

# AN ABSTRACT OF THE THESIS OF

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Title: THE PARTIAL EQUIVALENT CONDUCTANCES OF SALTS  
IN SEAWATER

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Abstract approved: \_\_\_\_\_  
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The partial equivalent conductances of the major salts in seawater have been determined over the temperature range from 0 to 25°C and the salinity range from 30 to 35.6‰. The data are presented below in terms of the partial equivalent conductance of NaCl,  $\bar{\Lambda}_{\text{NaCl}}$ , and the partial equivalent conductance differences,  $\bar{\Lambda}_{\Delta_i}$ , relative to  $\text{Na}^+$  and  $\text{Cl}^-$ .

$$\bar{\Lambda}_{\text{Bc}} = \bar{\Lambda}_{\text{NaCl}} + \bar{\Lambda}_{(\text{B} - \text{Na}^+)} + \bar{\Lambda}_{(\text{c} - \text{Cl}^-)}$$

$$\bar{\Lambda}_s (\text{S}\%_0 \text{ t}^\circ\text{C}) = a_{00} + a_{01}t + a_{02}t^2 + (a_{10} + a_{11}t)S \pm \epsilon \text{ cm}^2/(\text{ohm eq})$$

$\bar{\Lambda}_s$	$a_{00}$	$a_{01}$	$a_{02} \times 10^3$	$a_{10}$	$a_{11} \times 10^3$	$\epsilon$
$\bar{\Lambda}_{\text{NaCl}}$	51.36	1.73	6.37	-.200	-13.4	$\pm 0.18$
$\bar{\Lambda}_{(\text{K}^+ - \text{Na}^+)}$	10.80	0.464	-0.627	0.119	-4.41	$\pm 0.07$
$\bar{\Lambda}_{(\text{Ca}^{++} - \text{Na}^+)}$	-6.11	-.225	-2.66	0.0275	2.32	$\pm 0.06$
$\bar{\Lambda}_{(\text{Mg}^{++} - \text{Na}^+)}$	-5.15	-.391	-2.99	-.123	5.34	$\pm 0.02$
$\bar{\Lambda}_{(\text{SO}_4^{--} - \text{Cl}^-)}$	-18.65	-.445	-2.12	-.0235	-1.62	$\pm 0.10$

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$\bar{\Lambda}_{(\text{HCO}_3^- - \text{Cl}^-)}$	-18.6	-.663	-4.27	-.112	5.02	$\pm 0.23$
$\bar{\Lambda}_{(\text{NO}_3^- - \text{Cl}^-)}$	-.0754	-.246	-1.65	-.108	3.89	$\pm 0.13$
$\bar{\Lambda}_{\text{sea salt}}$	48.61	1.62	5.53	-.221	-12.6	$\pm 0.18$

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Seawater has been treated as a two-component system made up of "sea salt" and water. The partial equivalent conductance of "sea salt" calculated from  $\bar{\Lambda}_{\text{NaCl}}$  and  $\bar{\Lambda}_{\Delta_i}$  compares favorably with  $\bar{\Lambda}_{\text{sea salt}}$  calculated from specific conductance data.

The error in the conductance-density correlation is examined for the addition of 1 gm of salt to 1 kg of seawater assuming the partial conductance of the salt is the same as for "sea salt." At  $0^\circ\text{C}$  and 35‰ salinity, the error ranges from  $-0.07 \sigma_t$  units for NaCl to  $0.85 \sigma_t$  units for  $\text{MgSO}_4$ .

The Partial Equivalent Conductances  
of Salts in Seawater

by

Donald Nason Connors

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# THE PARTIAL EQUIVALENT CONDUCTANCES OF SALTS IN SEAWATER

## INTRODUCTION

The purpose of this investigation is to determine the partial equivalent conductances of the major salts in seawater over a range of temperatures and salinities encompassing those that commonly occur in the world ocean. We define the partial equivalent conductance of a salt in seawater the same way Sundheim (1957) did for molten salts.

$$\bar{\Lambda}_1 = \left( \frac{\partial L}{\partial n_1} \right)_{P, T, n_2, \dots}$$

where  $\bar{\Lambda}_1$  is the increase in the total conductance  $L$  of an infinitely large volume of seawater contained between two parallel plates one centimeter apart. This increase is due to the addition of one equivalent of salt.

A knowledge of the partial equivalent conductance of the major salts in seawater will lead to a better understanding of the physical chemistry of seawater. For example, a model can be constructed to account for the specific conductance of seawater. Seawater is regarded as a two-component system made up of "sea salt" and water. The concentrations of the various salts that make up "sea salt" are given by the artificial seawater formulas of Lyman and Fleming (1940) or Kester et al. (1967). The specific conductance of seawater then is

the sum of the partial equivalent conductances of the various salts times the number of equivalents of the salts per  $\text{cm}^3$  of seawater plus the partial specific conductance of the water times the concentration of the water. The result can be compared with the directly determined specific conductance data (e. g. Weyl, 1964). The data contained in this thesis can also be compared to the conductances of infinitely dilute solutions and of NaCl solutions of an ionic strength similar to seawater. These comparisons give an insight into the electrochemical complexity of seawater.

Probably the most important useful application of this investigation is that results together with partial volume data (Duedall and Weyl, 1967) will permit one to check how the density-conductance relationship is affected by changes in the relative chemical composition of seawater.

### Review of the Literature

The only previously published work on the partial equivalent conductance of salts in seawater was done by Park (1964). He studied major electrolytes in seawater of 35‰ salinity and at 23° C. The electrolytes studied were NaCl, KCl,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{MgSO}_4$ ,  $\text{NaHCO}_3$ ,  $\text{KHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{KH}_2\text{PO}_4$ , KBr, HCl and NaOH. Park (1964) used natural seawater with a salinity of 36.75‰. To 100 ml portions of the seawater, Park added small

increments of 1 M solutions of the above salts. He then diluted the seawater with distilled water to a final volume of 105 ml and a salinity of approximately 35 ‰, exclusive of the salt addition. Park used a Hytech Model 621 inductive salinometer to measure the change in the conductivity ratio of this water relative to standard seawater of 35 ‰ salinity.

He assumed that his salt additions were constant volume additions and that the partial equivalent conductance could be calculated from

$$\bar{\Lambda}_1 = \lim_{\Delta n_1 \rightarrow 0} \left( \frac{\Delta K}{\Delta n_1} \right)_{P, V, T, n_2, \dots} \quad (1)$$

A detailed critique which shows that Park's results for the partial equivalent conductances as defined by Equation 1 were 14.5% high has been presented by Connors and Park (1967).

