water was accomplished by B. V. Hamon in 1958 during his development of an In situ salinometer.[3]

He stated that his results should be taken as tentative primarily because of the very small amount of data upon which to base his conclusions. His experiments were conducted using artificial sea water of chlorinity 19.7 PPT which was diluted with deionized water to obtain lesser concentrations. Also, there was no control of temperature after the initial temperature was set prior to pressure application. Adiabatic compression was assumed and an appropriate adiabatic temperature correction was applied after the pressure increase. The pressure was increased from 1 atmosphere to approximately 1500 psi in three steps by introducing nitrogen gas into the pressure vessel.

The conductivity was quickly measured by means of a wheatstone bridge after each pressure increase. A total of four data points were gained for each experiment which showed the conductivity of the solutions to decrease with pressure. Hamon concluded the relationship between pressure and conductivity to be linear from his data.

In 1963 R. A. Horne and G. R. Frysinger conducted a thorough investigation of the properties of sea water under pressure, including electrical conductivity.[4] The specific conductance of three artificial

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[3] B. V. Hamon, "Effect of Pressure on Electrical Conductivity of Sea Water," Journal of Marine Research, XIV (August, 1955), pp. 83-89.

[4] G. R. Frysinger and R. A. Horne, "The Effect of Pressure on the Electrical Conductivity of Sea Water," Journal of Geophysical Research, VIII (April, 1963), pp. 1967-73.

solutions of sea water was measured at four temperatures over a pressure range of 1 bar to 1380 bars. The temperatures were $0^{o}C$, $5^{o}C$, $15^{o}C$ and $25^{o}C$. The standard solution was of chlorinity 19.376 PPT and solutions of 9.68 PPT and 17.61 PPT were prepared through the dilution of the standard solution as Hamon had done.

The temperature was controlled to $0.05^{o}C$ during the experiments which allowed the individuals to wait as long as required for the temperature to stabilize before measuring the conductivity after a pressure increase. From five to thirteen data pairs for each solution at each temperature were obtained with the results showing an increase of specific conductivity with pressure. The authors fit the data with a linear relationship. However, their data when placed on an expanded scale appears to be non-linear. A questionable conclusion reached by Horne and Frysinger is that the change in concentration of the solution as the solution volume is decreased during compression results in an increase of specific conductivity which is negligible compared to the observed specific conductivity. They claim the conductivity increases caused by concentration change are of a magnitude 1.0×10^{-4} mhos/cm while the observed changes are of magnitude 1.0×10^{-3}. The authors refer to the International Critical Tables as their source of compressibilities of sea water. The table from which the compressibility information was derived lists compressibilities corresponding to pressures in megabars. These values when compared to values for the compressibility coefficients of sea water calculated from the data presented by Riley and Skirrow, are totally incompatible.[5] The coefficients listed in the International

[5] J. P. Riley and G. Skirrow, "Chemical Oceanography," Academic Press, New York, New York, 1965, p. 111.

Critical Tables are an order of 10^6 smaller than those calculated. The calculated values utilized the results of Crease's work in 1962,[6] whereas the data listed in the International Critical Tables was the result of work done prior to 1928, thus more emphasis should be placed on the former. However, the preceding supports the idea that the listed units (megabars) in the International Critical Tables are incorrect and are actually bars. This would make the two sources of compressibilities compatible, and would also account for the small concentration changes noted by Horne and Frysinger and the resulting small conductivity changes due to compression.

The most recent study of the pressure effect upon electrical conductivity of sea water was conducted by A. Bradshaw and K. E. Schleicher at Woods Hole, Mass. in 1964.[7]

Three different solutions of salinities 31 PPT, 35 PPT and 39 PPT were used for their measurements and for the first time, true sea water was being used. The 31 PPT solution was prepared through dilution of Woods Hole Harbor water and 39 PPT solution was prepared by diluting Red Sea water. The 33 PPT salinity solution was prepared from Copenhagen standard sea water. Specific conductivities were measured for each solution at six temperatures, ranging from $0^{\circ}C$ to $25^{\circ}C$. The pressure range extended from 10 decibars to 10,338 decibars with measurements being made at approximately every 1720 decibars.

---

[6] J. Crease, "The Specific Volume of Sea Water Under Pressure As Determined by Recent Measurements of Sound Velocity," Deep Sea Research, IX (May, 1962), pp. 209-213.

[7] A. Bradshaw and K. E. Schleicher, "The Effect of Pressure on the Electrical Conductance of Sea Water," Deep Sea Research, XII (November, 1964), pp. 151-162.

Even though the pressure vessel was located in a constant temperature environment, the authors applied a correction to the measured conductivities if the temperature of the solution had increased during the course of a run. The maximum increase noted was $0.006^{\circ}C$. The conductivity correction for this temperature change is not listed, but a calculation, using the observation that specific conductivity increases 3% per degree Celcius increase in temperature shows this would amount to an increase by a factor of 0.00018 at $0^{\circ}C$.[8] The correction is approximately 6×10^{-6} mhos/cm which appears to be insignificant. The correction decreases from $0^{\circ}C$ to $25^{\circ}C$.

The results show a non-linear increase in relative specific conductivity as pressure is increased. It is not clear whether the relationship is parabolic or cubic.

A striking feature of the investigation was the absence of comments concerning the conductivity increase caused solely by concentration change during compression. This implies that Horne's and Frysinger's conclusion of negligible contribution was accepted without being questioned.

---

[8] J. P. Riley and G. Skirrow, op. cit., p. 103.

CHAPTER III

DESCRIPTION OF THE APPARATUS AND METHOD OF MEASUREMENT

Commercially manufactured conductivity cells are incapable of withstanding pressures much greater than 1 atmosphere, thus to carry out this research, a specially constructed cell was made. The specifications for the cell were that it should withstand pressures up to 400 atmospheres and be able to accurately measure resistances at this pressure.

I. CELL DESCRIPTION

The pressure vessel utilized to measure conductivities is a thick walled mild steel cylinder consisting of two parts coupled together by six bolts. A third component is a piston of the same material which is used to transmit the pressure. Through the center of the two pieces, comprising the cylinder, a hole of diameter approximately 1/3 that of the cylinder diameter, has been bored. The hole passes only 1/2 the distance through the bottom piece, such that a well is formed. Two electrodes protrude into the well very near the bottom, from opposite sides, enabling an external connection to a conductivity bridge.

The cell, when filled with solution, may have any desired pressure applied by means of the piston acting on the surface of the liquid. High pressures may be realized by placing the entire apparatus in a hydraulic press. The force exerted by the press on the large area or the piston face is transmitted through the piston

to the smaller area of the aqueous solution's surface. The pressure is amplified by a factor of two from the press to the solution thus, the pressure at the 1000 fathom depth of the ocean may be introduced into the cell by application of a press pressure less than 1700 psi.

The maintaining of a leakless cell at the high pressures expected was never a problem. A rubber O-ring was placed circumferencially around the well at the junction of the top and bottom pieces and another O-ring was fitted on to the piston protrusion entering the well. Since the cell, although operating under high pressures, was essentially static, the use of back-up O-rings was not found to be necessary.

The tendency to leak along the electrodes was eliminated by milling two small groves along the face of the bottom piece, extending radially outward from the well center to the perifery of the cylinder. The electrodes were wrapped with teflon tape and placed in these groves. This procedure resulted in an exceptionally satisfactory seal. Figure 1 is a schematic drawing of the cell.

Due to the material from which the pressure vessel was constructed, it was anticipated that a fairly large capacitance effect may be set up upon the application of an EMF across the electrodes. In minimizing this potential problem, platinum electrodes were used, with a circular platinimum strip tack welded to one end of each wire. The electrodes were carefully platinized with a solution of 3% platinum chloride dissolved in 0.025% lead acetate. To further minimize the capacitance effect, a polyethylene cup was fitted into the bottom of the well. The cell was filled with the solution to be measured until the electrodes were just submerged. A layer of less dense oil was placed above the

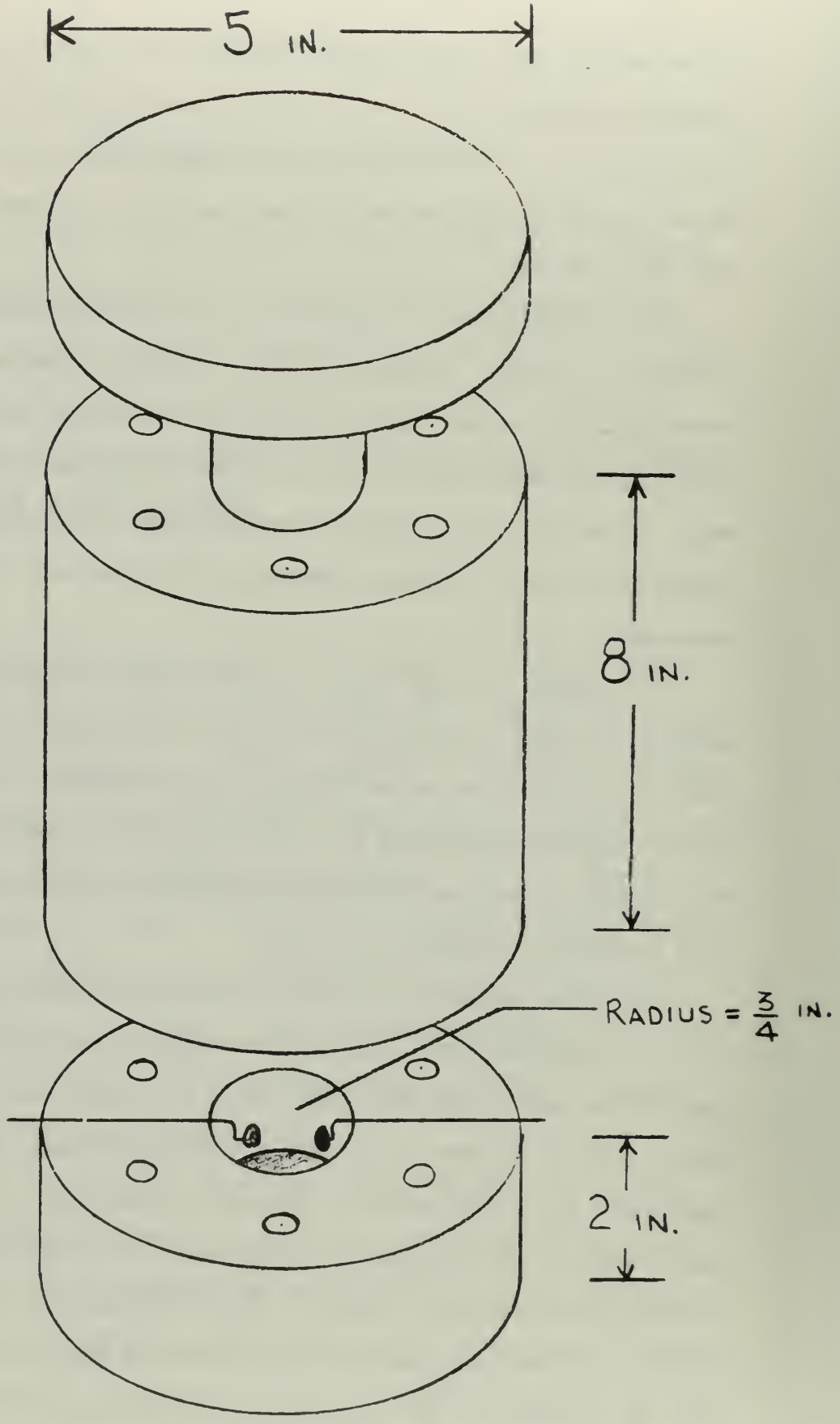

FIGURE 1. PRESSURE VESSEL ARRANGEMENT.

solution and it was upon the oil solution that the force was applied through the piston. This was successful in further minimizing the capacitance but it introduced errors in resistance readings by refracting the lines of current flux at the boundary of the oil-test solution due to the proximity of the boundary to the electrodes. Also, the oil frequently contaminated the electrodes during the solution removal.

The approach ultimately used with excellent result was to coat the well interior with polystyrene. The polystyrene and polyethlyene cup, provided a satisfactory insulation from the steel walls and enabled good bridge balancing.

The individual parts of the high-pressure-conductivity cell are shown in Figure 2.

II. CONDUCTIVITY MEASUREMENT

Temperature Control. To simulate conditions characteristic of the ocean's water column, the careful control of the aqueous sample's temperature was mandatory. This was accomplished through the use of a wide range ($-29^{o}C$ - $+70^{o}C$) constant temperature Forma-Temp bath with external outlets. The bath contained a mixture of pure water and methyl alcohol, the alcohol being used to depress the water's freezing point. To obtain lower temperatures, the refrigeration unit sometimes operated at as much as $20^{o}C$ below the desired bath temperature.

The cold water from the bath was circulated through copper tubing coils wrapped around the pressure vessel and through the upper and lower faces of the press upon which the vessel rested. As anticipated, it was necessary to maintain the bath solution at a temperature slightly

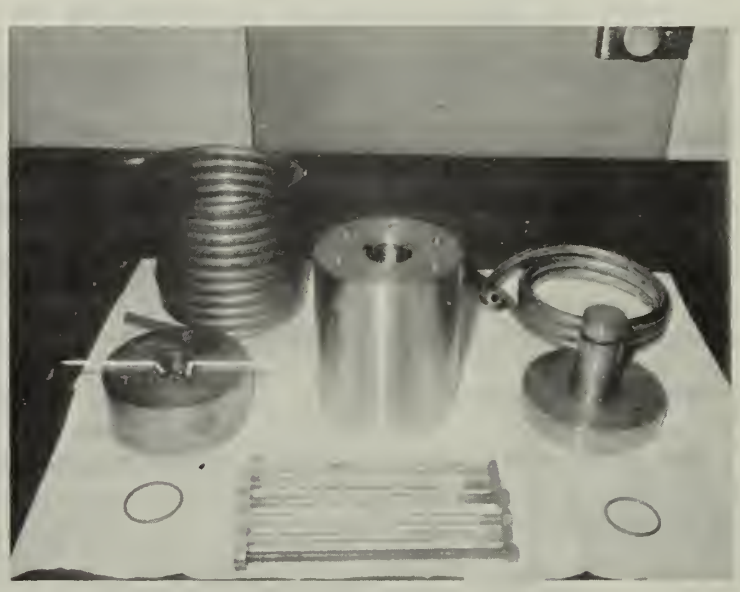

Figure 2. Components of the high pressure conductivity cell.

below the temperature desired within the pressure vessel due to the heat transfer between the copper cooling coils and the environment which was at room temperature (approximately 25°C). A cooling period of several hours was allowed before the cell was filled with an experimental sample.

After the cooling period, the cell was completely rinsed three times with distilled water followed by a 30 to 40 minute period of aspiration by means of a simple water aspirator. This was necessary to remove all residual distilled water remaining in the well. Following aspiration, two small volume rinses were made with the sample, to further insure against any dilution of the actual sample to be tested. The well was then filled with 165 milliliters of test solution.

A copper-constantan thermocouple in conjunction with a Leeds-Northrup millivolt potentiometer was utilized to measure the temperature of the sample within the cell. The thermocouple wire was introduced into the cell containing the solution followed by capping the well opening with a rubber stopper. Once the sample temperature had stabilized at the desired temperature, the stopper and thermocouple were removed and the pressure vessel piston was inserted into the well.

Pressure Application. Pressure was applied to the sample in the cell by means of a hydraulic press. The pressure applied by the press was measured by a direct reading bourdon tube pressure gauge which was easily converted to pressure acting within the cell by means of force per unit area relationships. The range of pressures capable of being applied by the press were from 1 atmosphere to approximately 12,000 psi in the cell. Figure 3 shows the pressure vessel and press arrangement.

The Conductivity Bridge. Resistance measurements were accomplished using a LKD Produkter conductivity bridge shown in Figure 4. The bridge resistance ranged from 11,110 ohms to 1 ohm. To gain further accuracy, three external decade resistors were also used. The first resistor was placed in series with the bridge variable resistance while the remaining two were in parallel with each other, but in series with the bridge and the other decade resistor. The circuitry is as shown in Figure 5. The addition of three external decade resisters enable resistance readings to be made to the third decimal place. The resistance of the sea water solutions could be measured to five significant figures and the less concentrated solutions of potassium chloride were measured to six significant figures.

The bridge had available two frequencies of alternating current, 1000 cps and 2000 cps. The best bridge balances were obtained using the higher frequency.

Although the capacitive effects, characteristic of any conductivity cell, were minimized through the arrangement of the electrodes inside the well, platinizing and insulating, a small amount remained. This was removed by use of a variable capacitor installed within the conductivity bridge's circuitry. The capacitor's range was from 0 farads to 10,500 pfarads. In general, the capacitances were removed with settings of 5000 pfarads or less on the bridge.

After the solution within the cell had come to the desired temperature, a resistance reading was taken at atmospheric pressure. The pressure was then increased by increments of 100 psi press pressure to 1000 psi. Above 1000 psi, the pressure was increased at 200 psi increments to 1600 psi press pressure. A 15 minute time interval was taken after each pressure increase before the resistance was

Figure 3. The hydaulic press and pressure vessel arrangement.