## EXPERIMENTAL METHOD

Consider a hypothetical conductance cell consisting of two parallel plate electrodes one centimeter apart containing one gram of seawater. Add  $\Delta n_1$  equivalents of salt 1. In the limit, as  $\Delta n_1$  approaches zero, the increase in the conductance per equivalent of added salt is equal to the partial equivalent conductance.

$$\bar{\Lambda}_1 = \lim_{\Delta n_1 \rightarrow 0} \frac{\Delta L}{\Delta n_1} = \frac{\partial L}{\partial n_1} \quad (2)$$

The partial specific conductance of water in seawater is defined in a similar manner. To the above hypothetical cell, add  $\Delta m$  grams of water to one gram of seawater. In the limit, as  $\Delta m$  approaches zero, the change in the conductance per gram of water added is equal to the partial specific conductance.

$$\bar{\Lambda}_w = \lim_{\Delta m \rightarrow 0} \frac{\Delta L}{\Delta m} = \frac{\partial L}{\partial m} \quad (3)$$

Since it is not practical to work with the hypothetical cell, we carried out the measurements in this work in Jones Electrolytic Conductivity Cells.<sup>1/</sup> These cells are completely filled and have constant geometry. The geometry, expressed by the cell constant A, can be established by measuring the conductance of a standard solution.

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<sup>1/</sup> Catalogue no. 4947 B, with cell constants of about  $150 \text{ cm}^{-1}$ .  
Leeds & Northrup Company, 4907 Stenton Avenue, Philadelphia 44,  
Pa.

The specific conductance of any solution can then be determined since the specific conductance is equal to the conductance times the cell constant.

$$K = L A$$

K is the specific conductance ( $\text{ohm}^{-1} \text{cm}^{-1}$ ), and L is the conductance ( $\text{ohm}^{-1}$ ).

The partial equivalent conductance can be determined in the following manner from the change in the specific conductance: the addition of  $\Delta n_1$  equivalents of salt 1 to a gram of seawater will change the specific volume, specific conductance, and total conductance.

	<u>Initial</u>	<u>After Addition</u>
specific conductance	K	$K + \Delta K$
specific volume	v	$v + \bar{v}_1 \Delta n_1$
total conductance	vK	$vK + \bar{\Lambda}_1 \Delta n_1$

Therefore

$$K + \Delta K = \frac{vK + \bar{\Lambda}_1 \Delta n_1}{v + \bar{v}_1 \Delta n_1}$$

since  $\frac{\bar{v}_1}{v} \Delta n_1 \ll 1$

$$\Delta K \approx \frac{\bar{\Lambda}_1 \Delta n_1}{v} - \frac{K \bar{v}_1 \Delta n_1}{v}$$

and 
$$\bar{\Lambda}_1 \approx \left( \frac{v \Delta K}{K \Delta n_1} + \bar{v}_1 \right) K \quad (4)$$

The units for partial equivalent conductance are  $\text{cm}^2/(\text{ohm eq})$ .

To determine  $\Delta K/K$ , fill two cells with the same seawater and obtain the ratio of their cell constants

$$r_1 = \frac{\text{Resistance of cell 1 with solution a}}{\text{Resistance of cell 2 with solution a}} = \frac{\text{Cell constant 1}}{\text{Cell constant 2}}$$

Fill cell 2 with seawater plus  $\Delta n_1$  equivalents of salt 1 per gram; determine the ratio  $r_2$

$$r_2 = \frac{\text{Cell constant 1} \cdot K}{\text{Cell constant 2} \cdot (K + \Delta K)}$$

Then

$$\frac{r_1}{r_2} - 1 = \frac{\Delta K}{K}$$

The partial specific conductance of water in seawater can be determined from specific conductance measurements in a like manner. Adding  $\Delta m$  grams of water per gram of seawater changes  $c$  (mass fraction of salt in seawater) to  $c - c\Delta m$  and the volume from  $v$  to  $v + \bar{v}_w \Delta m$ . The new specific conductance is

$$K + \Delta K = \frac{vK + \bar{\Lambda}_w \Delta m}{v + \bar{v}_w \Delta m}$$

or approximately

$$K + \Delta K \approx K + \frac{\Delta m}{v} (\bar{\Lambda}_w - K\bar{v}_w)$$

For small additions  $\Delta m \approx -\Delta c/c$ ; therefore

$$\frac{\frac{\Delta K}{K}}{\frac{\Delta c}{c}} = \frac{\Delta \ln K}{\Delta \ln c} = - \frac{1}{v} \left( \frac{\bar{\Lambda}_w}{K} - \bar{v}_w \right)$$

Weyl (1964) has shown that over a limited concentration range the specific conductance of seawater can be expressed by the following empirical equation:

$$K = A c^n$$

Therefore 
$$\frac{\Delta \ln K}{\Delta \ln c} = n$$

where n equals 0.892 for seawater with a salinity near 35‰ at 25°C <sup>2/</sup>.

$$n = - \frac{1}{v} \left( \frac{\bar{\Lambda}_w}{K} - \bar{v}_w \right)$$

$$\bar{\Lambda}_w = (\bar{v}_w - nv)K \quad (5)$$

The units for partial specific conductance are cm<sup>2</sup>/(ohm gm).

The partial equivalent conductance with the addition of a hydrated salt to seawater is

$$\bar{\Lambda}_{1 \cdot x H_2O} = \left( \frac{v \Delta K}{K \Delta n_{1 \cdot x H_2O}} + \bar{v}_{1 \cdot x H_2O} \right) K$$

where x equals the number of moles of water per equivalent of salt 1.

If we take MgSO<sub>4</sub> · 7H<sub>2</sub>O as an example, x would equal 3.5 moles per equivalent of salt. Then

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<sup>2/</sup> The slope, n, varies slightly with temperature; Δn/ΔT equals 3.2 × 10<sup>-4</sup> per deg, where T = 25°C - t° C.

$$\bar{v}_{1 \cdot xH_2O} = \bar{v}_1 + 3.5\bar{v}_w$$

and

$$\bar{\Lambda}_{1 \cdot xH_2O} = \bar{\Lambda}_1 + 3.5\bar{\Lambda}_w$$

The partial equivalent conductance of the salt ( $MgSO_4$ ) is

$$\bar{\Lambda}_1 = \frac{v\Delta K}{\Delta n_{1 \cdot 3.5H_2O}} + \bar{v}_1 K + 3.5\bar{v}_w K - 3.5\bar{\Lambda}_w$$

Substituting Equation 5 for  $\bar{\Lambda}_w$  we obtain

$$\bar{\Lambda}_1 = \left( \frac{v\Delta K}{K\Delta n_{1 \cdot 3.5H_2O}} + \bar{v}_1 + 3.5 \times 18.015v_n \right) K \quad (6)$$

where 18.015 is the gram molecular weight of water.

The specific conductance of seawater was calculated from Weyl's (1964) equation:

$$\log K = 0.57627 + 0.892 \log Cl(\text{‰}) - 10^{-4} \tau [88.3 + 0.55\tau + 0.0107\tau^2 - Cl(\text{‰})(0.145 - 0.002\tau + 0.0002\tau^2)] \quad (7)$$

where K is in millimhos per cm and  $\tau = 25 - t^\circ C$ . The equation is valid to 0.1% of the measured values (Thomas, Thompson and Utterback, 1934) over the range 17 - 20‰ in chlorinity and 0 - 25°C.

### Apparatus

Figure 1 is a diagram of the bridge and thermostat used in determining the partial equivalent conductances. The signal from an



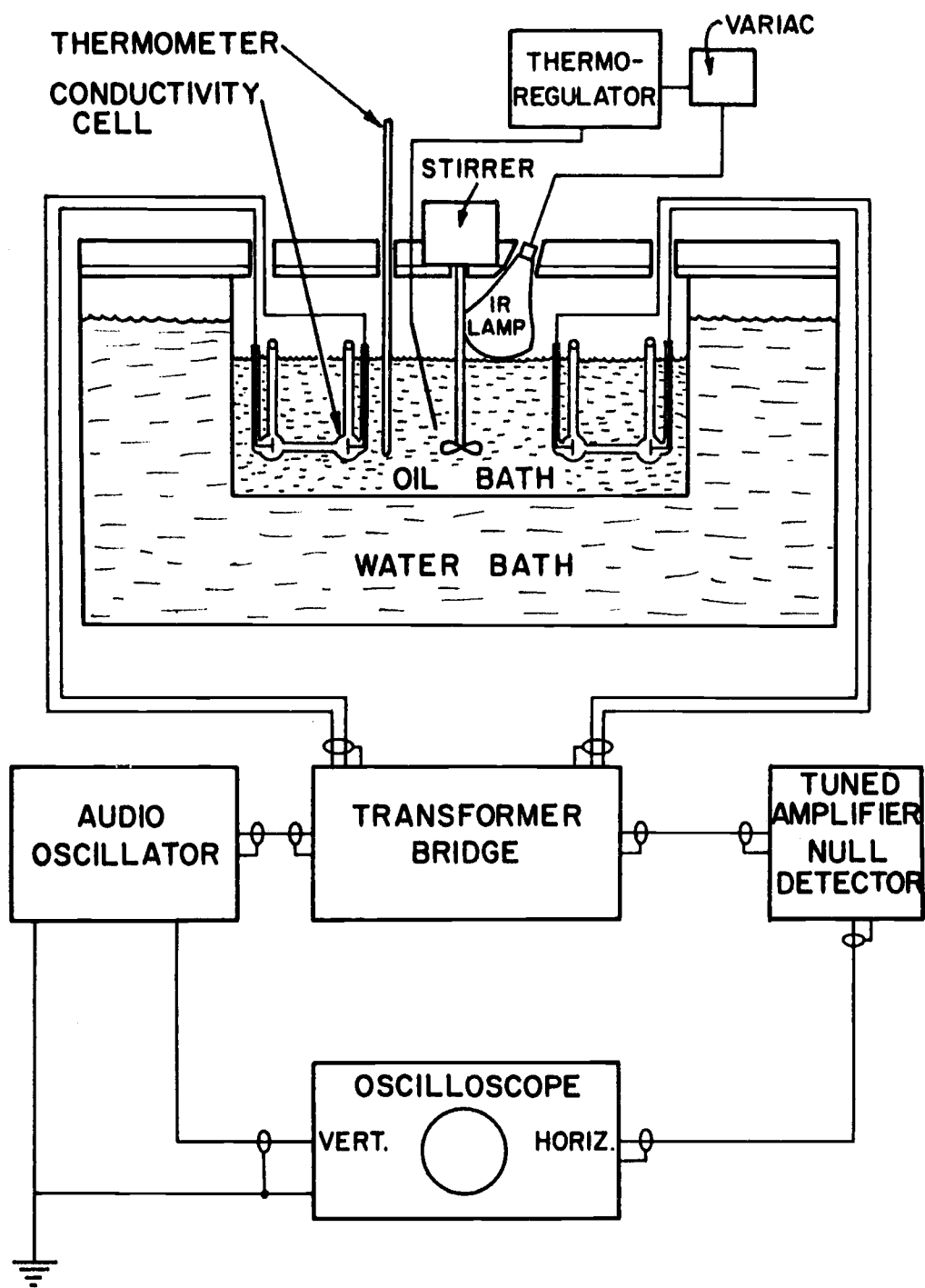


Figure 1. Instrumentation for Specific Conductance Measurements.

audio oscillator <sup>3/</sup> was used as the input to the voltage transformer of a transformer bridge <sup>4/</sup>. The output, from the current transformer of the bridge, was monitored on a tuned amplifier/null detector <sup>5/</sup>. The null point, for bridge balance, was more effectively monitored on a cathode ray oscilloscope <sup>6/</sup>. The vertical deflection of the CRO was driven by the audio oscillator while the horizontal signal was the amplified output of the tuned null detector. In this manner, both the phase and the amplitude of the output signal could be determined. Shielded and grounded leads were used throughout.

In order to prevent evaporation, we prepared the solutions in a wet box. The wet box consisted of a large insulated box with a front window of two clear (10 milthick) plastic sheets separated by a 0.25-inch dead-air space. Long flexible plastic gloves provided access to the wet box. The temperature was maintained constant at  $30 \pm 0.2^{\circ} \text{C}$  with a thermoswitch <sup>7/</sup> and a 100 watt light bulb. Air circulation was achieved with an 8-inch propeller attached to a small ac motor. The relative humidity was maintained between 90 and 94% with a 2x2 ft. cotton wick dipping into a trough of saline water.

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<sup>3/</sup> Model no. 201C Audio Oscillator from Hewlett-Packard Co., Page Mill Road, Palo Alto, California.

<sup>4/</sup> Model no. B821 High Precision Comparator from the Wayne Kerr Laboratories Limited, 44 Coombe Road, New Malden, Surrey, England.

<sup>5/</sup> Type 1232-A Tuned Amplifier and Null Detector from General Radio Company, West Concord, Massachusetts.

<sup>6/</sup> Model no. 102B Hewlett-Packard Oscilloscope.

<sup>7/</sup> Catalogue no. 17000-0 Thermoswitch from Fenwal Incorporated, Ashland, Massachusetts.

To fill the cells without air bubbles, we used the rotator shown in Figure 2b. The cell was mounted on the rotator and manipulated in such a way that during filling, the meniscus always advanced slowly in a vertical direction.