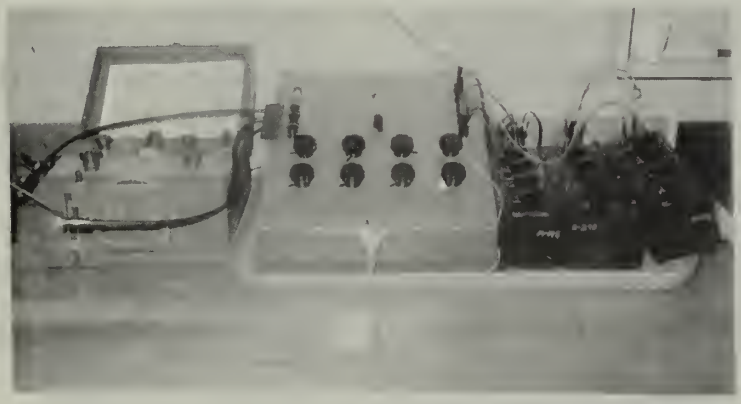

Figure 4. The LKD Produkter conductivity bridge.

measured to allow the solution to stabilize at the initial temperature since the pressure increase causes a slight increase in temperature due to the compression. As the pressure was relieved, the resistance was again measured at certain pressures during the decompression as a check.

Solutions. Three solutions of potassium chloride and two solutions of sea water were used for the experiments. The potassium chloride solutions were of concentration 0.010N, 0.100N and 1.000N, and were prepared in accordance with the procedure listed by Kortum.[1]

One sea water solution was prepared using the method recommended by Lyman and Fleming to obtain a salinity of 34.481 PPT.[2] The real sea water solutions were taken from Monterey Bay. The salinity of the samples ranged from 33.621 PPT to 33.645 PPT.

The purpose of using potassium chloride solutions was to establish the cell constant for the pressure vessel. KCl is in general used as a standardizing solution since its specific conductivity is accurately known. Also, the potassium chloride solutions served as a basis for comparison with the sea water solutions to determine if sea water responds in the same manner as the standard.

Figure 6 shows the entire system as it was used to conduct the experiments. The accuracy of the individual measurements are tabulated as follows:

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[1] J. Kortum, "Treatise on Electrochemistry," Elsevier Publishing Company, New York, New York, 1965, p. 6.

[2] H. U. Sverdrup, et al., The Oceans, Their Physics, Chemistry, and General Biology, (Englewood Cliffs: Prentice-Hall, Inc., 1928), p. 186.

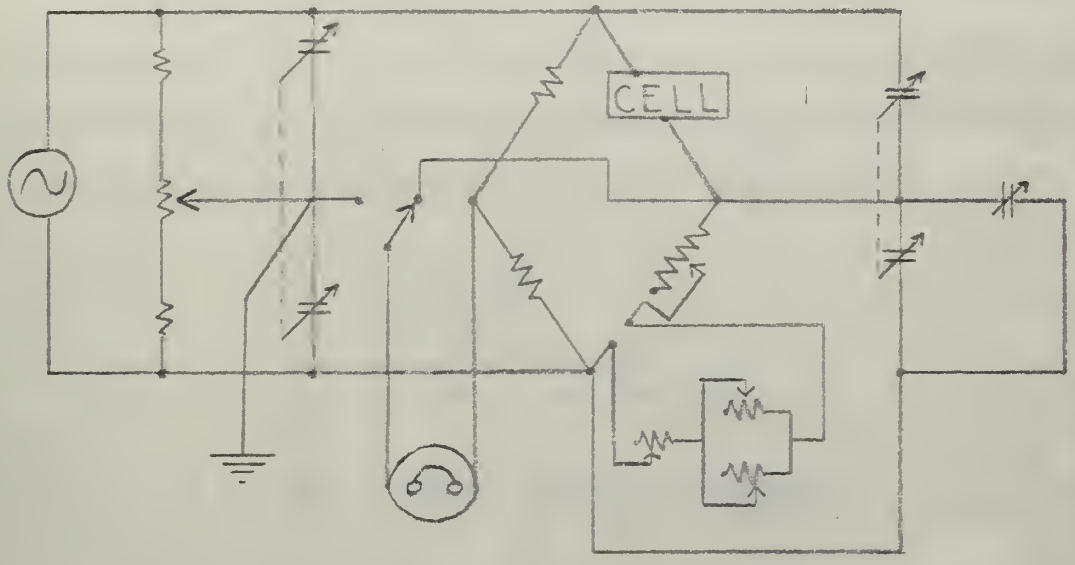

Figure 5. Basic bridge circuit with external decade resistors.

Figure 6. The system as it was used to measure electrical conductivity during pressure application.

Temperature (Bath)	Temperature (Cell)	Pressure Press	Resistance
$\pm 0.02^{\circ}C$	$\pm 0.25^{\circ}C$	± 5 psi	0.005 ohms

CHAPTER IV

EXPERIMENTAL RESULTS

A total of twenty experimental runs were conducted. At each temperature, $4^{o}C$, $10^{o}C$, $14^{o}C$ and $18^{o}C$, five sets of data for values of conductivity vs. pressure have been collected. The five sets are comprised of those values for the following solutions:

(1) 0.010 N KCl
(2) 0.100 N KCl
(3) 1.000 N KCl
(4) 34.481 PPT Artificial Sea Water
(5) 33.6 PPT Real Sea Water

I. DATA COLLECTED FROM THE EXPERIMENTS

The results of the experiments are tabulated in Tables I through V.

The specific conductivity of the distilled water used in the preparation of the standard potassium chloride solutions and the artificial sea water (S = 34.481 PPT) was measured at $4^{o}C$. The conductivity was found to be of magnitude 10^{-5} mhos/cm. The trend was an initial decrease in specific conductivity up to approximately 50 bars followed by an increase. This trend is very similar to that of the 0.010 KCl solution at temperatures below $18^{o}C$. This can be explained by the fact that the specific conductivity of 0.01N KCl is of magnitude 10^{-4} and the solution's response is greatly influenced by the solvent's reaction to the pressure.

TABLE I

SPECIFIC CONDUCTIVITY OF 0.010 N KCl SOLUTION
AT VARIOUS TEMPERATURES

Pressure in Bars	Temperature			
	4°C	10°C	14°C	18°C
Atmos.	0.000872000	0.0010250	0.00112166	0.0012226
10.73	0.000842998	0.0010213	0.00111805	
21.47	0.000841993	0.0010174	0.00110990	
26.83				0.0012298
32.20	0.000837900	0.0010182	0.00111117	
42.93	0.000838706	0.0010215	0.00111193	
53.6(	0.000839989	0.0010269	0.00111193	0.0012439
64.39	0.000841276	0.0010281	0.00111295	
75.13	0.000842710	0.0010293	0.00111396	
80.49				0.0012654
85.86	0.000844150	0.0010299	0.00111396	
96.59	0.000845630	0.0010307	0.00111396	
107.3	0.000846898	0.0010309	0.00111396	0.0012717
128.8	0.000849810	0.0010310	0.00111524	0.0012762
150.3	0.000852302	0.0010311	0.00111703	0.0012794
171.8	0.000854955	0.0010312	0.00111960	0.0012807
193.2				0.0012823

SPECIFIC CONDUCTIVITIES IN MHOS/CM

TABLE II

SPECIFIC CONDUCTIVITY OF 0.100 N KCl SOLUTION
AT VARIOUS TEMPERATURES

Pressure in Bars	Temperature			
	4°C	10°C	14°C	18°C
Atmos.	0.0080848	0.0094500	0.010375	0.011191
10.73	0.0080927	0.0094680		
21.47	0.0080948	0.0095016		
26.83			0.010438	0.011264
32.20	0.0081166	0.0095191		
42.93	0.0081397	0.0095191		
53.66	0.0081518	0.0095312	0.010485	0.011343
64.39	0.0081608	0.0095457		
75.13	0.0081648	0.0095535		
80.49			0.010497	0.011579
85.86	0.0081760	0.0095661		
96.59	0.0081770	0.0095692		
107.3	0.0081851	0.0095692	0.010508	0.011755
128.8	0.0082034	0.0095902	0.010525	0.011824
150.3	0.0082341	0.0096115	0.010542	0.011866
171.8	0.0082490	0.0096207	0.010565	0.011923
193.2			0.010576	0.011966

SPECIFIC CONDUCTIVITIES IN MHOS/CM

TABLE III

SPECIFIC CONDUCTIVITY OF 1.000 N KCl SOLUTION
AT VARIOUS TEMPERATURES

Pressure in Bars	Temperature			
	4°C	10°C	14°C	18°C
Atmos.	0.072700	0.083800	0.091250	0.098200
10.73	0.072873	0.084105		
21.47	0.073047	0.084543		
26.83			0.091906	0.098200
32.20	0.073091	0.084543		
42.93	0.073091	0.084543		
53.66	0.073161	0.084731	0.091997	0.098490
64.39	0.073161	0.084731		
75.13	0.073459	0.084731		
80.49			0.092191	0.099218
85.86	0.073574	0.084844		
96.59	0.073574	0.084967		
107.3	0.073574	0.085042	0.092272	0.099475
128.8	0.073974	0.085271	0.092272	0.099864
150.3	0.073974	0.085367	0.092386	0.10013
171.8	0.074045	0.085491	0.092386	0.10052
193.2			0.092386	0.10052

SPECIFIC CONDUCTIVITIES IN MHOS/CM

TABLE IV

SPECIFIC CONDUCTIVITY OF ARTIFICIAL SEA WATER
AT VARIOUS TEMPERATURES. SALINITY = 34.481 PPT

Pressure in Bars	Temperature			
	4°C	10°C	14°C	18°C
Atmos.	0.032140	0.037523	0.041393	0.045277
10.73	0.032411	0.037622	0.041550	
21.47	0.032460	0.037821	0.041667	
26.83				0.045608
32.20	0.032460	0.037981	0.041786	
42.93	0.032480	0.038072	0.041833	
53.66	0.032485	0.038123	0.041905	0.045918
64.39	0.032496	0.038158	0.042025	
75.13	0.032558	0.038072	0.042025	
80.49				0.046180
85.86	0.032558	0.038089	0.042073	
96.59	0.032578	0.038123	0.042085	
107.3	0.032578	0.038184	0.042145	0.046365
128.8	0.032707	0.038184	0.042205	0.046578
150.3	0.032786	0.038225	0.042266	0.046632
171.8	0.032906	0.038266	0.042266	0.046712
193.2				0.046902

SPECIFIC CONDUCTIVITIES IN MHOS/CM

TABLE V

SPECIFIC CONDUCTIVITY OF REAL SEA WATER AT VARIOUS TEMPERATURES. SALINITY = 33.645 PPT

Pressure in Bars	Temperature			
	4°C	10°C	14°C	18°C
Atmos.	0.031220	0.037832	0.040474	0.044298
10.73	0.031354	0.038479	0.040673	0.044897
21.47	0.031530	0.038551	0.040673	0.044957
32.20	0.031562	0.038607	0.040706	0.044973
42.93	0.031588	0.038624	0.040722	0.045049
53.66	0.031640	0.038699	0.040722	0.045141
64.39	0.031688	0.038728	0.040772	0.045202
75.13	0.031688	0.038829	0.040939	0.045264
85.86	0.031759	0.038847	0.040974	0.045264
96.59	0.031847	0.038847	0.041280	0.045279
107.3	0.031847	0.038885	0.041347	0.045304
128.8	0.031901	0.038923	0.041486	0.045304
150.3	0.031970	0.038997	0.041521	0.045356
171.8	0.031987	0.039110	0.041590	0.045409

SPECIFIC CONDUCTIVITIES IN MHOS/CM

CHAPTER V

MATHEMATICAL DETERMINATIONS AND CONVERSIONS

Prior to a detailed analysis of the data collected during the investigations, several conversions and determinations were required. The raw data, consisting of press pressures and resistances, was meaningless until the conversions had been accomplished.

I. PRESSURE CONVERSION

The press pressure in psi was converted to equivalent pressure inside the pressure vessel and expressed in bars. This established a perspective concerning depth since 1 bar is approximately the pressure of the ocean's water column at 10 meters depth. The conversion was made using the relation that applied pressure is equal to force divided by the area over which the force is applied.

$$F = (\text{Pressure})\ (\text{Area})$$

The force through the pressure vessel piston can be computed from the measured press pressure and the area of the small piston face. The gauge measuring press pressure is calibrated against a surface area of 2.7464 in^2. The pressure felt by the electrolyte inside the well can be determined from the quotient of force and small piston face area. The area of the small piston face is 1.7671 in^2.

$$\text{Internal Pressure (psi)} = \frac{\text{Press Pressure (psi)}\ (2.7464\ in.^2)}{(1.7671\ in.^2)}$$

The internal pressure in psi was converted to bars using the relation that 14.67 psi = 1.013 bars.

II. CONVERSION OF RESISTANCE TO CONDUCTIVITY

The conductivity bridge measures the resistance across the electrodes which can be converted to specific conductivity. The following equalities were used to determine the specific conductivity from resistance:

$$\text{Measured Resistance} = \frac{\sigma \ell}{a}$$

where σ is specific resistance in ohm-cm.
ℓ is the distance between the electrode faces.
a is the cross-sectional area of one electrode face.

The specific conductivity is defined as the reciprocal of specific resistance. Thus, if the resistance and quotient ℓ/a are known, the specific conductivity (κ) can be calculated.

$$\kappa = \frac{1}{\sigma} = \frac{\ell}{aR} \text{ ohms}^{-1} \text{ cm}^{-1}$$

The factor ℓ/a, is commonly referred to as the "cell constant" and can be very accurately determined by measuring the resistance of a standard solution such as potassium chloride for which the specific conductivity has been measured accurately in the past. As previously mentioned, potassium chloride solutions were prepared using the standards recommended by Kortum and the cell constant for the pressure vessel was derived from his listed specific conductivities.[1]

$$\text{Cell Constant} = \frac{\ell}{a} = (\kappa_{KCl}) \quad \text{(Resistance)}$$

$$\text{Thus, } \kappa = \frac{\text{Cell Constant}}{\text{Resistance}} \text{ in mhos/cm}$$

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[1] J. Kortum, "Treatise on Electrochemistry," Elsevier Publishing Company, New York, New York, 1965, p. 6.

III. DETERMINATION OF CONDUCTIVITY CAUSED BY CONCENTRATION CHANGES DUE TO COMPRESSIBILITY OF THE SOLUTIONS

Molar Conductance Determination. The determination of specific conductivity resulting from increase in concentration due to the compressibility of the sample is fairly simple for the potassium chloride solutions but rather complex for the sea water. The calculation is made through an equation which relates the molar conductance (Λ) of the solution to the specific conductivity:

$$\Lambda = \kappa V$$

where V is the volume, in cubic centimeters, of one mole of the electrolytic solution.

If the solution concentration is expressed in moles per liter, the molar conductance is:

$$\Lambda = \frac{(\kappa)\ (1000)}{C}\ \text{ohms}^{-1}\ \text{cm}^{2}$$ *

where C is the concentration in moles/liter

Since potassium chloride solutions expressed in concentration units of equivalents per liter are numerically equal to their concentrations in molar units (moles per liter), the molar conductance of the KCl solutions may be readily calculated.

Determination of Conductivity Caused by Concentration Change. The molar conductance of the sea water solutions was calculated using the same equation, but after the concentration units, parts per thousand, had been converted to moles per liter.

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*J. Kortum, "Treatise on Electrochemistry". Elsevier Publishing Company, New York, New York, 1965, p. 7.

Table VI lists the concentrations of the eleven major ions in a solution of sea water of salinity 35 PPT. The concentration of each ion in moles per liter was computed after correcting the original concentration to that corresponding to the salinity of the sample used. This was done by first determining the densities of the sea water solutions for each salinity and temperature to be analyzed using Knudsen's Hydrographical Tables.[1] With this information, the actual volume of sea water present can be found as shown below:

$$(1)\quad \left[\frac{1000 \text{ gms sea water}}{1 \text{ kg sea water}}\right]\left[\overbrace{\frac{1 \text{ cm}^3 \text{ sea water}}{\text{"x" gms sea water}}}^{1/\rho}\right]\left[\frac{1 \text{ ml real sea water}}{1 \text{ cm}^3 \text{ sea water}}\right] = \frac{1000}{x}$$

The units of expression (1) are $\frac{\text{ml of sea water}}{\text{kg of sea water}}$

The concentration, Y gms per kg sea water, of an ion a^+ in a solution of sea water whose salinity is $\bar{S}$(PPT) may be converted to moles per liter in the following manner:

$$(2)\quad \left[S(\text{PPT})\right]\left[\frac{Y \text{ gms } a^+/\text{kg sea water}}{35.0 \text{ PPT}}\right]\left[\frac{1 \text{ mole } a^+}{\text{"z" gms } a^+}\right] = \frac{B \text{ moles } a^+}{\text{kg sea water}}$$

Where "z" is the molecular weight of ion a^+. The product from the results of equations (1) and (2), is the concentration of a^+ in moles/liter.

$$\left[\frac{B \text{ moles } a^+}{\text{kg sea water}}\right]\left[\frac{1 \text{ kg sea water}}{\frac{1000}{x} \text{ ml sea water}}\right] = \left[a^+\right] \frac{\text{moles}}{\text{liter}}$$

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[1] M. H. C. Knudsen, Hydrographical Tables, (Copenhagen: G. E. C. GAD, 1901), 63 pp.