The conductance varies about 2 to 3%/°C. The temperature of the cells must be within 0.002°C of each other in order to measure the conductivity ratio of the solutions to 2 parts in 10<sup>5</sup>. This was accomplished by immersing the cells in an oil bath, which in turn was placed in a constant temperature bath<sup>8/</sup> set 0.3 to 0.5°C below the desired temperature of the run (see Figure 1). The oil bath consisted of a 40-liter aluminum tub, half full of Diala Oil AX<sup>9/</sup>. A rotary pump<sup>10/</sup> and the thermistor of a temperature regulator<sup>11/</sup> which actuated an infrared lamp were centrally located in the oil bath. The amounts of power to the pump and lamp were controlled with variacs. The temperature range over the whole oil bath was 0.003°C (at 25°C). The temperature range for any particular point in the oil bath was 0.002°C for a period of time encompassing a

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<sup>8/</sup> Model no. 4-8605 Wide Range Constant Temperature Bath, from American Instrument Co., Inc., 8030 Georgia Avenue, Silver Springs, Maryland.

<sup>9/</sup> Shell Oil Company, Shell Building, San Francisco, California.

<sup>10/</sup> Model no. 4-603S Rotary Pump from American Instrument Company.

<sup>11/</sup> Model no. 44 Fisher Temperature Control from Fisher Scientific, 461 Riverside Avenue, Boston, Massachusetts.

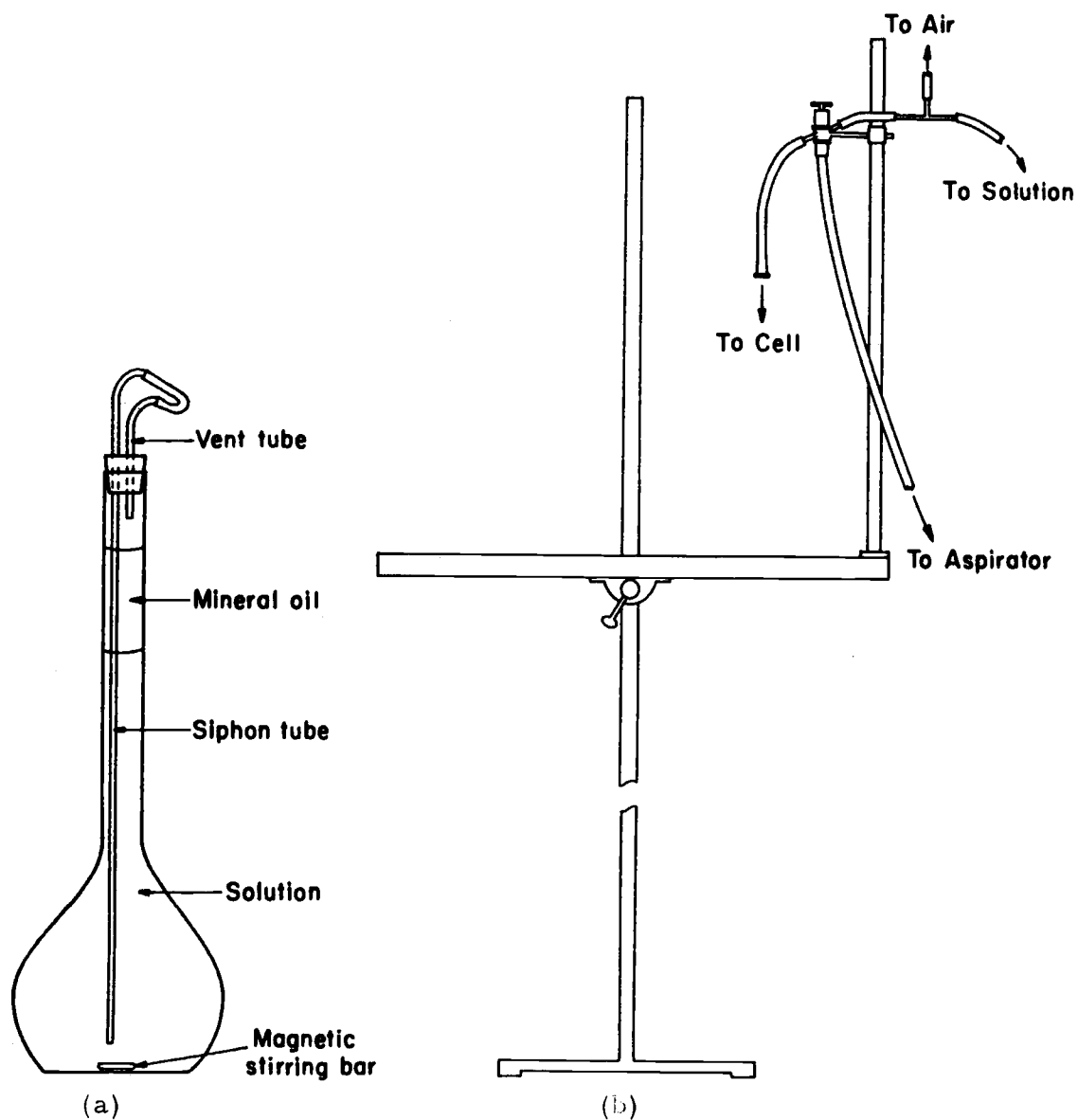


Figure 2. Handling of Solutions: (a) Set-up for Delivery of Solutions to Conductance Cells, and (b) Rotator for Filling Conductance Cells.

number of cycles of the infrared lamp, and the heater/refrigerator of the water bath. The temperature and temperature ranges were determined with a Beckmann-type differential thermometer, which was calibrated with a platinum resistance thermometer.

### Conductivity Cells

The Jones-type conductivity cells used were manufactured according to the criteria established by Jones and Bollinger (1931). The cells, as received from the manufacturer, were cleaned in sequence with benzene, acetone, distilled water, fuming nitric acid, and finally distilled water. The platinum electrodes were platinized to a light gray color according to the procedure of Jones and Bollinger (1935) with 3% chloroplatinic acid containing a 0.025% lead acetate additive. Each electrode in the cell was made the cathode, relative to an auxiliary platinum electrode, for the passage of 65 milliamps of high voltage dc. The effectiveness of platinization in reducing polarization effects was evaluated from the change in the ratio of the cell constants,  $R_{obs}$ , as the frequency,  $f$ , was varied according to the formula  $R_{obs} = R_{true} + \text{const}/\sqrt{f}$  (see Jones and Bollinger, 1935). A plot of  $R_{obs}$  vs.  $1/\sqrt{f}$  for the pairs of cells used is a straight line of essentially zero slope between five and ten kc <sup>12/</sup>.

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<sup>12/</sup> For the pair of cells used in about 95% of the runs,  $R_{obs}$  varied from 0 to 3 parts in  $10^5$ .  $R_{obs}$  varied 2 to 3 parts in  $10^5$  for a second pair of cells used in a few runs.

The frequency test was carried out periodically to check the adequacy of platinization.