TABLE VI*

CONCENTRATIONS OF MAJOR IONS COMPOSING SEA WATER OF SALINITY 35 PPT AT 0°C.

Constituent	Concentration in gms/kg of Sea Water
Chloride (Cl^-)	19.353
Sodium (Na^+)	10.76
Sulphate ($SO_4^=$)	2.712
Magnesium (Mg^{++})	1.294
Calcium (Ca^{++})	0.413
Potassium (K^+)	0.387
Bicarbonate (HCO_3^-)	0.142
Bromide (Br^-)	0.067
Strontium (Sr^{++})	0.008
Boron (B)	0.004
Flouride (F^-)	0.001

*J. P. Riley and G. Skirrow, Chemical Oceanography, (New York: Academic Press, 1965), p. 647.

The summation of concentrations was taken as the concentration of the sea water in moles per liter. The molar conductivity of each solution was computed at atmospheric pressure and was assumed to remain constant over the range of pressure application.

The increase in concentration caused by compression of the sample in the conductivity cell was determined utilizing the results of J. Crease's studies of sea water compressibility in 1962. His data has been listed by Riley and Skirrow as the percent reduction in volume of sea water of salinity 35 PPT for temperatures $0^{o}C$, $10^{o}C$, $20^{o}C$ and $30^{o}C$, at 1000 decibars pressure. The compressibility may be considered directly proportional to pressure over the range 1 to 1000 decibars allowing linear computation of compressibilities for lower pressures.[2] The coefficients of compressibilities for pressures in excess of 1000 decibars are those determined by Heck and Service while conducting sound velocity studies in sea water for the U. S. Coast and Geodetic Survey.[3] It was then necessary to extrapolate the values to conform to the temperatures being investigated during this project. Table VII lists the percent reduction in volume of sea water over the pressure range and temperatures of interest.

The percent reduction in volume values for salinity of 35 PPT were used throughout. The difference between values at 35 PPT and those for salinity of 33.64 PPT is less than .002% which results in an error less than the error (0.5%) in measuring the pressure.

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[2] J. P. Riley and G. Skirrow, Chemical Oceanography, (New York: Academic Press, 1965), p. 112.

[3] N. H. Heck and Jerry H. Service, Velocity of Sound in Sea Water, U. S. Coast and Geodetic Survey, United States Department of Commerce, Special Publication No. 108 (Washington: Government Printing Office, 1924), pp. 7-9.

The new concentration (c') resulting after each pressure increase is equal to the product of the initial concentration (c) in molar units and the quotient of initial and final volume of the sample.

$$c' = (c)\ (V_o/V) \qquad \text{moles/liter}$$

The specific conductance resulting from the changed concentration is:

$$\kappa' = \frac{\Lambda c'}{1000} \qquad \text{mhos/cm}$$

The mathematical expressions required for all determinations and conversions were programed for execution by the Navy Postgraduate School's IBM 360 digital computer. A copy of the program has been included in Appendix B.

TABLE VII

THE PERCENT REDUCTION IN VOLUME
FOR SEA WATER OF SALINITY 35 PPT

Pressure in Bars	Temperature			
	4°C	10°C	14°C	18°C
1	0.0000	0.0000	0.0000	0.0000
10.7	0.0504	0.0503	0.0491	0.0484
21.5	0.1010	0.1000	0.0983	0.0969
26.8	0.1260	0.1250	0.1229	0.1211
32.2	0.1516	0.1502	0.1486	0.1456
42.9	0.2019	0.1999	0.1975	0.1938
53.7	0.2522	0.2495	0.2455	0.2420
64.4	0.3024	0.2994	0.2945	0.2904
75.1	0.3528	0.3488	0.3432	0.3384
80.5	0.3783	0.3743	0.3683	0.3630
85.9	0.4035	0.3994	0.3929	0.3872
96.6	0.4541	0.4495	0.4420	0.4353
107.3	0.4896	0.4846	0.4766	0.4694
128.8	0.5994	0.5934	0.5846	0.5750
150.3	0.6942	0.6881	0.6774	0.6667
171.8	0.7924	0.7846	0.7706	0.7597
193.2	0.888	0.878	0.865	0.852

CHAPTER VI

COMPARISON OF THE RESULTS

I. OBSERVATIONS

The data collected during the experiments has been graphically presented as curves of specific conductivity vs. pressure. To obtain the general trend of the response of each electrolyte when pressure is applied, a scale was used such that a large range of values could be presented. This enabled the family of temperature curves for each solution to be shown together. The effect of such scale selection is to minimize deviation of individual curves. The standard KCl solutions are shown in Figures 7, 8, and 9. The curves are least squares fits to the data points. Three fits are presented, linear, parabolic and cubic, for the purpose of determining whether the relationship between pressure and conductivity is linear as previous researchers propose it to be, or non-linear. Also, a standard trend can be established from the potassium chloride solutions for comparison with the sea water solutions to decide if sea water responds to pressure normally, as the standards do, or abnormally, different than the standards.

Figures 7 and 8 show the specific conductivity of the standard KCl solutions to increase with increasing pressure. The largest increase occurs at the higher temperature with the increases becoming less pronounced and nearly equal as temperature decreases. Also, the greatest increase in specific conductivity occurs within the 1 to 150 bar pressure internal. At pressure greater than 150 bars, the rate of

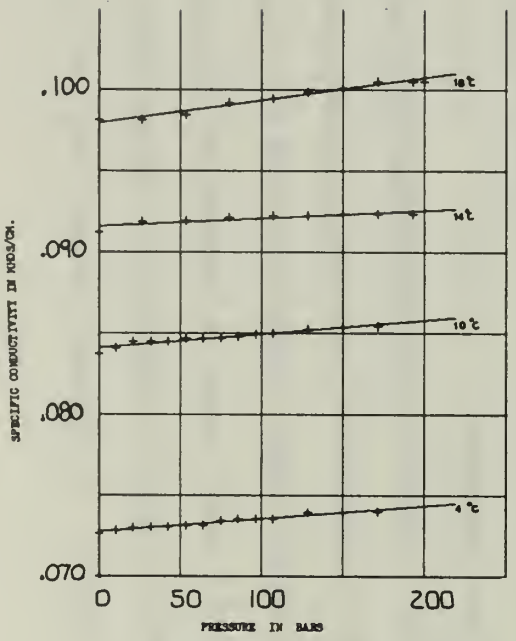

FIGURE 7A LINEAR FIT.

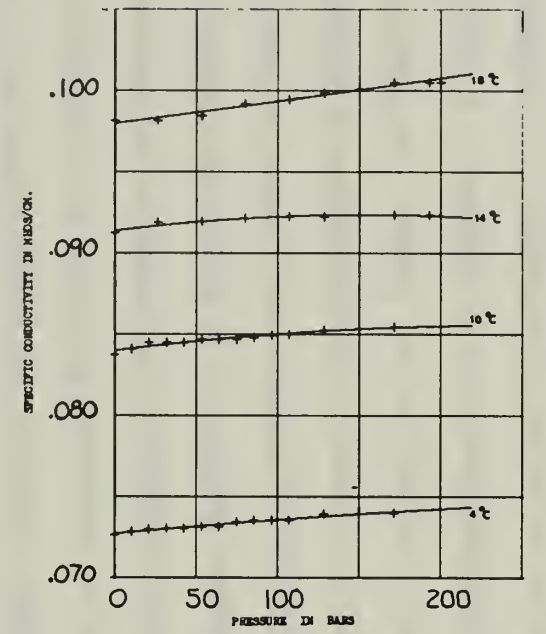

FIGURE 7B 2ND DEGREE FIT.

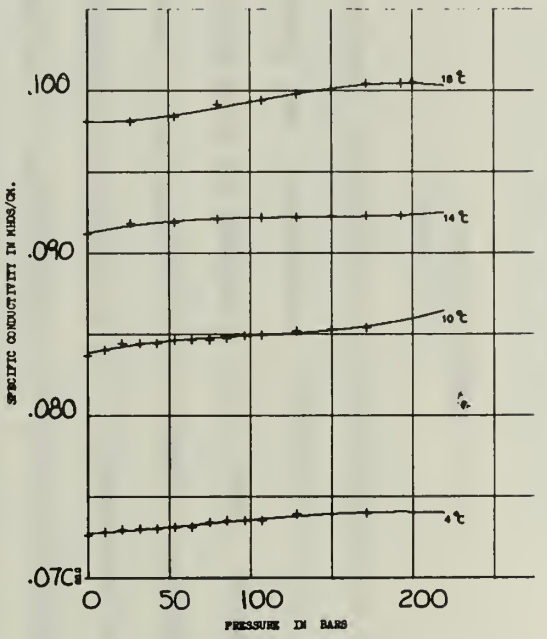

FIGURE 7C. 3RD DEGREE FIT.

FIGURE 7

SPECIFIC CONDUCTIVITY VS. PRESSURE
FOR A SOLUTION OF 1.0M KCl AT
VARIOUS TEMPERATURES

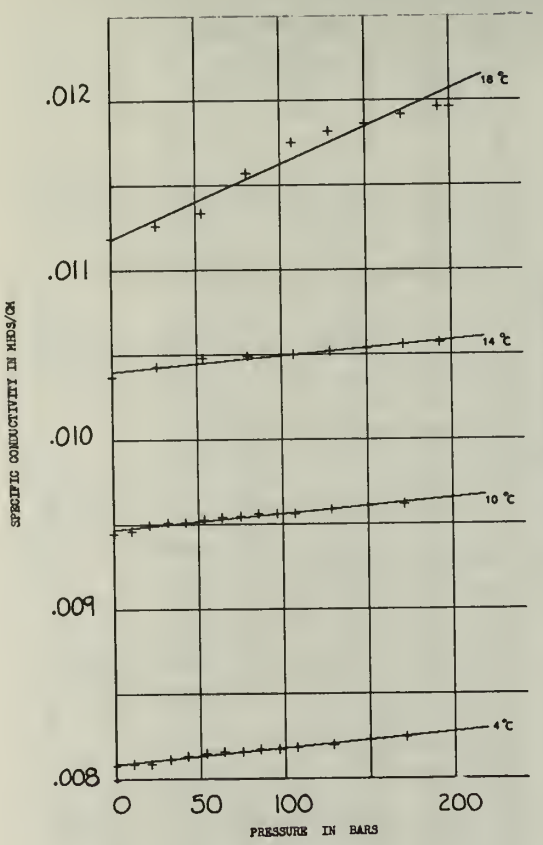

FIGURE 8A. LINEAR FIT.

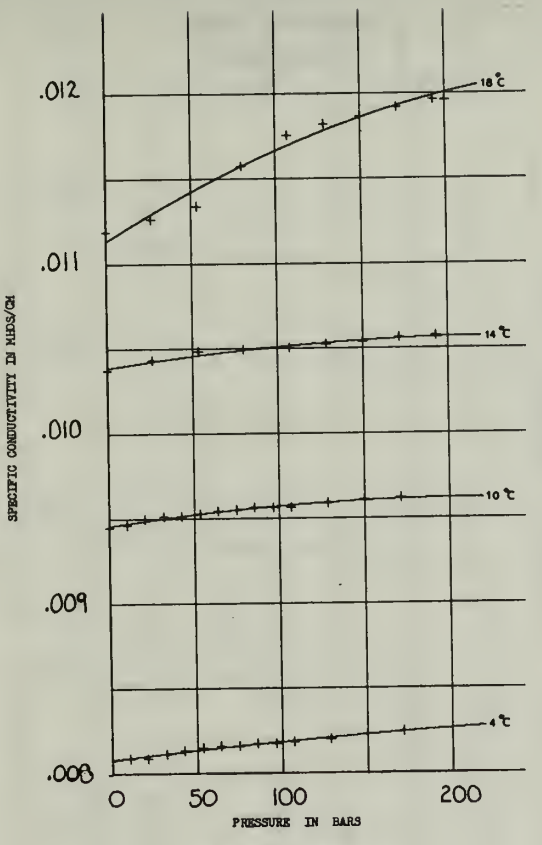

FIGURE 8B. 2ND DEGREE FIT.

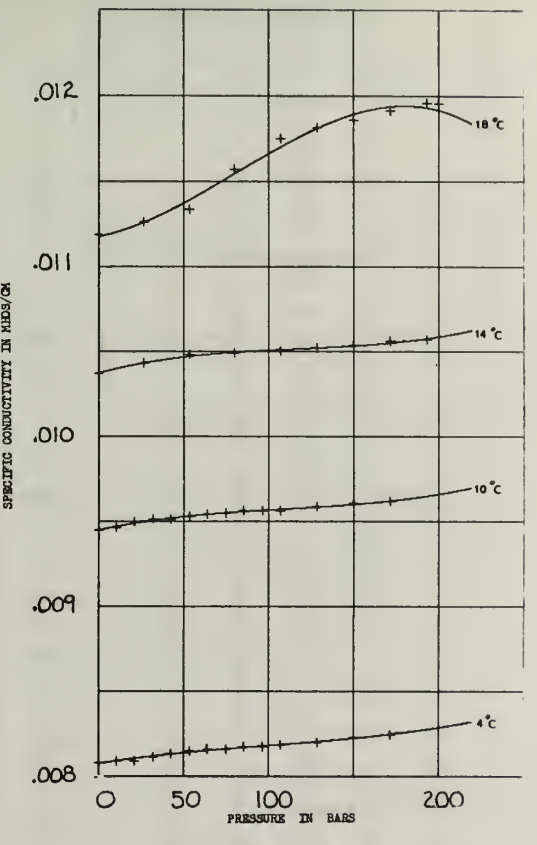

FIGURE 8C. 3RD DEGREE FIT.

FIGURE 8

SPECIFIC CONDUCTIVITY VS. PRESSURE
FOR A SOLUTION OF 0.1N KCl AT
VARIOUS TEMPERATURES

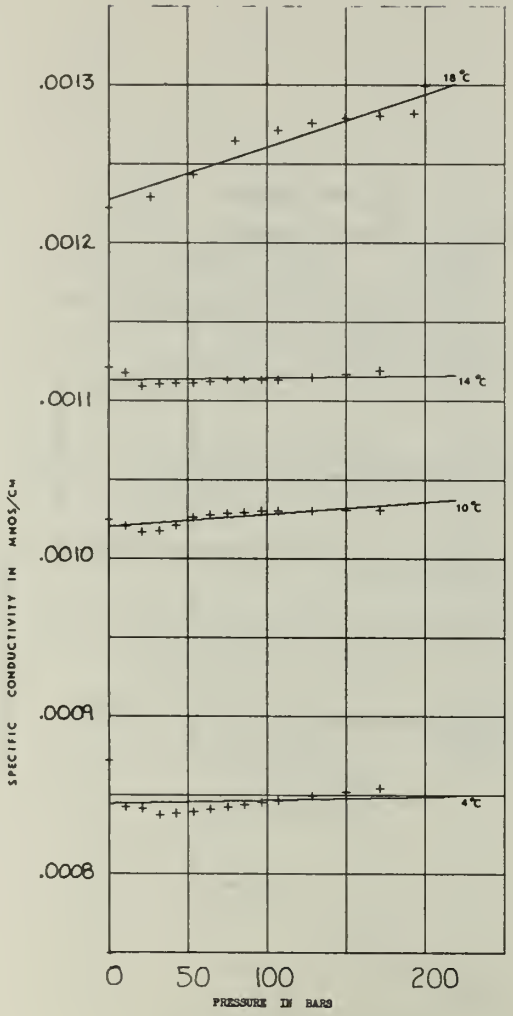

FIGURE 9A LINEAR FIT.

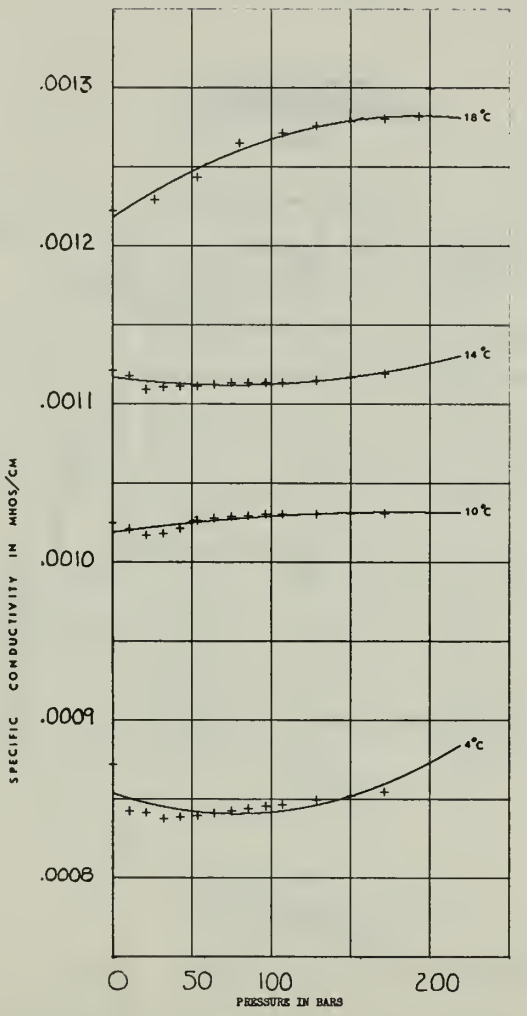

FIGURE 9B. 2ND DEGREE FIT.