### Preparation of Artificial Seawater

Artificial seawater was used, since partial equivalent conductances of the major salts in seawater are mainly influenced by the abundance and interactions of the major ions in seawater. Artificial seawater minimizes the contamination of the platinized electrodes of the conductivity cells; it provides a reproducible ionic media containing the major electrolytes found in natural water; and it is less susceptible to biological modification than natural seawater (which contains a small amount of organic matter).

The seawater was made according to the recipe of Lyman and Fleming (1940) and the procedure outlined by Kester et al. (1967). However, we made one modification: we filtered the seawater through a 0.45 micron Millipore filter prior to equilibration with laboratory air. The artificial seawaters were quite stable; after three or four months storage there was little change in salinity and only a slight decrease in pH. The salinity was determined with a Hytech Inductive Salinity and Conductivity Meter, which was standardized with Copenhagen seawater. Precision was  $\pm 0.003\text{‰}$  and accuracy was estimated to be about  $\pm 0.005\text{‰}$ .

### Preparation and Handling of Solutions

The ratios of conductances were very sensitive to evaporation, and special handling procedures had to be developed. To obtain an accuracy of 1 in  $10^5$ , one cannot lose more than 1 part in  $10^5$  of water by evaporation. For one kilogram of solutions this is 10 milligrams of water, or the amount of water vaporized into dry air at  $25^{\circ}\text{C}$  that occupies about  $400\text{ cm}^3$ . A quantity of salt was weighed out and delivered to a one-liter volumetric flask; a teflon-coated magnetic stirring bar of known volume was inserted, and the flask closed off with a siphon. The flask (with salt) and a large reservoir of seawater, for the run, was then placed in a constant temperature wet box. The temperature in the wet box was maintained constant at about  $30 \pm 0.2^{\circ}\text{C}$ , and the relative humidity was between 90 and 94%. The volumetric flask and the seawater (fitted with a siphon and covered with a layer of mineral oil) were thermostated overnight in the wet box. The siphon was removed and the flask filled to the mark with seawater. The salt and seawater were mixed with a magnetic stirrer and, with the siphon tube partially in, mineral oil was added (see Figure 2a). A liter of unaltered seawater was handled in a similar manner with a comparable exposure time in the wet box, without stirring.

The conductivity cells were filled with one of the above solutions

in the following manner. The cell is clamped to a cell holder. <sup>13/</sup>. The cell holder is clamped to the table of the cell rotator, and one tube of the cell is attached to a two-way stopcock. The two-way stopcock leads to an aspirator and to the siphon of the solution being evaluated plus an air bleeder valve. The cell is first slowly drained (the cells are not stored empty). As the cell is emptied, the table is rotated to minimize the air/solution interface. The cell is then filled with the new solution. Again, the table is rotated and the solution moves through the cell. When the cell is half-full, the siphon is clamped off and the air bleeder valve is opened. This rinse solution is drained as before. The above procedure is repeated three or four times to insure complete rinsing. The cell is then slowly filled to over-flowing and is visually checked for air bubbles trapped on or between the electrodes. Some of the solution is drained out so that the level within the cell will coincide with the level of the cell's immersion in the oil bath.

#### Measurement of Conductance Ratio

The optimum operating conditions for the bridge were determined at 25°C with the cells filled with the same seawater. With input voltages of 4, 8, and 15 volts, we varied the input frequency from 1 to 10 kc in steps of 1 kc. The conductance ratios varied

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<sup>13/</sup> Catalogue no. 4990 Mounting Stand, from Leeds & Northrup Co.



from 3 and 6 parts in  $10^5$  (from 1 to 5 kc) and from 0 and 2 parts in  $10^5$  (from 5 to 10 kc). The ratios varied from 0 and 1 in  $10^5$  for input voltages of 4, 8, and 15 volts at 7 kc. Four volts at 7 kc were used for all conductance measurements as the input to the primary of the voltage transformer of the bridge.

Null was obtained on the bridge in the following manner. When the cells had come to thermal equilibrium, the gain on the amplifier was decreased and the bridge unbalanced. The input frequency was adjusted to match that of the null detector. The bridge is then re-balanced and the amplifier gain increased. A variable capacitor ( $\pm 5$  pF), parallel to the secondary of the input transformer (on the "standard" side of the bridge), was varied slightly to get a minimum deflection on the null detector/oscilloscope display. The above procedure was repeated until a zero or minimum reading was obtained on the detector (one repetition was usually sufficient).

Two experiments were carried out to determine the repeatability and reproducibility of the conductance ratios. The conductance ratio of two cells filled with the same seawater was determined at  $25^{\circ}\text{C}$ . One of the cells was then removed from the oil bath and manipulated as-in-filling without opening the cell. The cell was returned to the oil bath and the conductance ratio redetermined. This procedure was repeated nine times with one cell or the other. The standard deviation for the ratio was 1 in  $10^5$ . The other experiment went a

step further: the cell was rinsed two or three times and refilled with the same seawater. The standard deviation for seven tries was 1 in  $10^5$ . Finally, for all partial equivalent conductance measurements made, the ratio of the cell constants was determined before and after every set of four seawater vs. seawater plus salt solutions. The cell was rinsed four or five times between each determination. The standard deviation for these data was 2 in  $10^5$ .

Our initial intention was to make a series of salt additions to seawater at a particular salinity and temperature and to extrapolate the ratio of the change in conductance to the equivalents of salt added to zero salt addition. Eight such runs were made, two each for NaCl, KCl,  $K_2SO_4$ , and  $Na_2SO_4$ . A set of solutions was made up in the wet box from a liter of seawater plus salt and a liter of unaltered seawater. Fifty ml automatic pipettes were used to make solutions of 250, 150, 100, 50, and 0 ml seawater plus salt diluted respectively with 0, 50, 100, 150 and 250 ml of unaltered seawater. The conductance ratios were determined, and  $\Delta K/K\Delta n$  was plotted against  $\Delta n$  (Figure 3). It can be seen from the figure that over the range of additions of NaCl the ratio does not change significantly. The same held for the salts KCl,  $K_2SO_4$  and  $Na_2SO_4$ . Since there was no difference in  $\Delta K/K\Delta n$ , within experimental error, between the original single salt addition and the extrapolated value, single salt additions were used in all subsequent determinations of the partial