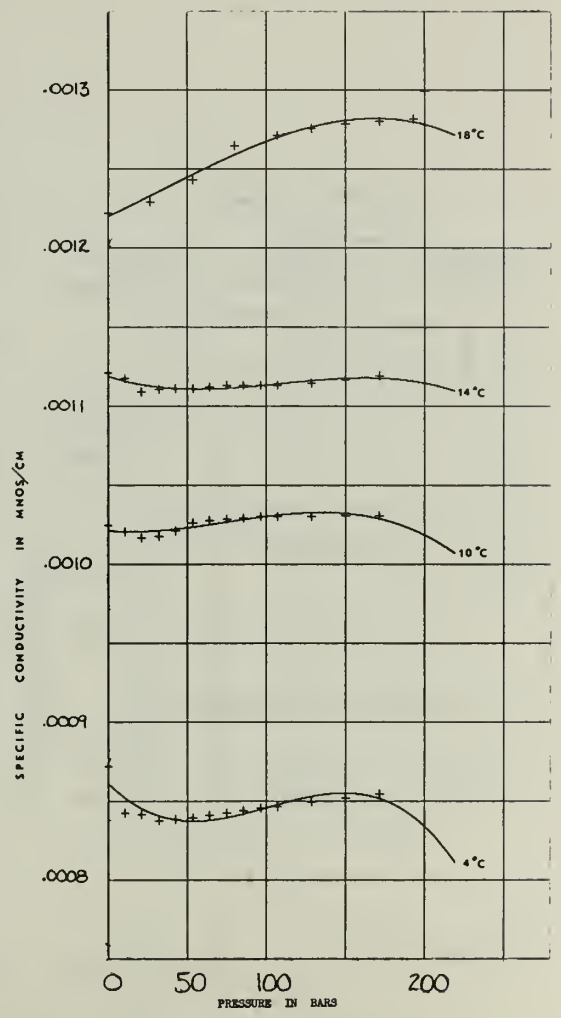

FIGURE 9C. 3RD DEGREE FIT.

FIGURE 9

SPECIFIC CONDUCTIVITY VS. PRESSURE
FOR A SOLUTION OF 0.01M KCl AT
VARIOUS TEMPERATURES

increase of conductivity is decreased in comparison. There appears then to be a dependence upon temperature of the standard solution's response to pressure, as well as a range of pressures where the increase is greatest.

It is difficult to decide if the relationship between pressure and conductivity is linear or non-linear since all fits seem good when presented on a small scale. Linear fits appear satisfactory for the $10^{o}C$ and $4^{o}C$ curves but less satisfactory for the higher temperatures. Parabolic and cubic fits appear to best describe the entire family of curves, however.

The trends exhibited by the 0.01N KCl solution in Figure 9, are quite dissimilar in comparison to the 1.0 and 0.1 normal KCl solutions. Curves representing temperatures of $4^{o}C$, $10^{o}C$ and $14^{o}C$ show the specific conductivity passing through a minimum value at about 40 bars pressure, followed by an increase over the remaining pressure range. The minimum becomes less pronounced with increasing temperature and ceases to exist at temperature $18^{o}C$.

The phenomenon is felt to be caused by the specific conductivity of the distilled water used in preparing the 0.01N KCl solution.

The conductivity of the water was measured at $4^{o}C$ and found to be of magnitude 10^{-5} mhos/cm. The specific conductivity was noted to initially decrease, over the pressure range 1 to 50 bars, and then increase. The magnitude of the specific conductance for 0.01N, KCl ranges from 8×10^{-4} to 11×10^{-4} mhos/cm over the temperature range $4^{o}C$ to $10^{o}C$. There is reasonable evidence to support the belief that the conductivity changes of the 0.01 KCl solution is being greatly influenced by the conductivity of the solvent at these temperatures. Also, because the molar concentration of sea water is approximately

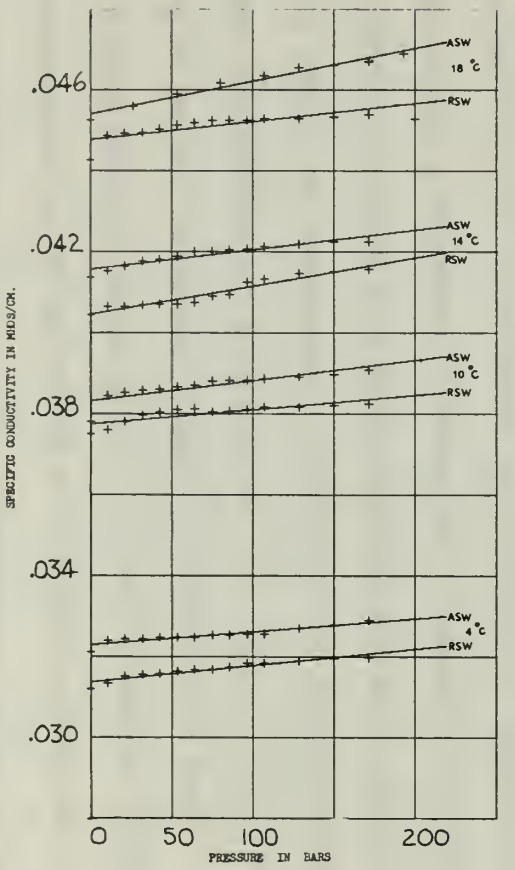

FIGURE 10A. LINEAR FIT.

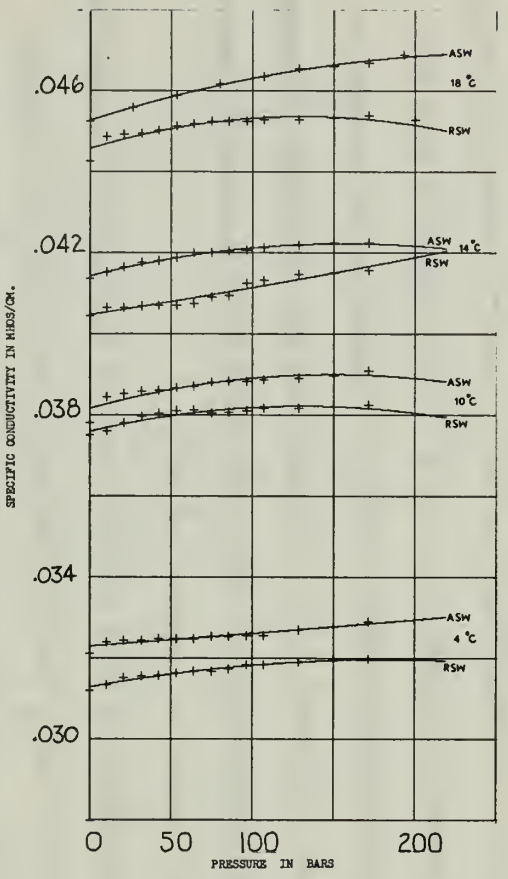

FIGURE 10B. 2ND DEGREE FIT.

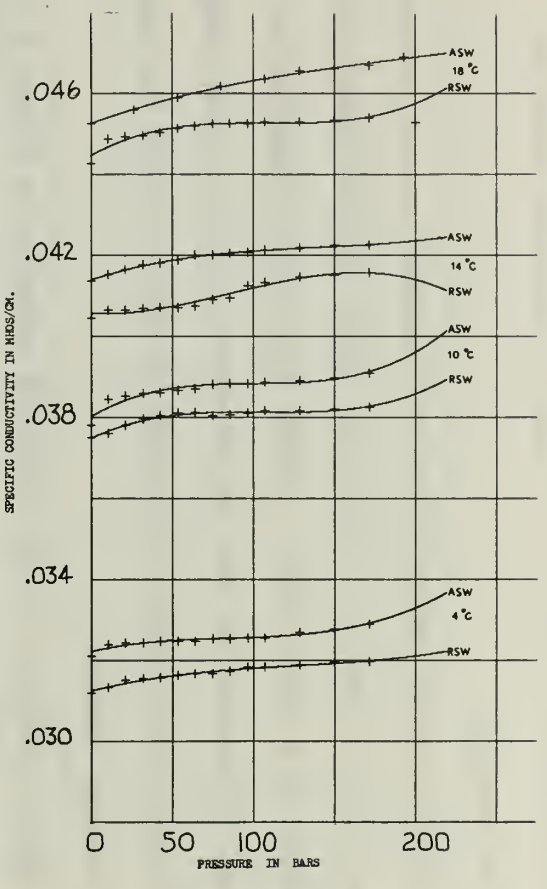

FIGURE 10C. 3RD DEGREE FIT.

FIGURE 10

SPECIFIC CONDUCTIVITY VS. PRESSURE
FOR SOLUTIONS OF REAL AND
ARTIFICIAL SEA WATER AT
VARIOUS TEMPERATURES

1.0, very little emphasis should be placed on comparisons with a dilute KCl solution. 1.00N KCl and 0.10N KCl are much more meaningful for comparison purposes.

Figure 10 is a graphical display of pressure vs. conductivity for real sea water and artificial sea water. The scale is again selected such that all isotherms could be presented on a single plot. The specific conductivity increases with pressure, as expected, with the most rapid increase occurring over the first 100 bars.

The total conductivity change over the pressure range appears to increase slightly with decreasing temperature for the real sea water solutions, at 4°C, while the total conductivity change for artificial sea water over the pressure range decreases slightly with decreasing temperature.

A further interesting observation is the shifting toward lower pressures of the curve segments representing the greatest rate of increase of conductivity as temperature is increased. This is the case for both real and artificial sea water with the possible exception of the artificial solution at 18°C.

As with the standard KCl solutions, three least square fits are shown for the data. The parabolic and cubic fits appear better than the linear fit.

II. COMPARISON WITH PREVIOUS MEASUREMENTS

Standard Potassium Chloride Solutions. L. H. Adams and R. E. Hall,[1] in 1931 conducted experiments in measuring the resistances of

[1] L. H. Adams and R. E. Hall, "The Effect of Pressure on the Electrical Conductivity of Solutions of Sodium Chloride and other Electrolytes," Journal of Physical Chemistry, LXXXV (August, 1931), pp. 2145-2163.

solutions of sodium chloride at high pressures. Their results are presented as the ratio of resistances, R/R_o, where R_o is the resistance at atmospheric pressure and R is the cell resistance at the given pressure. The authors corrected for the increase in concentration by dividing the relative resistance ratio at each pressure by the relative volume change, V/V_o, for the pressure change. The corrections, resulted in significant changes to the resistance ratio. The results of Adams and Hall are suitable for comparing the standard KCl solutions used during the investigation, since trends are of interest rather than absolute conductivity values. Also, KCl and NaCl are both strong electrolytes (nearly completely dissociating in aqueous solutions even at relatively high concentrations), ionizing at a 1:1 ratio.

The values of resistance ratios observed by Adams and Hall for a 0.583% (0.10N) NaCl solution are listed in Table VIII with the corresponding values measured for a 0.10N KCl solution during this research.

On the basis of Table VIII, the two sources of data compare reasonably well. The greatest deviation between any two resistance ratios is 0.006. At all pressures, the ratio for the KCl solution is less than the NaCl solution. This is attributed to the smaller tendency KCl has toward ion pairing at this concentration than has NaCl and by the differing effects pressure has on the two electrolytes in altering this tendency.[2]

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[2] C. I. Martynova, et al., "Electrolytic Properties of Aqueous Solutions of Some Electrolytes at High Parameters," Teploemergetika, XII (August, 1963), pp. 91-95.

TABLE VIII

COMPARATIVE RESULTS FOR RESISTANCE RATIOS, R/R_o, OF 0.10N KCl AND 0.10M NaCl

Pressure in Bars	Adams and Hall 0.10 NaCl	Mays 0.10 KCl
Atmos.	1.000	1.000
27	.998	.994
54	.995	.989
80	.994	.988
107	.992	.987
129	.989	.986
150	.987	.984
172	.986	.982
193	.985	.981

Sea Water Comparisons. The experimental results in general support the findings of Horne and Bradshaw,[3] in that all show an increase in specific conductivity of sea water with pressure. However, comparisons with the results shown by B. V. Hamon are completely incompatable. The incompatability may be the result of misinterpretation of his results as they are presented in a confusing manner. He uses the terms, resistance of solution and conductance of solution synonymously

[3] R. A. Horne and G. R. Frysinger, "The Effect of Pressure on the Electrical Conductivity of Sea Water," Journal of Geophysical Research, VII (April, 1963), pp. 1967-1973; A. Bradshaw, et al., "The Effect of Pressure on the Electrical Conductance of Sea Water," Deep Sea Research, XII (November, 1964), pp. 151-162.

throughout his paper, when in actuality, they are reciprocals. His measurements of resistance consistently show an increase with increasing pressure which must be interpreted as a conductivity decrease with pressure. Hamon's data in this respect agrees with none of the other researchers results in the field. The unusual resistances measured by Hamon may possibly be due to his lack of temperature control, especially since the pressure application was accomplished by introducing nitrogen gas into the pressure vessel. The increase in temperature of the nitrogen when compressed is much greater than the temperature increase which would result if the pressure was applied directly to the solution. There may have been considerable heat transfer from the gas to the solution and the increased solution temperature should have resulted in a decrease in resistance. Thus, the increasing resistance is unexplained.

Figure 11 represents the relation between temperature and specific conductivity for sea water, salinity = 34.481 PPT. The data points have been fitted with isobaric lines and show just the opposite of Hamon's results, in that the conductivity increases with temperature rather than decreases.

Horne and Frysinger's experimental results and the results of this study are in general complimentary,[4] showing a rapid increase in conductivity over the first 100-200 bars pressure then increasing at a lesser rate. The change in specific conductivity over the first 150 bars pressure observed by Horne is also, very close in comparison

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[4]R. A. Horne, op. cit., p. 1968.

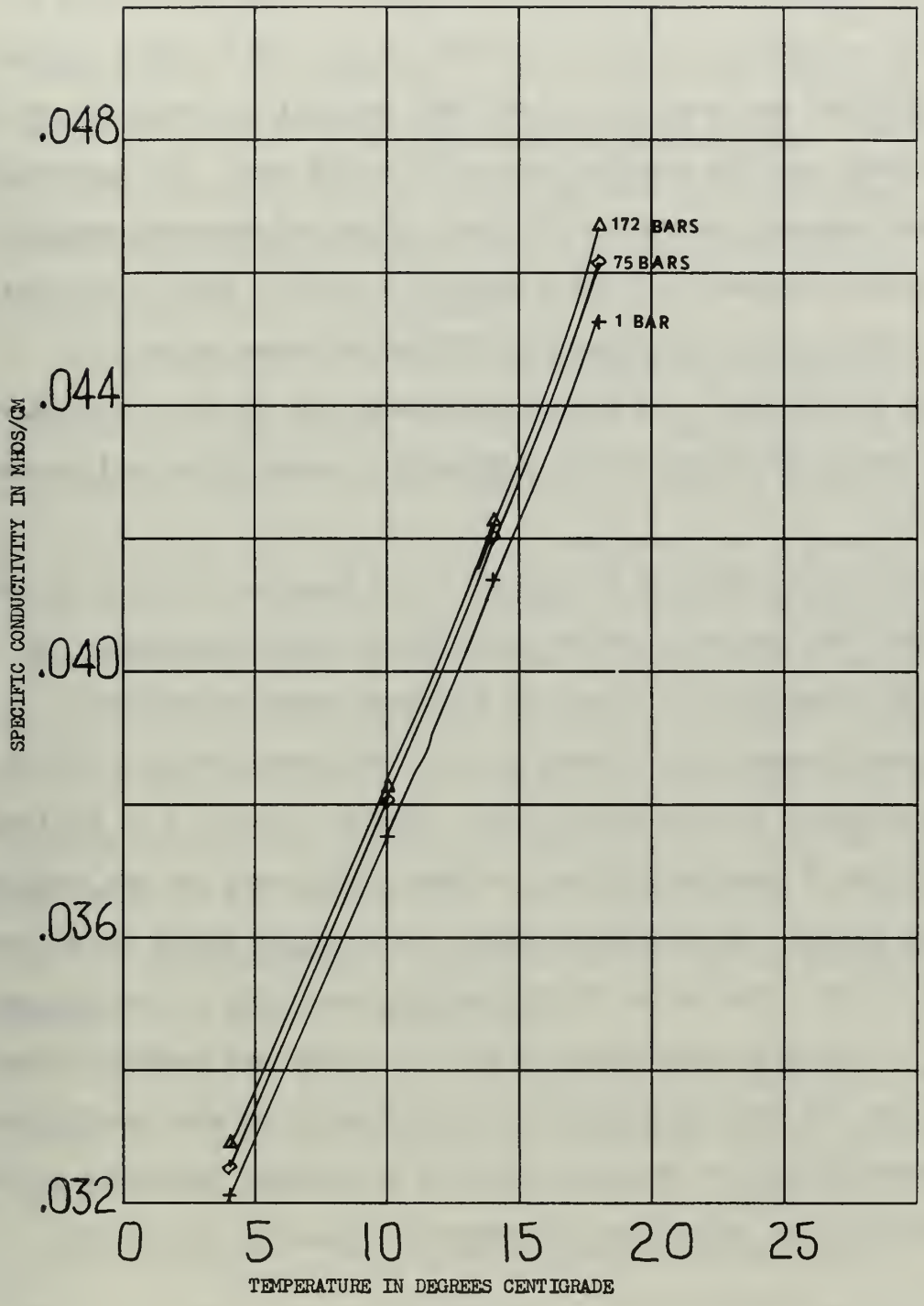

FIGURE 11

SPECIFIC CONDUCTIVITY VS. TEMPERATURE FOR SEA WATER (S = 34.481 PPT) AT DIFFERENT PRESSURES

to the change measured during this research project. Unfortunately, Horne has only one data point for pressures less than 200 bars to use for comparison. Tables IV and V on page 31 show an increase in specific conductivity at 4°C of 0.000567 mhos/cm and 0.000681 mhos/cm for artificial sea water (S = 34.481 PPT) and real sea water (33.695 PPT) respectively over the pressure interval 1 to 128 bars. For approximately the same pressure interval (1-138 bars), Horne and Frysinger measured a conductivity increase of 0.00073 mhos/cm at 4.82°C. Their electrolyte was a slightly more concentrated artificial sea water solution of salinity 34.907 PPT.[5] The difference between the values of conductivity change can be attributed to the difference in temperatures and concentrations.

There is considerable difference in the specific conductivity values resulting from the new solution concentration after compression. A graphical presentation by Horne and Frysinger shows the specific conductance change for sea water (S = 35.0 PPT, temperature = 0°C) to be approximately 0.00008 mhos/cm for a pressure interval 1 to 200 bars.[6] Their source of compressibilities to make calculations was the International Critical Tables. As previously stated, the Critical Tables are believed to be in error. The source of compressibilities cited in the Critical Tables is a special publication of the U. S. Coast and Geodetic Survey by Heck and Service. This publication has listed the same coefficients of compressibility for sea water relative to pressure increasing in bars that the Critical Tables have for pressure increasing in megabars.

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[5] Ibid.

[6] Ibid. p. 1971.

The conductivities calculated by Horne and Frysinger to determine the concentration effect of the experiments are much smaller in comparison to those determined while conducting this investigation. The cause may be the result of the apparently mislabeled table in the International Critical Tables. There is no justification in assuming the conductance contributed by a concentration change of the solution, as it is compressed, is negligible as Horne and Frysinger do.

The investigation conducted by Bradshaw and Schleicher is essentially a duplication of Horne's work. The results are presented as percent increases in ionic conductivity over the pressure interval 1 to 1000 bars with, again only one measurement at a pressure less than 200 bars.[8] The percent increases in specific conductivity calculated by Bradshaw and Schleicher are consistently smaller by about 1.0% than those calculated from the data listed in Table V. It is difficult to derive any significance from these differences because the absolute values of the specific conductivities measured by Schleicher are not available. The compressibility of the solutions was not considered thus no comparison can be made concerning the concentration effect on conductivity.

The effect of pressure on the electrical conductivity observed during the experiments compares most favorably with the results of Horne and Frysinger with the exception of the concentration effect during compression. Lack of data for pressures less than 138 bars made it necessary to use approximate values for the comparisons, but are felt to be meaningful.

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[8] A. Bradshaw, et. al., loc.cit.

CHAPTER VII

EXPLANATION OF RESULTS

The electrical conductivity of an electrolytic solution depends upon several parameters, and many of these parameters are functions of other variables. For sea water, the conductivity is essentially dependent upon four quantities. These are:

(1) Nature of the Solution
(2) Applied Electromotive Force
(3) Interionic Reactions
(4) Viscosity

Of these four quantities, the viscosity generally appears to have the greatest influence on conductivity, but under certain conditions, the others may be equally as important.

To determine the pressure dependence of specific conductivity of sea water or any electrolyte, one must closely examine effects pressure has on the above quantities.

I. NATURE OF SOLUTION

An aqueous electrolytic solution may be characterized by the nature of its solute, solvent, and its concentration. For the purpose of this study, the solvent was water and in the standard solutions, the solute was potassium chloride. The artificial sea water contained as solute, specific amounts of the eleven major constituents found in real sea water. This resulted in a solution of 34.481 PPT concentration. Real sea water is justifiably assumed to contain every known element in its composition.[1] The concentrations ranged from 33.642 to 33.646 PPT.

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[1] J. P. Riley and G. Skirrow, "Chemical Oceanography," Academic Press, New York, New York, 1965, 712 pp.

The electrical conductivity of the aqueous solutions, when considering only the solution constituents, is dependent upon the concentration, degree of dissociation, and ionic mobilities of its constituents.

Conductivity, being basically a measure of the rapidity with which ions in solution migrate toward the electrode of opposite charge when a potential is applied across the solution, naturally depends upon the number of ions in the solution and their velocities resulting from the electromotive force. The number of ions present in solution is a function of the concentration and dissociation constant. An increase in concentration places a greater number of molecules into the solution and assuming they completely ionize, there would be an increase in the number of charge carrying species which would result in a conductivity increase. Electrolytes are generally classified by the number of ion pairs formed when placed in solution. An electrolytic solution which contains a relatively small number of ions and many ion pairs is called weak while a strong electrolyte contains a great number of ions and few ion pairs. Solutions of potassium chloride and sea water are strong electrolytes and have characteristically high conductivities for this reason.

The velocity of ions in solution is characteristic for a given species and is directly proportional to the valence of the ion. Thus, in a solution of high valence ions, one would expect a greater conductance. However, most electrolytes which ionize to high valence anions and cations have relatively high association constants and tend to form neutral ion pairs in solution. This is especially true for some of the major constituents of sea water.

II. APPLIED VOLTAGE

The measurement of a solution's conductivity requires that a voltage be applied across the electrodes in the solution. The voltage produces an electric field in the solution. It is this field which causes the ions to move toward their attracting electrodes. The LKD Producter conductivity bridge used for the resistance measurements is characterized by a constant electromotive force at the balance point. Thus, the applied voltage had no effect on the variation of the solution's conductivity.

III. INTERIONIC REACTIONS

Three interionic reaction effects are possible in an electrolytic solution. Ions of opposite sign may interfere with each other's motion in an electrostatic manner, or they may restrict one anothers movement through mechanical interference. If the solution is a sufficiently complex mixture of several components, an anion and cation may join together by means of a purely electrostatic bond to form a neutrally charged ion pair.

The first two effects have been extensively studied and are referred to as the relaxation and electrophoretic effects respectively.[2]

The electrostatic interactions or, relaxation effect, are caused by the tendency of an ion with its hydration atmosphere, to assume an asymmetrical shape if an ion of like or opposite charge passes sufficiently close to it during the migration process. This will result

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[2]J.O'M. Bockris, Modern Aspects of Electrochemistry No. 2 (London: Butterworths Scientific Publications, 1959), p. 51.

in a change of the ion's mobility and the resulting specific conductivity of the solution. The electrophoretic effect is a mechanical alteration of an ion's motion. It is based upon the theory that an ion moving in a medium of viscosity, μ, will tend to carry the adjacent medium along with it. Ions, in the vicinity will be influenced by the fluid's movement and will either be retarded or assisted in their movement. Neither effect is critical unless the solution is of high concentration.

The third interionic effect, ion pairing, is the least known but could play a prominent role explaining the pressure effect on electrical conductivity of sea water at high pressure. The ionic association theory of B. Jerrum has become most widely accepted.[3] The theory is based on a probability function that a cation and an anion of equal valence will form an electrically neutral ion through electrical attractive forces if they pass within a specified distance of each other in a solution. The number of ions in a cubic centimeter of the solution must be sufficiently large, however, if this is to occur. As can be seen, these requirements rely heavily upon the concentration and degree of dissociation of the solution.

Garrels and Thompson,[4] in 1962 determined that approximately 9% of the calcium, 13% of the magnesium, 1% of the sodium, 1/2 of the sulphate, 1/3 of the bicarbonate, and 90% of the carbonate found in sea water exist as ion pairs, at atmospheric pressure. One may only speculate as to what effect pressure has on the formation of these ion pairs.

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[3]Herbert S. Harned and Benton B. Owen, The Physical Chemistry of Electrolytic Solutions (New York: Reinhold Publishing Corporation, 1958), 803 pp.

[4]Riley, op.cit., p. 121.

IV. VISCOSITY

With the exception of pure water at low temperatures, most liquids show an exponential increase in viscosity with increasing pressure.[5] The viscosity of water is known to pass through a minimum in viscosity with increasing pressure at 0°C and 10°C. This minimum occurs at approximately 500 bars pressure. However, the presence of a dissolved electrolyte in the solvent water, removes the phenomenon,and for many years the belief existed that pressure caused the viscosity of sea water to increase.[6] This is not the case as has been shown by Horne and Johnson during a recent investigation of the subject.[7]

The viscosity of any aqueous solution is basically dependent upon the degree of association of the solvent molecules, degree of solvation of solute ions, solution temperature and concentration. Pressure has a significant effect upon each of the variables.

The Solvent. In a solution with water as a solvent, the water molecules tend to arrange themselves into two groups, ordered and disordered. In 1957, M. S. Frank and W. Y. Wen determined that liquid water exists as a mixture of weak, hydrogen bonded clusters and monomeric molecules.[8] The clusters consist of 4 water molecules

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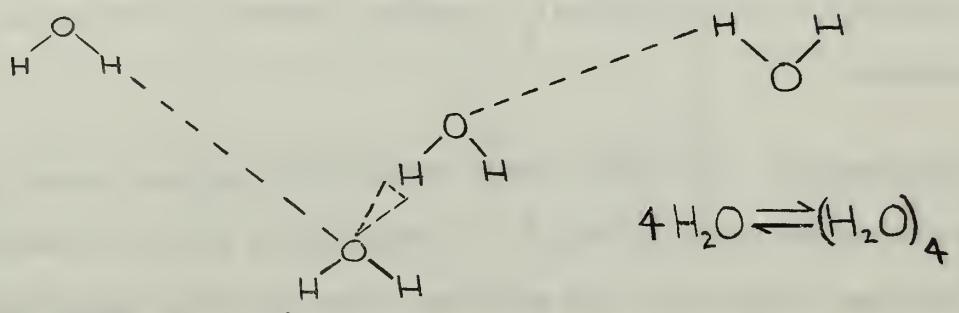
[5] S. D. Hamann, Physico-Chemical Effects of Pressure (New York: New York Academic Press, Inc., 1957), p. 81.

[6] Ibid., p. 82.

[7] R. A. Horne and D. S. Johnson, "The Viscosity of Compressed Sea Water," Journal of Geophysical Research, LXXXI (November, 1966), p. 5276.

[8] Ibid., p. 5275-5277.

tied together by 3 hydrogen bonds. The structure of the clusters is apparently invariant and offers a serious obstruction to a solute ion passing through the solution. The diagram below shows the three dimensional arrangement of such a cluster.



Those water molecules which do not form clusters become free molecules in the solution, forming a disordered array. They are available to become members of the hydration atmospheres surrounding the solute ions.

The Solvation Effect. A second factor determining the viscosity of an electrolytic solution is the solvation effect. The solvation effect results from the tendency of the polarized, free water molecules to orient themselves around the cations and to a small extent the anions in the solution. The orientation results in the formation of a hydration sphere which effects the motion of the ions in two ways. They are retarded in their travel due to their increased circumference and the opportunity for interionic reactions is greater. The number of water molecules composing the hydration atmosphere has been most commonly found to be between 6 and 10.[9]

Temperature. The temperature effect upon viscosity of an aqueous solution is well known. The viscosity decreases with increasing

[9]John P. Hunt, Metal Ions in Solution (New York: W. A. Benjamin, Inc. 1965), p. 27.

temperature except for the special case of liquid water at $0^{\circ}C$ and $10^{\circ}C$.[10] The explanation for this is that a rise in temperature decreases the number of Frank-Wen clusters resulting in a decreased resistance to the ions moving through the solution. This partially accounts for the conductivity increase observed by temperature increases.

Concentration. The final factor contributing to the viscosity problem is the solution concentration. In the case of highly concentrated solutions (saturated), the solution essentially has insufficient solvent molecules to meet the demands of the solute ions in filling their hydration atmospheres. The result is a rapid increase in viscosity. Since sea water is not considered to be a saturated solution, an increase in concentration results in a conductivity increase because the above effect is not considered to be significant in altering the viscosity.

V. THE EFFECTS OF PRESSURE ON VISCOSITY AND CONDUCTIVITY

The application of pressure to an electrolytic solution results in significant changes to the ionic conductance of the solution. The solution experiences a marked change in concentration and ionic mobility. The latter is primarily caused by viscosity changes.*

Previous investigations have either neglected the concentration changes or concluded they were not significant. Figures 12 through 15 are expanded scale plots of specific conductivity vs. pressure showing

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[10] Hamann, op. cit., p. 81.

* Infra, p. 66.

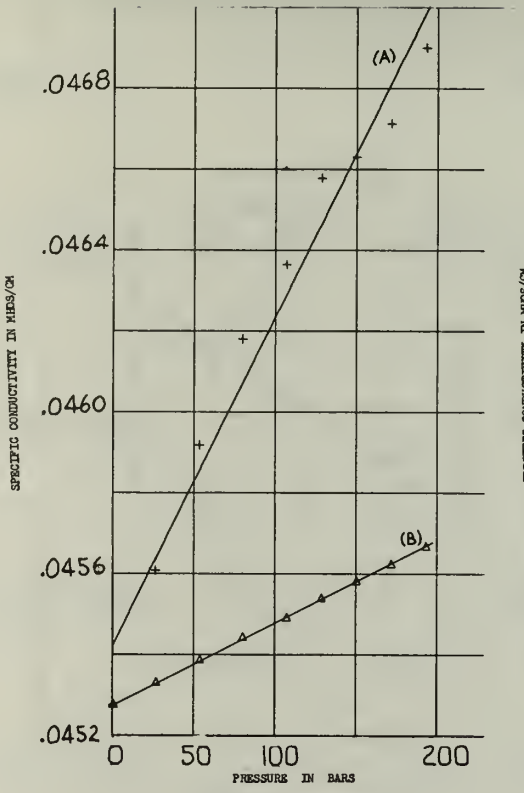


FIGURE 12A. LINEAR FIT.

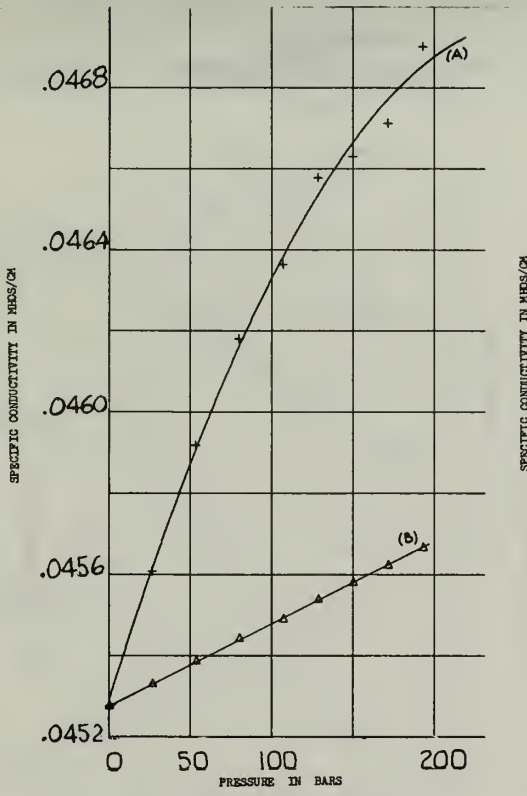


FIGURE 12B. 2ND DEGREE FIT.