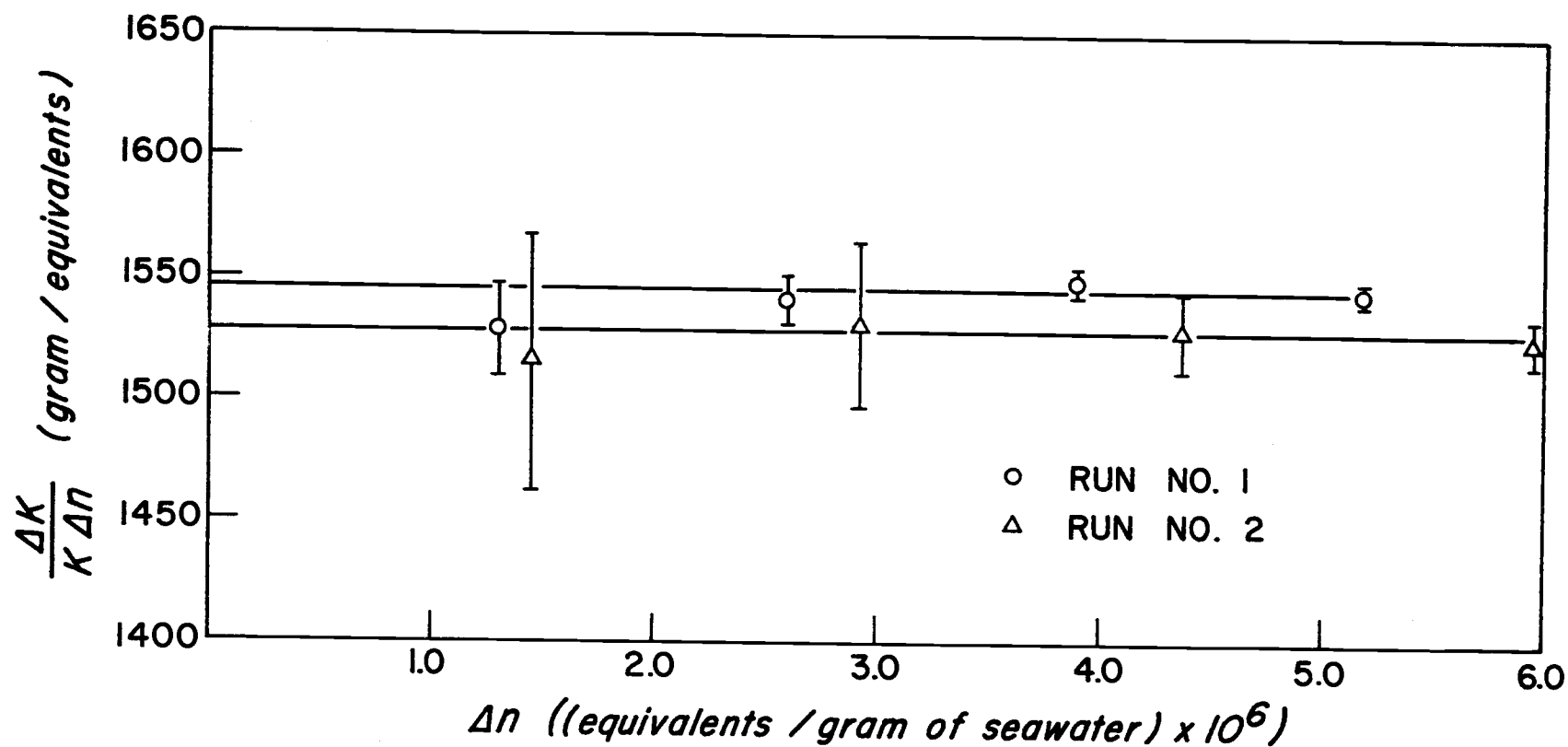
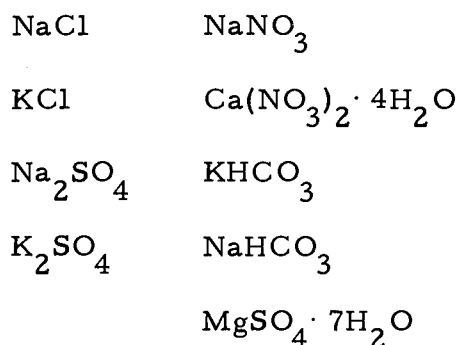


Figure 3. The Change in the Specific Conductance for Small Additions of NaCl to a Seawater of 34.430‰ Salinity at 24.955°C.

equivalent conductance.

### Salts Investigated

The salts used in this investigation were;



All the salts have at least one ion common to the major ions in seawater. All can be weighed with precision and accuracy on an analytical balance without perceptible deliquescence or efflorescence. Most of them can be added to seawater in amounts suitable for conductivity measurements without causing major phase changes in seawater (*i. e.* CO<sub>2</sub> gas bubbles or CaCO<sub>3</sub> precipitation); KHCO<sub>3</sub> and NaHCO<sub>3</sub> were exceptions. When enough KHCO<sub>3</sub> was added to cause the desirable 1% change in the conductance ratio, the nucleation time for carbonate precipitation was several weeks (see Pytkowicz, 1965). For NaHCO<sub>3</sub>, a 0.5 to 0.6% change in the conductivity ratio had a nucleation time of a few hours. As a result, only three runs were made.

All of the salts were reagent grade Baker and Adamson<sup>14/</sup> and were not further purified.  $\text{KCl}$  and  $\text{Na}_2\text{SO}_4$  were fused prior to use, and  $\text{NaCl}$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{NaNO}_3$  were dried for several hours at temperatures of 100 to 150°C. These five salts were stored in a covered evacuated dessicator between uses and were redried periodically.  $\text{KHCO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  were used as obtained from the manufacturer because of our uncertainty of the composition and the stability of the dried form.

The error introduced by not purifying the dryable salts is beyond the limits of detection of the bridge. The hydrated salts have a larger potential source of error. The minimum assay for  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  is 99.5%; the maximum amount of water as an impurity is 0.5%. This could lead to a 0.5% error in the determination of

$\bar{\Lambda}_{\text{MgSO}_4}$

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<sup>14/</sup> Baker and Adamson Quality, Allied Chemical, General Chemical Division, Morristown, New Jersey.

## EXPERIMENTAL RESULTS

To calculate the partial equivalent conductances of NaCl, KCl,  $K_2SO_4$ ,  $Na_2SO_4$ ,  $KHCO_3$ ,  $NaNO_3$ ,  $Ca(NO_3)_2$  and  $MgSO_4$ , we used the changes in the conductance ratio, the specific conductance of seawater from Weyl's (1964) formula, and the partial equivalent volume data of Duedall and Weyl (1967). A sample calculation is given in Appendix 1.