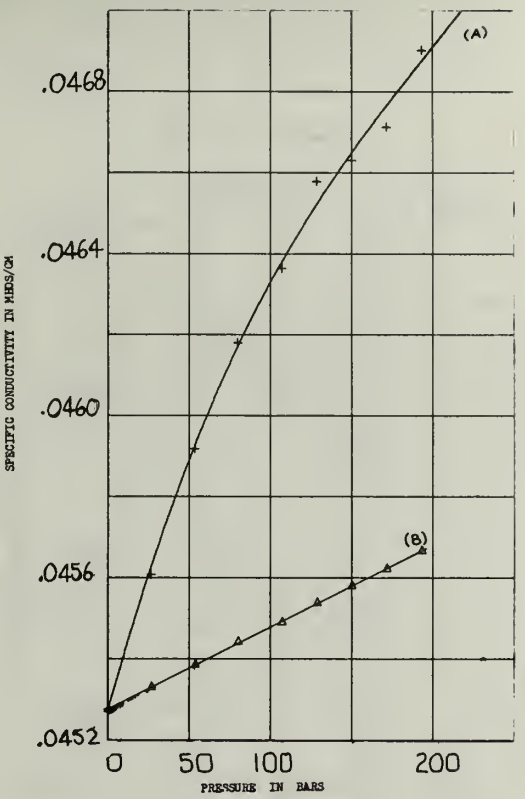
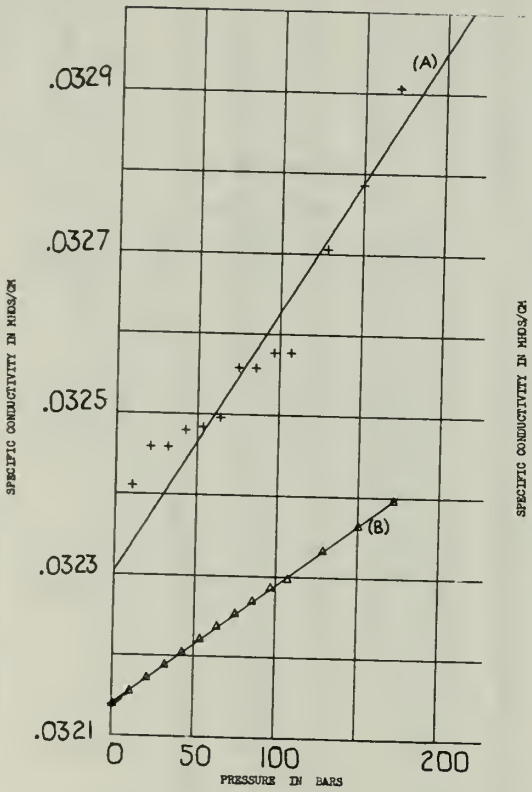


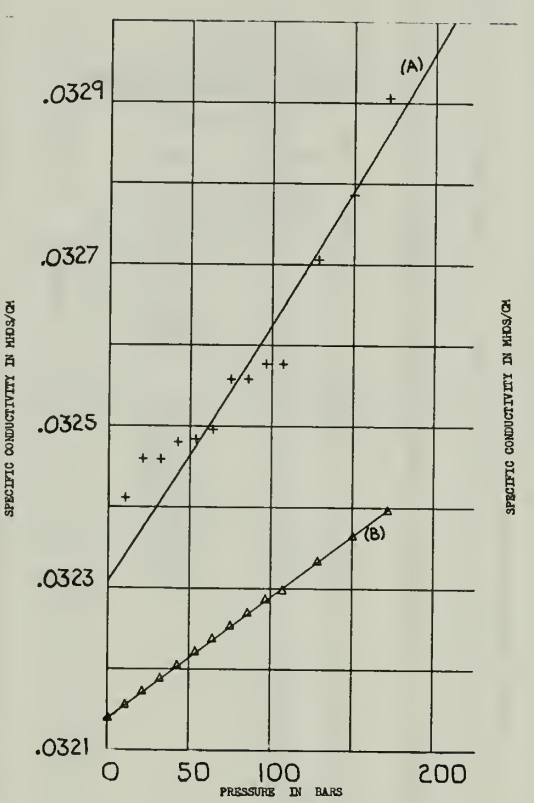
FIGURE 12C. 3RD DEGREE FIT.

FIGURE 12

SPECIFIC CONDUCTIVITY VS. PRESSURE FOR
ARTIFICIAL SEA WATER (S = 34.481 PPT; T = 18°C)
(A) OBSERVED
(B) COMPRESSION EFFECT



PIGURE 13A. LINEAR FIT.



PIGURE 13B. 2ND DEGREE FIT.

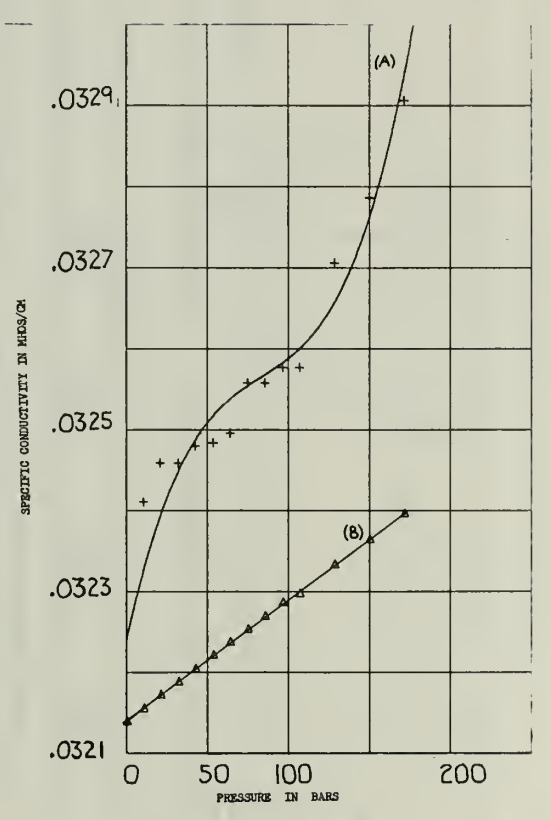


FIGURE 13C. 3RD DEGREE FIT.

FIGURE 13

SPECIFIC CONDUCTIVITY VS. PRESSURE FOR
ARTIFICIAL SEA WATER (S = 34.481 PPT; T = 4°C)
(A) OBSERVED
(B) COMPRESSIDN EFFECT

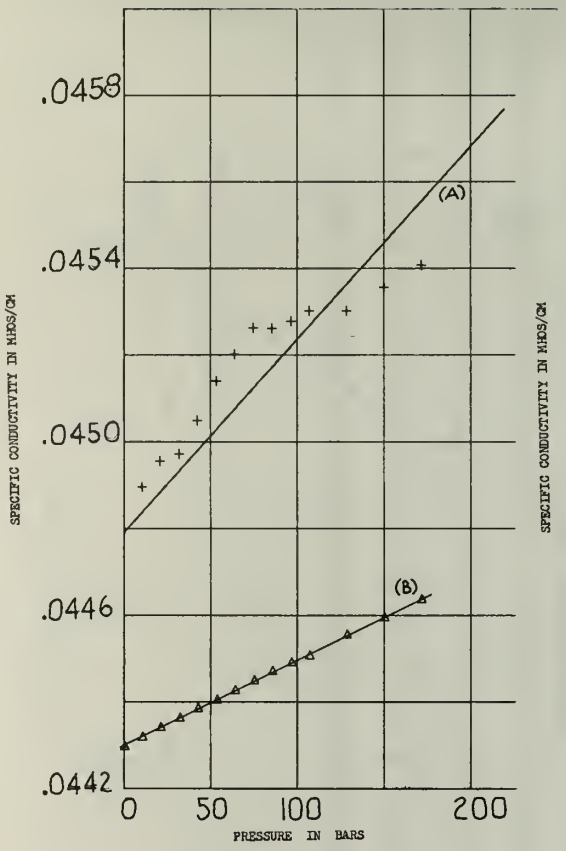


FIGURE 14A. LINEAR FIT.

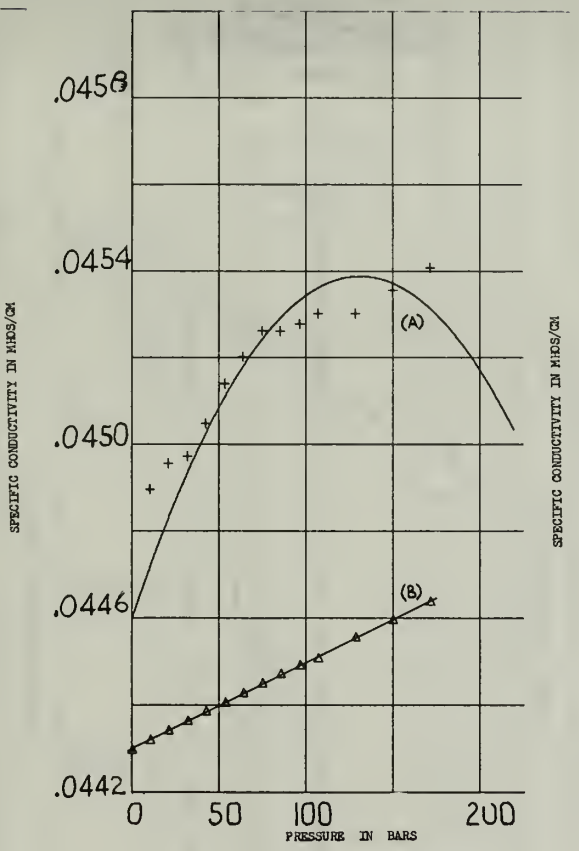


FIGURE 14B. 2ND DEGREE FIT.

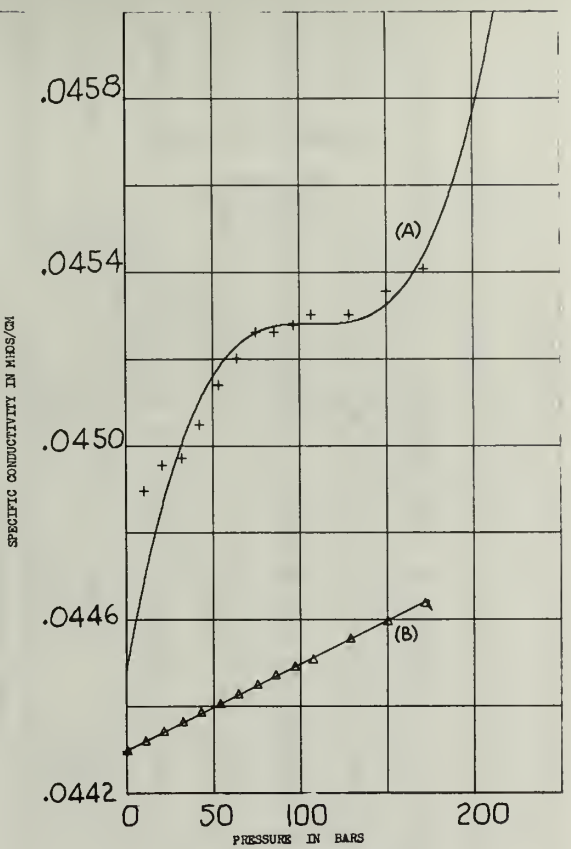


FIGURE 14C. 3RD DEGREE FIT.

FIGURE 14

SPECIFIC CONDUCTIVITY VS. PRESSURE FOR
REAL SEA WATER (S = 33.646 PPT; T = 18°C)
(A) OBSERVED
(B) COMPRESSION EFFECT

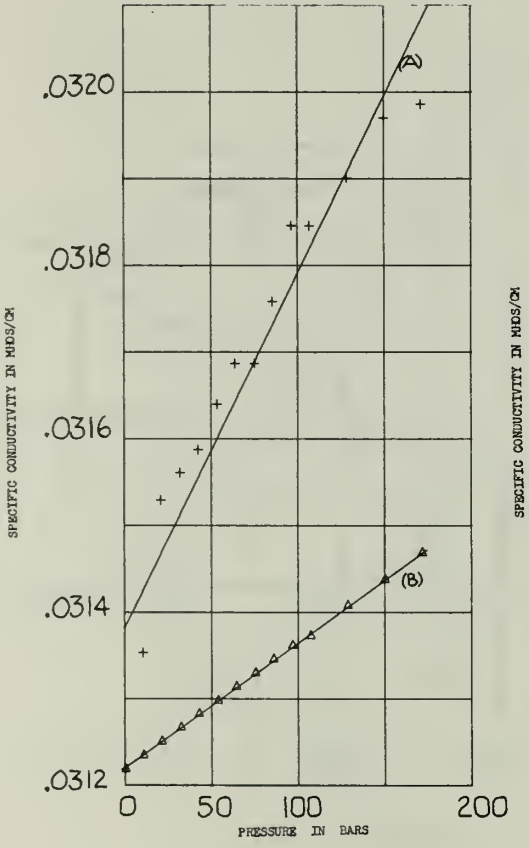


FIGURE 15A. LINEAR FIT.

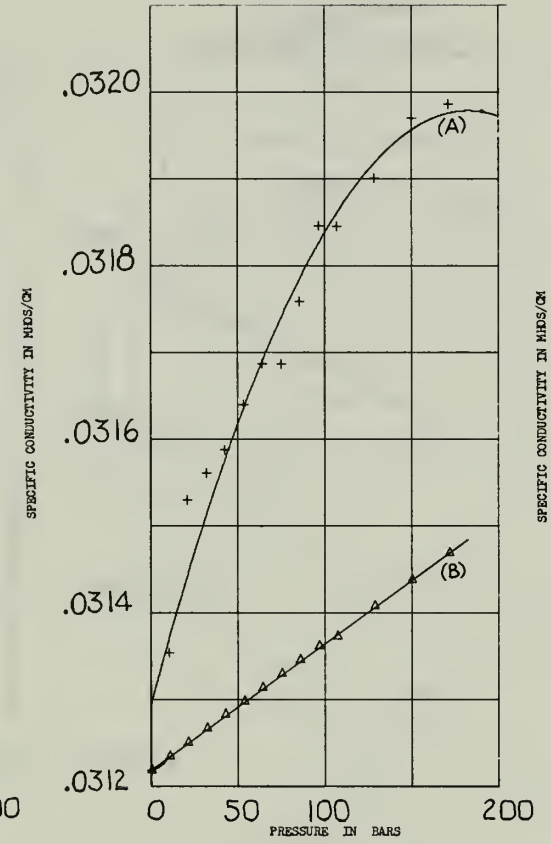


FIGURE 15B. 2ND DEGREE FIT.

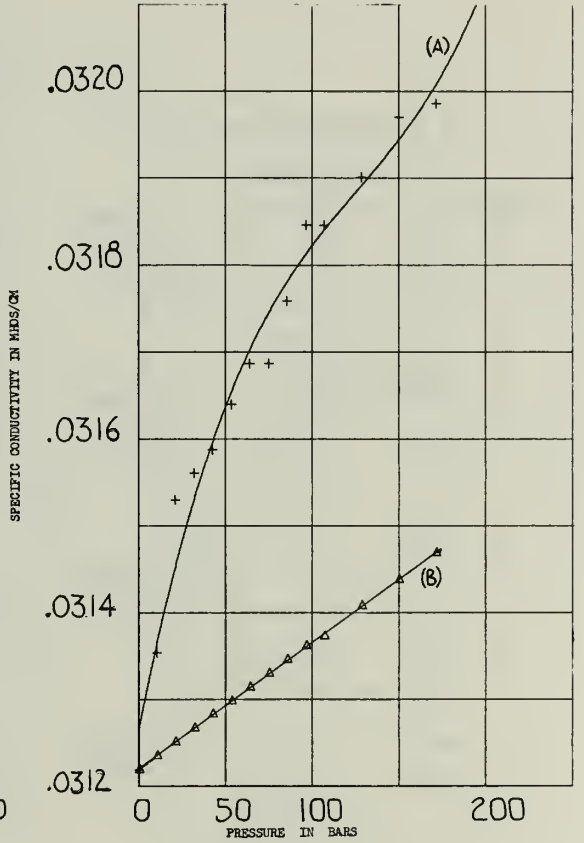


FIGURE 15C. 3RD DEGREE FIT.

FIGURE 15

SPECIFIC CONDUCTIVITY VS. PRESSURE FOR
REAL SEA WATER (S = 33.646 PPT; T = 4°C)
(A) OBSERVED
(B) COMPRESSION EFFECT

the observed conductivity and the calculated values resulting solely from the compression effect on the solution. The corrections to the observed data are important, even at these comparatively low pressures.

The pressure has little effect upon the degree of ionization of strong electrolytes, such as NaCl. However, the magnesium ion and sulphate ion are found in fairly high concentrations in sea water. Magnesium sulphate is also a strong electrolyte but has a much greater tendency toward ion pairing. Work by S. D. Hamman determined that the degree of ionization of several electrolytes which tend to form ion pairs in solution increases steadily with pressure up to several thousand bars.[11] This effect undoubtedly contributes to the conductance of solutions of sea water at great depths, but it is doubtful if there was much contribution during this research because of the lower pressures investigated.

The pressure normally would act to increase the electromotive force within the cell, and alter the measurements of resistance. The nature of the conductivity bridge used during the experiments precluded this from occurring.**

The compression of an electrolyte, dissolved in water, results in extreme changes in the solution's viscosity. Pressure is almost as powerful as temperature in dissolving the weakly bonded Frank-Wen clusters. The resulting dissociation of the clusters may initially act to cause a decrease in viscosity by increasing the volume available

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[11] Hamann, op. cit., p. 124.

** Supra, p.56.

for an ion to move through the solution. Further increases in pressure continues to break the ordered water molecules but at the same time moves the disordered, free water molecules closer to one another leaving less and less volume for ions to pass in the solution.

The degree of solvation is also influenced by pressure. The hydration atmosphere composed of several polarly oriented water molecules is compressed by the contracting solution which in essence appears to enhance the movements between electrodes. This is due to a reduction in the solvent shell radius. It may be that under sufficiently high pressures the solvent shell radius is decreased to such an extent that there is insufficient space for all the water molecules in the hydrated atmosphere and one is released. It is not known how great an effect this would have on electrical conductivity.

The final effect which pressure has on viscosity is indirectly tied to the temperature of the solution. Unlike most simple electrolytes dissolved in water, the viscosity of sea water passes through a minimum value at all temperatures from $-2^{o}C$ to slightly greater than $20^{o}C$.[12] The viscosity minimum becomes less pronounced and is shifted toward lower pressures with increasing temperature. The minimum occurs at approximately 500 bars for solutions at $0^{o}C$ and 200 bars for solutions at $15^{o}C$ and higher.

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[12] Horne and Johnson, Ibid.

CHAPTER VIII

ANALYSIS OF GRAPHICAL DISPLAYS AND CONCLUSIONS

Analysis. Figures 16 through 19 are graphical displays of specific conductivity vs. pressure. Each figure contains a curve through the observed data and the curve resulting after a correction for concentration change was made. Linear and cubic fits for the data are presented for comparison. The expanded scale enables the viewing of details which were obscured in Figure 10.

The rapid increase of specific conductivity over the first 100 bars pressure is striking for both real and artificial sea water at both high and low temperatures. The solutions at 18°C appear to have ended their high rate of conductivity increase at about 200 bars. The low temperature solutions still appear to be experiencing the rapid conductance increase at 200 bars.

The rapid increase noted in conductivity can best be accounted for by the minimum in viscosity which sea water experiences when subjected to pressures. The solutions at 18°C have nearly reached the minimum viscosity point at 150-200 bars and continues to increase at a lesser rate. The lower temperature solutions may have approximately 300 bars more applied to them before they pass through the viscosity minimum.[1] This helps in explaining the expected continuance of the high rate of conductivity increase. This is inferred from the position of the data point at 172 bars. The conductivity change over the interval of pressure increase, 1 to 150 bars, can be explained in more detail

[1] R. A. Horne and D. S. Johnson, "The Viscosity of Compressed Sea Water," Journal of Geophysical Research, LXXXI (November, 1966), pp. 5275-5277.

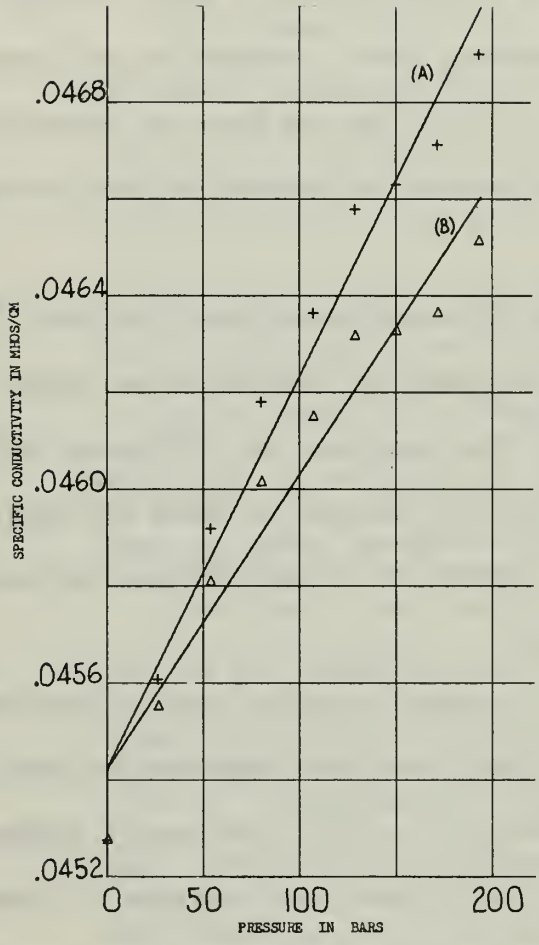

FIGURE 16A. LINEAR FIT.

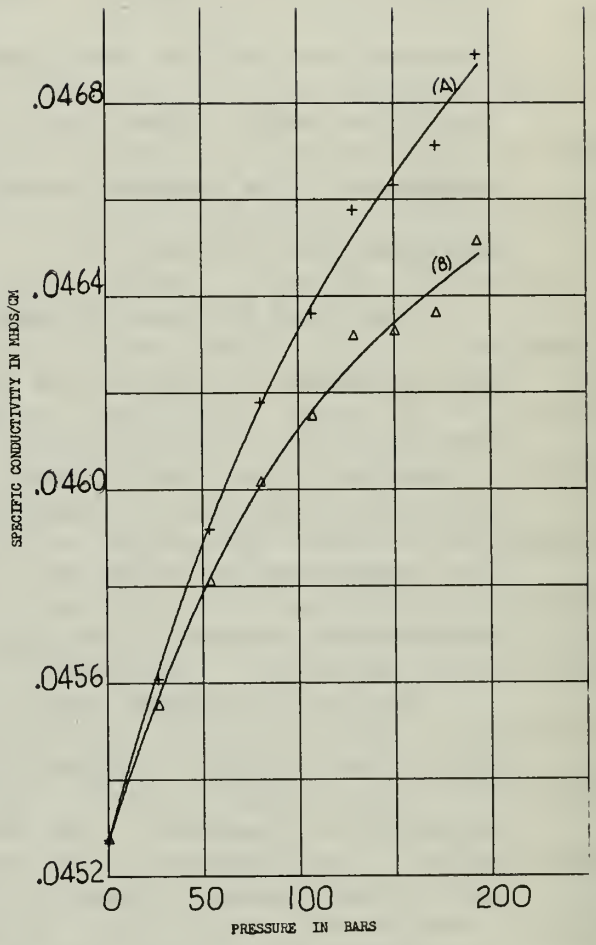

FIGURE 16B. 3RD DEGREE FIT.

FIGURE 16

SPECIFIC CONDUCTIVITY VS. PRESSURE FOR
ARTIFICIAL SEA WATER (S = 34.481 PPT; T = 18°C)
(A) OBSERVED
(B) CORRECTED FOR COMPRESSION

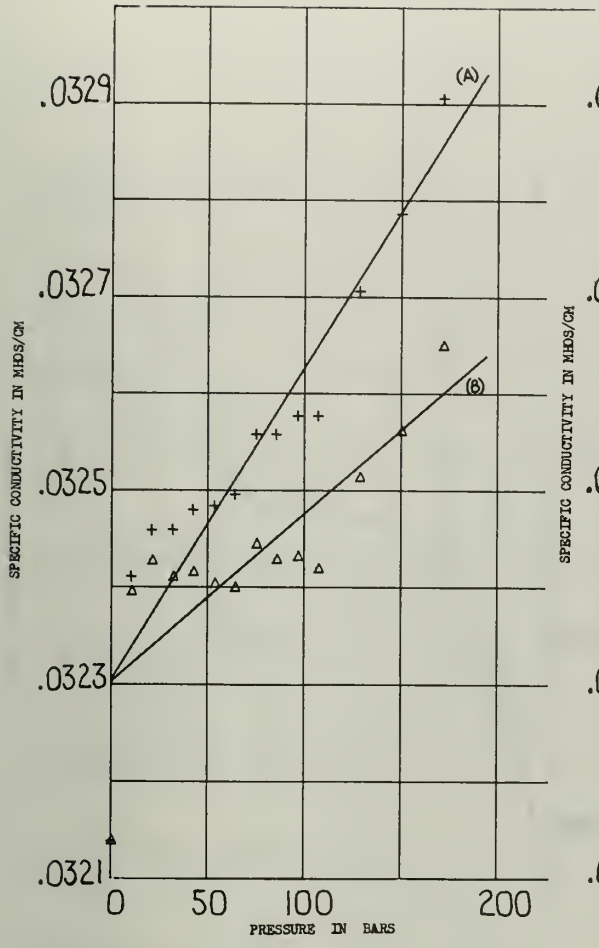

FIGURE 17A. LINEAR FIT.

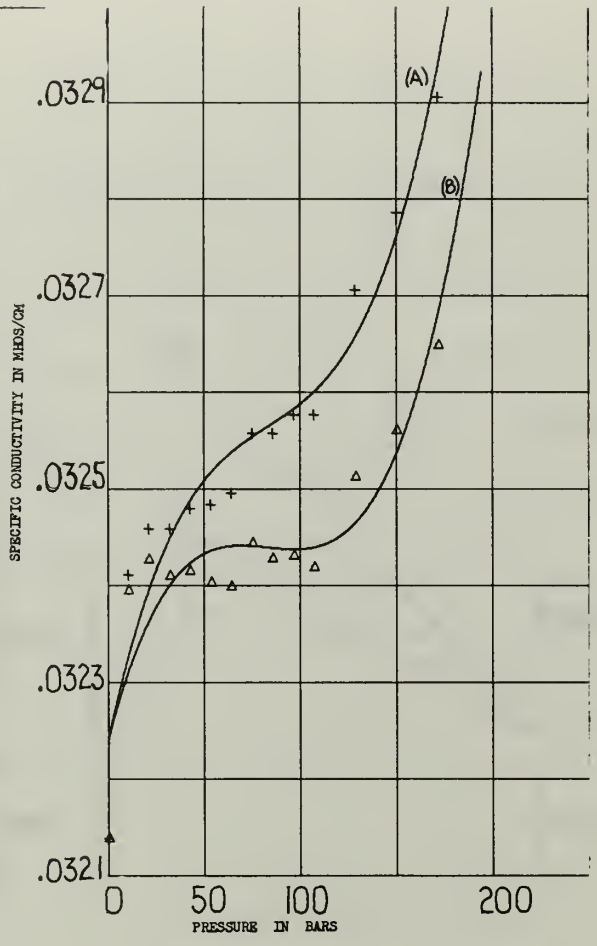

FIGURE 17B. 3RD DEGREE FIT.

FIGURE 17

SPECIFIC CONDUCTIVITY VS. PRESSURE FOR
ARTIFICIAL SEA WATER (S = 34.481 PPT; T = 4°C)
(A) OBSERVED
(B) CORRECTED FOR COMPRESSION

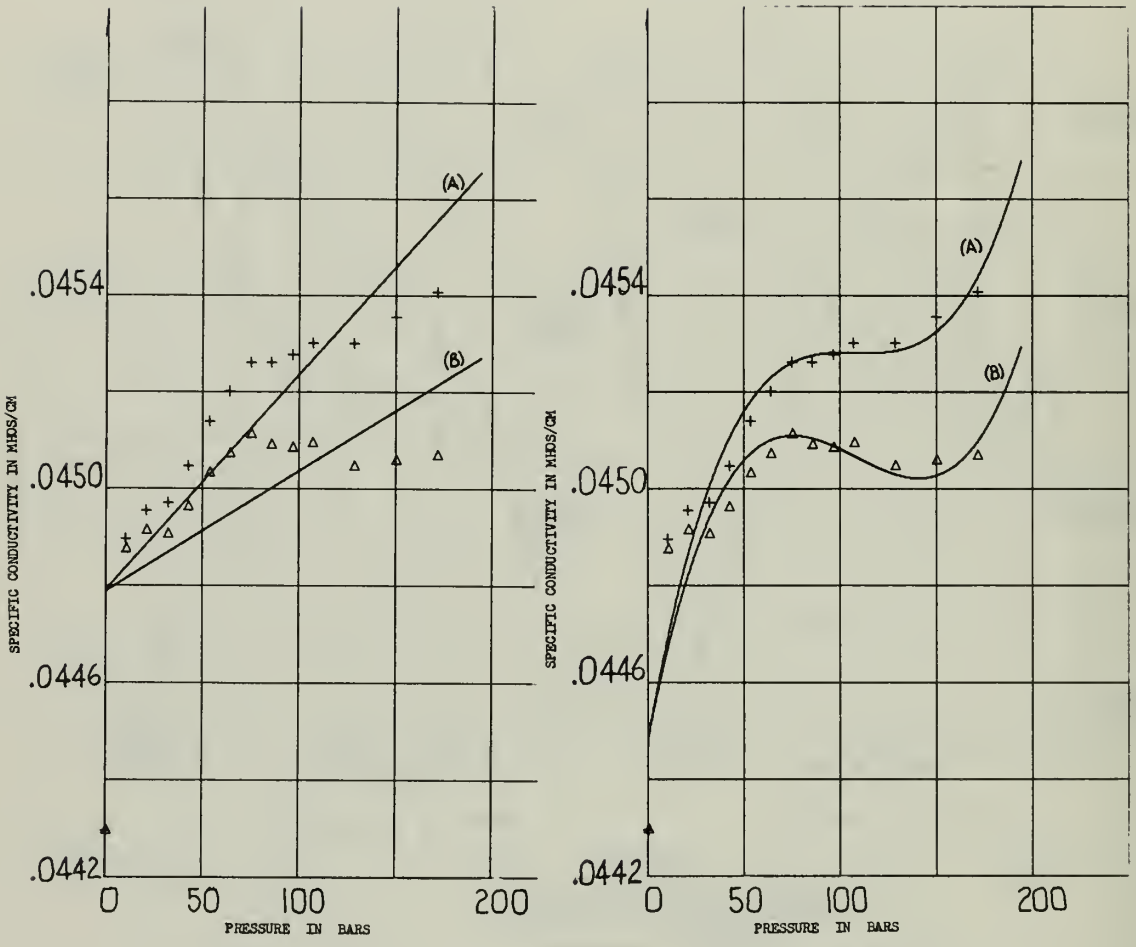

FIGURE 18A. LINEAR FIT.

FIGURE 18B. 3RD DEGREE FIT

FIGURE 18

SPECIFIC CONDUCTIVITY VS. PRESSURE FOR
REAL SEA WATER (S = 33.646 PPT; T = 18°C)
(A) OBSERVED
(B) CORRECTED FOR COMPRESSION

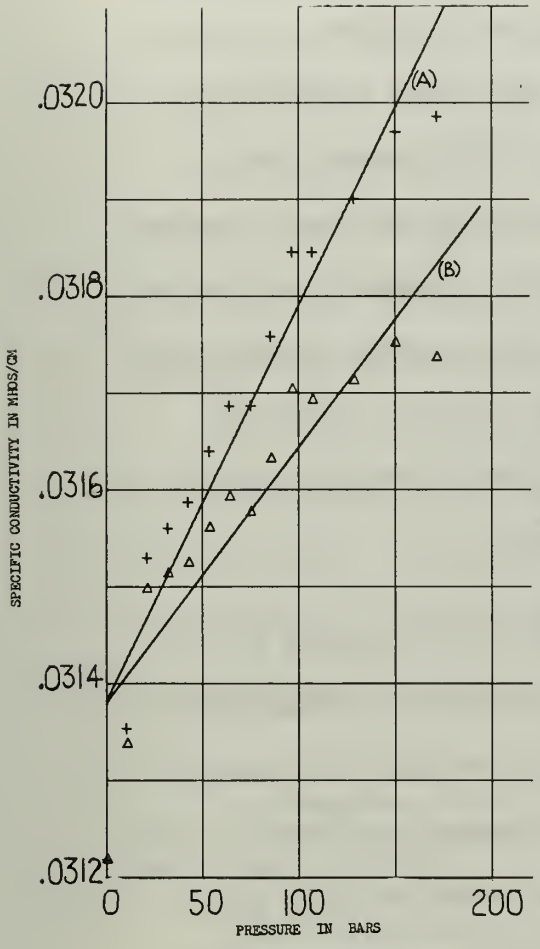

FIGURE 19A. LINEAR FIT.

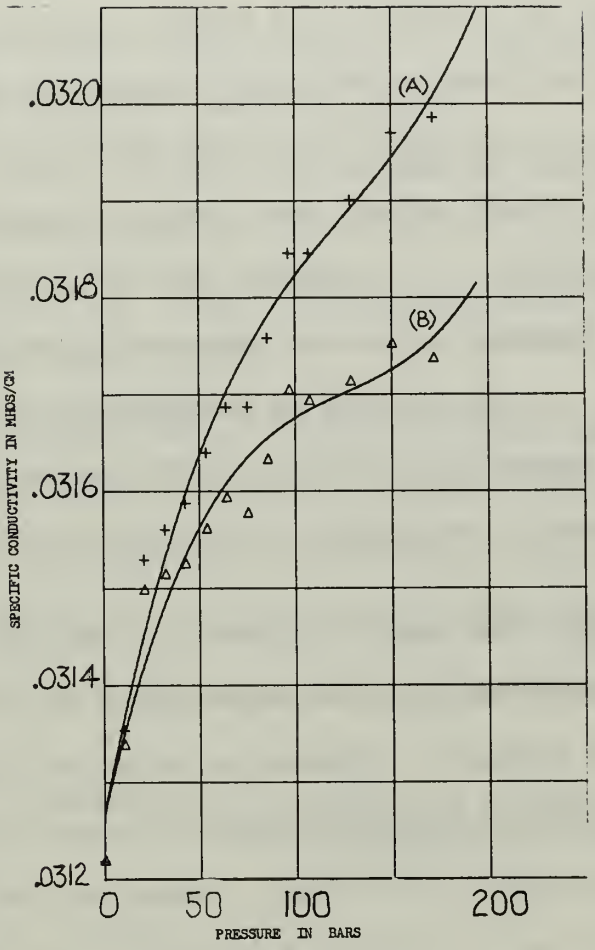

FIGURE 19B. 3RD DEGREE FIT.

FIGURE 19

SPECIFIC CONDUCTIVITY VS. PRESSURE FOR
REAL SEA WATER (S = 33.646 PPT; T = 4°C)
(A) OBSERVED
(B) CORRECTED FOR COMPRESSION

through considerations of the solution's structure. At the low temperature, the pressure acts to destroy the associated Frank-Wen clusters. Apparently, at 150 bars, the volume between bulk water molecules (free H_2O's) has been reduced to such an extent that solvated ions begin to have difficulty passing through the solution.

The solutions at the higher temperature have fewer clusters to be dissolved than the $4^{\circ}C$ solutions due to the temperature effect which has already reduced their number. Since there are fewer clusters to be dissolved, it is expected that the viscosity minimum would occur at lower pressure and have a corresponding effect upon the conductivity increase. As the pressure is increased beyond 100 bars, resulting specific conductivity changes probably become more dependent upon the electrophoretic, relaxation, and solvation effects.**

Conclusions. The specific conductivity of sea water solutions at a representative salinity and temperatures for the ocean, increases with increasing pressure. Mathematical relationships for the variations indicate that the variations are not linear. Parabolic or cubic polynomials best fit the data. Conductivities determined from these polynomials for a solution of salinity 34.481 PPT, temperature $18^{\circ}C$ at a pressure of 100 bars show a difference of 0.000097 mhos/cm between the values determined using a linear polynomial and a cubic polynomial. A difference of 0.000096 mhos/cm was found between linear and parabolic expressions. This would amount to an uncertainty in the salinity measurement of 0.04 PPT.[2] If an accuracy to 4 significant

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** Supra, p. 56.