The original data were normalized to common salinities and temperatures for comparison purposes and for determination of the partial equivalent conductance differences. This was done for each salt by fitting the data, by least squares, to power series in temperature and salinity.

$$\bar{\Lambda}_s (S\text{‰}, t^{\circ}\text{C}) = \sum_{ij} a_{ij} S^i t^j \quad (8)$$

$i = 0 \text{ ---}, n$

$j = 0 \text{ ---}, m$

where  $S$  is salinity in ‰ and  $t$  is temperature in  $^{\circ}\text{C}$ . The significant terms were evaluated from: graphs of the partial equivalent conductance of the salts vs. temperature and salinity and the equation of  $\bar{\Lambda}_{\text{sea salt}}$  determined from specific conductance of seawater and partial specific volume data of water in seawater (see below). The standard deviation between calculated and predicted values of  $\bar{\Lambda}_{\text{sea salt}}$  is

0.03 cm<sup>2</sup>/(ohm eq) comparable to the error in determining the specific conductance from Weyl's (1964) equation. The coefficients of the equations

$$\bar{\Lambda}_s = a_{00} + a_{01}t + a_{02}t^2 + (a_{10} + a_{11}t)S \quad (9)$$

used to adjust the measured partial equivalent conductances are given in Appendix II. Predicted values from the above equations fell within duplicate run error. The adjusted measured values are given in Table 1, and duplicate runs are indicated by  $\pm$ . The correction factors applied to the observed partial equivalent conductances, in normalizing to common salinities and temperatures, were less than 1% of the observed values.

#### Partial Equivalent Conductance Differences

The validity of the measurements in this work can be checked by determining the partial equivalent conductance differences for sets of four salts with common anions and cations. For the group of salts NaCl, KCl, K<sub>2</sub>SO<sub>4</sub>, and Na<sub>2</sub>SO<sub>4</sub>, the following relationships were found, within experimental error, for the salinity and temperature ranges studied:

$$\bar{\Lambda}_{(K^+ - Na^+)Cl^-} = \bar{\Lambda}_{(K^+ - Na^+)SO_4^-}$$

$$\bar{\Lambda}_{(SO_4^{2-} - Cl^-)K^+} = \bar{\Lambda}_{(SO_4^{2-} - Cl^-)Na^+}$$

Table I. Summary of the Adjusted Measured Partial Equivalent Conductances of Salts in Seawater ( $\text{cm}^2/(\text{ohm eq})$ ).

Salt	$S^0/\text{oo} = 34.325$			$S^0/\text{oo} = 32.248$		$S^0/\text{oo} = 30.126$		
	$24.958^{\circ}\text{C}$	$14.986^{\circ}\text{C}$	$0.00^{\circ}\text{C}$	$24.958^{\circ}\text{C}$	$0.00^{\circ}\text{C}$	$24.958^{\circ}\text{C}$	$0.00^{\circ}\text{C}$	
NaCl	$80.13_{\pm.04}$	$64.96_{\pm.04}$	$44.54_{\pm.14}$	81.39	$44.84_{\pm.30}$	$82.38_{\pm.03}$	$45.36_{\pm.32}$	
KCl	$102.64_{\pm1.42}$	$84.36_{\pm.10}$	$59.40_{\pm.12}$	103.47	$59.74_{\pm.06}$	$104.74_{\pm.02}$	$59.86_{\pm.26}$	
$\text{K}_2\text{SO}_4$	$69.14_{\pm.40}$	$56.98_{\pm.02}$	$39.86_{\pm.06}$	70.65	$40.34_{\pm.08}$	$71.62_{\pm.02}$	40.28	
$\text{Na}_2\text{SO}_4$	$46.93_{\pm.33}$	$37.48_{\pm.02}$	$25.04_{\pm.04}$	48.30	$25.68_{\pm.02}$	$49.33_{\pm.08}$	$26.09_{\pm.25}$	
	$S^0/\text{oo} = 35.567$			$S^0/\text{oo} = 33.953$		$S^0/\text{oo} = 30.180$		
	$24.920^{\circ}\text{C}$	$14.950^{\circ}\text{C}$	$0.00^{\circ}\text{C}$	$24.920^{\circ}\text{C}$	$14.950^{\circ}\text{C}$	$24.920^{\circ}\text{C}$	$14.950^{\circ}\text{C}$	$0.00^{\circ}\text{C}$
$\text{KHCO}_3$	$64.25_{\pm.33}$	$53.00_{\pm.26}$	36.68	$65.74_{\pm.06}$	$53.96_{\pm.14}$	67.19	$54.94_{\pm.24}$	$37.92_{\pm.14}$
$\text{NaNO}_3$	$71.64_{\pm.38}$	$58.40_{\pm.28}$	40.28	$72.82_{\pm.04}$	$59.47_{\pm.17}$	$74.72_{\pm.02}$	$60.79_{\pm.10}$	$42.02_{\pm.15}$
$\text{Ca}(\text{NO}_3)_2$	$61.34_{\pm.42}$	$50.51_{\pm.34}$	35.18	$62.36_{\pm.06}$	$51.48_{\pm.09}$	$63.86_{\pm.32}$	$52.71_{\pm.10}$	$36.70_{\pm.06}$
$\text{MgSO}_4$	$29.79_{\pm.10}$	$23.70_{\pm.10}$	15.24	$30.72_{\pm.01}$	$24.46_{\pm.06}$	$32.82_{\pm.19}$	$26.25_{\pm.03}$	$17.20_{\pm.07}$



The above relationship follows directly from the definition of partial equivalent conductance and from the fact that the properties of a solution depend only on its composition and not on the salts from which it was prepared. The conductance difference for  $(K^+ - Na^+)HCO_3^-$  at the salinity and temperatures run is also equal to the above within experimental error.

Equally valid comparisons can be made for  $MgSO_4$ ,  $Ca(NO_3)_2$ , and  $NaNO_3$  by means of Equation 9 and Park's (1964) work (re-evaluated by Connors and Park, 1967) with a salinity of 35.04‰ and at 23°C.

In general terms one can write

$$\bar{\Lambda}_{Xa} - \bar{\Lambda}_{Xb} = \bar{\Lambda}_{Aa} - \bar{\Lambda}_{Ab} \equiv \bar{\Lambda}_{(a-b)}$$

independent of the common ion. It is more convenient to present the results of this work as ionic conductance differences relative to the sodium and the chloride ions. For example, the partial equivalent conductance for the salt Bc can be determined from

$$\bar{\Lambda}_{Bc} = \bar{\Lambda}_{NaCl} + \bar{\Lambda}_{(B-Na^+)} + \bar{\Lambda}_{(c-Cl^-)} \quad (10)$$

The partial equivalent conductance differences determined in this work at various salinities and temperatures are

$$\bar{\Lambda}_{(K^+ - Na^+)} \quad \bar{\Lambda}_{(SO_4^{=2} - Cl^-)}$$

$$\begin{array}{cc} \bar{\Lambda}_{(\text{Mg}^{++} - \text{Na}^+)} & \bar{\Lambda}_{(\text{HCO}_3^- - \text{Cl}^-)} \\ \bar{\Lambda}_{(\text{Ca}^{++} - \text{Na}^+)} & \bar{\Lambda}_{(\text{NO}_3^- - \text{Cl}^-)} \end{array}$$

These differences, as well as data for NaCl, are presented in Table II for salinities and temperatures requiring a minimum amount of extrapolation or interpolation of the original data. The error, where listed, is  $\pm$  the standard deviation of the original data. The data in the table can be used to determine the partial equivalent conductance of 16 cation-anion pairs.