[2] B. D. Thomas, et. al., "The Electrical Conductivity of Sea Water," Journal of The Council for the International Exploration of the Seas, IX (March, 1934), pp. 28-35.

figures is required for salinity values determined using In situ salinometers, the linear relation would not be acceptable at this pressure. A linear relation is justifiable perhaps through the upper 1000 meters of the ocean's water column. The slopes of all the curves of Figures 16 through 19 are very nearly equal and the curves themselves over the interval 1 to 100 bars are essentially linear.

For real sea water, pressure becomes less effective in causing conductivity increases as the temperature is raised. The loss of effectiveness, however, was not as apparent during this investigation as a previous investigation found it to be.[3]

The change in solution concentration resulting from the experimental methods required to measure specific conductivity response to pressure is significant. Errors in the experimental results were found to be approximately 1% if the concentration effect was not considered. This is equivalent to an error of 0.1 PPT in the salinity determination.[4]

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[3] A. Bradshaw and K. E. Schleicher, "The Effect of Pressure on the Electrical Conductance of Sea Water," Deep Sea Research, XII (November, 1964), pp. 151-162.

[4] B. D. Thomas, et. al, loc. cit.

CHAPTER IX

RECOMMENDATIONS

The results of the study of pressure effects on electrical conductivity of sea water through the upper 2000 meters of the ocean's water column indicate that important details may be obscured by measuring conductivity only once over large pressure increases. To insure that the complete pressure effect is known, this research should be continued to pressures equivalent to those characterizing the very deep regions of the ocean but the increments of pressure should be kept small, not greater than 25 to 30 bars.

Only 4 temperatures and a narrow range of salinities have been examined. The investigation should be extended to encompass the complete range of salinities commonly found in the world oceans, as well as the temperatures characterizing the water column to the depth of practical In situ conductivity measurements.

To gain a better insight concerning the causes of the conductance changes due to pressure, an investigation of the effect pressure has on the individual constituents of sea water would be worthwhile.

Very little importance has been placed on the formation of ion pairs in sea water in explaining the conductance changes with pressure. An investigation of the phenomenon may show it to be an important aspect of the problem.

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APPENDIX A

GLOSSARY OF TERMS

Specific Conductivity - Specific Conductivity is the measure of a solution's ability to conduct electricity. The numerical value is equivalent to the length in centimeters of a conductor with a cross sectional area of 1 cm^2 and resistance 1 ohm. Conductivity, conductance and specific conductivity are used synonymously in the report. The mathematical definition is: Specific conductivity = $\kappa = \frac{\ell}{aR}$ where ℓ/a is the cell constant and R is resistance.

Ion Pair - An ion pair is an uncharged molecule consisting of a positive and negatively charged ion being held together by an electrostatic bond.

Ionize - The creation of charged entities from the atoms of a neutral molecule.

Dissociate - The destruction of a covalent bond to produce ions from a neutral molecule.

Associate - The attraction of charged (or uncharged) molecules or ions resulting in the formation of an electrostatic bond. The attraction present with an electrostatic bond is much smaller in magnitude than that of a covalent bond.

APPENDIX B

```
THIS COMPUTER PROGRAM IS DESIGNED TO TAKE THE MEASURED VALUES OF
RESISTANCE FOR THE ELECTROLYTIC SOLUTION, AND THE PRESSURES AT WHICH
THE MEASUREMENTS WERE MADE AND CONVERT THEM TO SPECIFIC CONDUCTIVITIES.
THE PROGRAM ALSO DETERMINES OTHER USEFUL QUANTITIES NEEDED TO
DETERMINE THE EFFECT OF PRESSURE ON THE IONIC CONDUCTANCE THROUGH
THE UPPER 2000 METERS OF THE OCEAN'S WATER COLUMN.



      IMPLICIT REAL*8(A-H,P-Z)
      REAL*8 INTVOL,COMPRE(14),LABEL/8H        /,ITITLE(12),LAMBDA
      REAL*4 SIGMA,DELY,SB,ST,SC,W,XF(2),YF(2)
      REAL*4 XX(900),YY(900),XXX(14),YYY(14),YCOMP(14)
      DIMENSION SEDUCE(8),FAKE(2),CFAKE(2)
      DIMENSION TMCOND(14),RATIO(14),CRATIO(14),BATIO(9),CBATIO(9)
      DIMENSION REDUCE(13),DIFF(14)
      DIMENSION COND(14),RES(14),PRESS(14),FORCE(14),PP(14),D(14)
      DIMENSION W(14),Y(14),DELY(14),B(6),SB(6),V(6),ST(6),X(6),SC(6),
     *U(30,30)
      DIMENSION RRES(9),PBAR(14),CC(10),ATWT(10),CON(10)

C     NN IS THE NUMBER OF SETS OF DATA TO BE ANALYZED.  FOR EXAMPLE,
C     1 DATA SET WOULD BE A SOLUTION OF 34.481 PPT SEA WATER AT
C     14 DEGREES CENTIGRADE.

      READ(5,40) NN
   40 FORMAT(I5)

C     CC REPRESENTS THE CONCENTRATIONS OF THE 11 MAJOR IONS IN SEA WATER
C     OF SALINITY 35 PPT.

      READ(5,131) CC

C     ATWT REPRESENTS THE MOLECULAR WEIGHTS OF THE 11 MAJOR CONSTITUENTS
C     OF SEA WATER.

      READ(5,131) ATWT
  131 FORMAT(5F10.3)

C     FAKE AND CFAKE ARE DUMMY VALUES OF CONDUCTIVITY AND PRESSURE
C     WHICH ESTABLISH THE X AND Y SCALES OF GRAPHS PLOTTED BY THE DRAW
C     SUBROUTINE.  THESE ARE ONLY USEFUL IF MORE THAN ONE CURVE IS TO BE
C     DRAWN ON A GRAPH.

      READ(5,777) FAKE
  777 FORMAT(2F10.6)
      CFAKE(1)=0.0
```

```
      CFAKE(2)=200.0
      DO 650 I=1,2
      XF(I)=CFAKE(I)
  650 YF(I)=FAKE(I)
      DO 25 N=1,NN

C     CELCON IS THE VALUE OF THE CELL CONSTANT.

      READ(5,4) CELCON
    4 FORMAT(F10.6)

C     DENS IS THE SOLUTION DENSITY.

      READ(5,130) DENS
  130 FORMAT(F10.5)

C     M IS THE NUMBER OF DATA POINTS COLLECTED FOR THE PARTICULAR
C     EXPERIMENT.

      READ(5,30) M
   30 FORMAT(I5)

C     T IS THE TEMPERATURE OF THE SOLUTION.

      READ(5,8) T

C     C IS THE SOLUTION CONCENTRATION IN MOLES PER LITER OR PARTS PER
C     THOUSAND

      READ(5,3)C
    3 FORMAT(F10.3)
    8 FORMAT(F10.2)
      IF(M.LT.14) GO TO 191

C     REDUCE AND SEDUCE ARE THE PERCENT REDUCTION IN VOLUME OF THE
C     SOLUTION OVER THE PRESSURE RANGE.

      READ(5,148) REDUCE
      GO TO 190
  191 READ(5,148) SEDUCE
  148 FORMAT(5F10.5)
  190 WRITE(6,5) C,T
    5 FORMAT('1',T25,'CONCENTRATION OF SOLUTION=',F7.3,5X,'SOLUTION TEMP
     *ERATURE=',F5.2)
      GO TO 501
 3000 WRITE(6,2)
    2 FORMAT(//,T2,'PRESS PRESSURE',T21,'RESISTANCE',T42,'CONDUCTIVITY',
     *T61,'WATER PRESSURE',T84,'DEPTH',/,T5,'IN PSI',T22,'IN OHMS',
```

```
     *T43,'IN MHOS/CM',T65,'IN BARS',T82,'IN METERS',T100,'R/R(1)',T110,
     *'R/R(1) CORRECTED')
  501 IF(M.LT.14) GO TO 66
C
C       RES AND RRES ARE THE VALUES OF RESISTANCE FOR THE SOLUTION
C       MEASURED DURING THE EXPERIMENT.
C
        READ(5,131) RES
        GO TO 67
   66   READ(5,131) RRES
C
C       A    IS THE AREA FOR WHICH THE PRESSURE GAUGE IS CALIBRATED.
C
   67   A=2.74646526
C
C       AA    IS THE AREA OF THE PRESSURE VESSEL PISTON.
C
        AA=1.76709375
C
C       R AND PRESCON ARE CONVERSION FACTORS CONVERTING ATMOSPHERES TO
C       DECIBARS AND BARS.
C
        R=10.13/14.67
        PRSCON=1.013/14.67
        PRESS(1)=0.0
        IF(C.LT.2.0) GO TO 136
        VOL=1.0/DENS
        SF=C/35.0
        CONCEN=0.0
C
C       CONVERSION OF CONCENTRATIONS IN PARTS PER THOUSAND TO MOLES
C       PER LITER.
C
        DO 135 I=1,10
        CON(I)=((SF)*(CC(I)/ATWT(I)))/VOL
  135   CONCEN=CONCEN+CON(I)
C
C       DETERMINATION OF SPECIFIC CONDUCTIVITIES FROM RESISTANCE.
C
  136   DO 20 I=1,M
        IF(M.LT.14) GO TO 60
        COND(I)=CELCON/RES(I)
        GO TO 17
   60   COND(I)=CELCON/RRES(I)
   17   IF(I.EQ.1) GO TO 10
        IF(M.LT.14) GO TO 44
        IF(I.GT.11) GO TO 19
        PRESS(I)=PRESS(I-1)+100.0
```

```
      GO TO 10
   19 PRESS(I)=PRESS(I-1)+200.0
      GO TO 10
   44 IF(I.GT.5) GO TO 19
      PRESS(I)=PRESS(I-1)+250.0

C     CONVERSION OF PRESS PRESSURE TO INTERNAL PRESSURE, PRESSURE IN
C     BARS, AND REPRESENTATIVE DEPTH IN METERS.

   10 FORCE(I)=PRESS(I)*A
      PP(I)=FORCE(I)/AA
      D(I)=PP(I)*R
      PBAR(I)=PRSCON*PP(I)
   20 CONTINUE
      IF(C.LT.2.0) GO TO 137
      VOLUME=(1.0/CONCEN)*1000.0
      GO TO 138
  137 VOLUME=(1.0/C)*1000.0

C     DETERMINATION OF THE SOLUTION'S MOLAR CONDUCTANCE.

  138 LAMBDA=COND(1)*VOLUME
      INTVOL=0.165000
      COMPRE(1)=COND(1)
      RATIO(1)=1.0000
      CRATIO(1)=1.0000
      BATIO(1)=1.0000
      CBATIO(1)=1.0000
      L=M-1

C     DETERMINATION OF THE VOLUME CHANGE FOR EACH INTERVAL PRESSURE
C     INCREASE.  INTVOL IS THE INITIAL VOLUME, AND FVOL IS THE FINAL
C     VOLUME.

      DO 141 I=1,L
      IF(M.LT.14) GO TO 150
      VOLCOR=INTVOL*(REDUCE(I)*0.01)
      GO TO 181
  150 VOLCOR=INTVOL*(SEDUCE(I)*0.01)
  181 FVOL=INTVOL-VOLCOR
      IF(M.LT.14) GO TO 700
      RATIO(I+1)=RES(I+1)/RES(1)
      CRATIO(I+1)=RATIO(I+1)*(INTVOL/FVOL)
      GO TO 701
  700 BATIO(I+1)=RRES(I+1)/RRES(1)
      CBATIO(I+1)=BATIO(I+1)*(INTVOL/FVOL)
  701 IF(C.LT.2.0) GO TO 139
      STR=(INTVOL/FVOL)*CONCEN
```

```
      GO TO 132
  139 STR=(INTVOL/FVOL)*C

C     COMPRE REPRESENTS THE SPECIFIC CONDUCTANCE OF THE SOLUTION WHICH
C     RESULTS SOLELY FROM THE INCREASED CONCENTRATION DUE TO COMPRESSION

  132 COMPRE(I+1)=(LAMBDA*STR)/1000.0
  141 CONTINUE
      DO 145 I=1,M
      DIFF(I)=COMPRE(I)-COMPRE(1)

C     TMCOND IS THE SOLUTION SPECIFIC CONDUCTIVITY AFTER THE COMPRESSION
C     EFFECT HAS BEEN REMOVED.

  145 TMCOND(I)=COND(I)-DIFF(I)
      GO TO 502
 3001 DO 12 I=1,M
      IF(M.LT.14) GO TO 61
      WRITE(6,7) PRESS(I),RES(I),COND(I),PBAR(I),D(I),RATIO(I),CRATIO(I)
    7 FORMAT(//,T4,F7.1,T21,F8.3,T36,D20.10,T62,F10.3,T81,F10.3,
     *T100,F10.4,T113,F10.4)
      GO TO 12
   61 WRITE(6,7) PRESS(I),RRES(I),COND(I),PBAR(I),D(I),BATIO(I),CBATIO(I
     *)
   12 CONTINUE
  502 CONTINUE

C     THE REMAINDER OF THE PROGRAM INVOLVES CONVERSION OF VARIABLES
C     FROM DOUBLE PRECISION TO SINGLE PRECISION TO USE THE DRAW
C     SUBROUTINE AND LEAST SQUARES POLYNOMIAL FIT SUBROUTINE.

      DO 80 I=1,M
      YCOMP(I)=COMPRE(I)
      XXX(I)=PBAR(I)
   80 YYY(I)=COND(I)
      GO TO 503
 3002 WRITE(6,142)
  142 FORMAT('1',T2,'WATER PRESSURE',5X,'OBSERVED SPECIFIC',10X,'SPECIFI
     *C CONDUCTIVITY',10X,'CORRECTED SPECIFIC',/,T8,'IN',T22,'CONDUCTIVI
     *TY IN',T49,'DUE TO COMPRESSION',T80,'CONDUCTIVITY IN',/,T7,'BARS',
     *T26,'MHOS/CM',T53,'IN MHOS/CM',T84,'MHOS/CM',//)
      DO 143 I=1,M
      WRITE(6,144) PBAR(I),COND(I),COMPRE(I),TMCOND(I)
  144 FORMAT(T3,F10.3,T18,D20.10,T47,D20.10,T76,D20.10)
  143 CONTINUE
  503 CONTINUE
```

```
C      KM IS THE INDEX PARAMETER REPRESENTING THE DEGREE FIT TO THE DATA
C      POINTS.  FOR EXAMPLE, KM=3 WILL RESULT IN A THIRD DEGREE FIT.

       DO 500 KM=1,3
       READ(5,11) (ITITLE(I),I=1,12)
    11 FORMAT(6A8)
       CALL DRAW(M,XXX,YYY,1,2,LABEL,ITITLE,0,0,0,0,1,2,8,9,1,LAST)
       WRITE(6,13) LAST
    13 FORMAT(//,2X,'LAST= ',I2)
       CALL DRAW(M,XXX,YCOMP,2,5,LABEL,ITITLE,0,0,0,0,1,2,9,15,1,LAST)
       WRITE(6,13) LAST
       CALL LSQPOL(M,KM,0,0,0,SIGMA,PBAR,COND,W,Y,DELY,B,SB,V,ST,X,SC,U)
       DX=220.0/900.0
       RR=0.0
       DO 100 I=1,900
       XX(I)=RR
       IF(KM.EQ.2) GO TO 45
       IF(KM.EQ.3) GO TO 46
       YY(I)=B(1)+B(2)*RR
       GO TO 100
    45 YY(I)=B(1)+B(2)*RR+B(3)*(RR**2)
       GO TO 100
    46 YY(I)=B(1)+B(2)*RR+B(3)*(RR**2)+B(4)*(RR**3)
   100 RR=RR+DX
   882 CALL DRAW(900,XX,YY,3,0,LABEL,ITITLE,0,0,0,0,1,2,8,9,1,LAST)
       WRITE(6,13) LAST
   500 CONTINUE
    25 CONTINUE
  1000 CONTINUE
       RETURN
       END
```

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13. ABSTRACT

The specific conductivity of 5 different electrolytic solutions over a pressure range of 1 to 200 bars has been measured. The solutions were 0.01N, 0.10N and 1.00N KCl and 2 solutions of sea water. One sea water solution was real sea water, the other artificial. Each solution was tested at 4 temperatures, ranging from 4°C to 18°C. The pressure caused the specific conductivity of all solutions to increase in a non-linear fashion. First, second and third degree least square curves have been fitted to the data for comparisons. The specific conductivity caused by solution concentration changes during compression has been determined and found to be a significant error source. Explanations are offered to account for the conductivity changes considering the manner in which pressure alters the chemical structure of the solution. The areas discussed are solution concentration, applied voltage, interionic reactions and viscosity.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Conductivity Electrical Sea Water Pressure						

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