The conductances of the salts NaCl, KCl,  $\text{K}_2\text{SO}_4$ , and  $\text{Na}_2\text{SO}_4$  are overdetermined. If  $\bar{\Lambda}_s$ 's are available for three of the salts, the fourth can be calculated from Equation 10. As a result, the averages of the differences are given for  $\bar{\Lambda}_{(\text{K}^+ - \text{Na}^+)}$  and  $\bar{\Lambda}_{(\text{SO}_4^{=} - \text{Cl}^-)}$  in Table II (underlined values), and the averages are used in all subsequent calculations.

The partial equivalent conductance differences from Table II were fitted by a least-squares polynomial approximation to the power series (Equation 9), and the coefficients were calculated. The results appear in Table III. The errors,  $\epsilon$ , listed in Table III are  $\pm$  the standard deviation between predicted values from the equations given and the adjusted measured results. The five coefficients for each  $\bar{\Lambda}_\Delta$  were determined with the seven or eight data points

Table II. Measured Partial Equivalent Conductance Differences  $\text{cm}^2/(\text{ohm eq})$ .

Partial Equivalent Conductance	$S^\circ/\infty = 34.325$			$S^\circ/\infty = 32.248$		$S^\circ/\infty = 30.126$		
	$24.958^\circ\text{C}$	$14.986^\circ\text{C}$	$0.00^\circ\text{C}$	$24.958^\circ\text{C}$	$0.00^\circ\text{C}$	$24.958^\circ\text{C}$	$0.00^\circ\text{C}$	
$\bar{\Lambda}_{\text{NaCl}}$	$80.13_{\pm.04}$	$64.96_{\pm.04}$	$44.54_{\pm.14}$	81.39	$44.84_{\pm.30}$	$82.38_{\pm.03}$	$45.36_{\pm.32}$	
$\bar{\Lambda}_{(\text{K}^+ - \text{Na}^+)\text{Cl}^-}$	$22.51_{\pm 1.42}$	$19.40_{\pm.09}$	$14.86_{\pm.18}$	22.08	$14.90_{\pm.31}$	$22.36_{\pm.04}$	$14.50_{\pm.41}$	
$\bar{\Lambda}_{(\text{K}^+ - \text{Na}^+)\text{SO}_4^{=}}$	$22.21_{\pm.52}$	$19.50_{\pm.03}$	$14.82_{\pm.08}$	22.35	$14.66_{\pm.10}$	$22.29_{\pm.08}$	$14.19_{\pm.35}$	
$\bar{\Lambda}_{(\text{K}^+ - \text{Na}^+)\text{Ave}}$	<u><math>22.36_{\pm 1.08}</math></u>	<u><math>19.45_{\pm.09}</math></u>	<u><math>14.84_{\pm.14}</math></u>	<u><math>22.22_{\pm.14}</math></u>	<u><math>14.78_{\pm.25}</math></u>	<u><math>22.32_{\pm.10}</math></u>	<u><math>14.34_{\pm.40}</math></u>	
$\bar{\Lambda}_{(\text{SO}_4^{=}-\text{Cl}^-)\text{Na}^+}$	$-33.20_{\pm.33}$	$-27.48_{\pm.04}$	$-19.50_{\pm.14}$	-33.09	$-19.16_{\pm.30}$	$-33.05_{\pm.09}$	$-19.27_{\pm.43}$	
$\bar{\Lambda}_{(\text{SO}_4^{=}-\text{Cl}^-)\text{K}^+}$	$-33.50_{\pm 1.47}$	$-27.38_{\pm.10}$	$-19.54_{\pm.12}$	-32.82	$-19.40_{\pm.10}$	$-33.12_{\pm.03}$	$-19.58_{\pm.26}$	
$\bar{\Lambda}_{(\text{SO}_4^{=}-\text{Cl}^-)\text{Ave}}$	<u><math>-33.35_{\pm 1.30}</math></u>	<u><math>-27.43_{\pm.10}</math></u>	<u><math>-19.42_{\pm.17}</math></u>	<u><math>-32.96_{\pm.14}</math></u>	<u><math>-19.28_{\pm.25}</math></u>	<u><math>-33.08_{\pm.07}</math></u>	<u><math>-19.42_{\pm.40}</math></u>	
	$S^\circ/\infty = 35.567$			$S^\circ/\infty = 33.953$		$S^\circ/\infty = 30.180$		
	$24.920^\circ\text{C}$	$14.950^\circ\text{C}$	$0.00^\circ\text{C}$	$24.920^\circ\text{C}$	$14.950^\circ\text{C}$	$24.920^\circ\text{C}$	$14.950^\circ\text{C}$	$0.00^\circ\text{C}$
$\bar{\Lambda}_{(\text{Mg}^{++} - \text{Na}^+)\text{SO}_4^{=}}$	$-16.40_{\pm.35}$	$-13.20_{\pm.11}$	-9.55	$-16.45_{\pm.01}$	$-13.14_{\pm.06}$	$-16.44_{\pm.20}$	$-13.00_{\pm.03}$	$-8.87_{\pm.26}$
$\bar{\Lambda}_{(\text{Ca}^{++} - \text{Na}^+)\text{NO}_3^-}$	$-10.30_{\pm.57}$	$-7.89_{\pm.44}$	-5.10	$-10.46_{\pm.07}$	$-8.05_{\pm.19}$	$-10.86_{\pm.32}$	$-8.08_{\pm.14}$	$-5.32_{\pm.16}$
$\bar{\Lambda}_{(\text{HCO}_3^- - \text{Cl}^-)\text{K}^+}$	$-37.69_{\pm 1.47}$	$-30.86_{\pm.26}$	-22.64	$-36.94_{\pm.07}$	$-30.47_{\pm.17}$	$-37.45_{\pm.03}$	$-30.80_{\pm.25}$	$-21.94_{\pm.29}$
$\bar{\Lambda}_{(\text{NO}_3^- - \text{Cl}^-)\text{Na}^+}$	$-7.77_{\pm.38}$	$-6.01_{\pm.28}$	-3.96	$-7.48_{\pm.04}$	$-5.58_{\pm.18}$	$-7.57_{\pm.04}$	$-5.78_{\pm.10}$	$-3.32_{\pm.35}$

Table III. The Partial Equivalent Conductances of Salts in Seawater: Salinity Range 30 to 35.6 ‰, Temperature Range 0 to 25° C.

$$\bar{\Lambda}_{\text{Bc}} = \bar{\Lambda}_{\text{NaCl}} + \bar{\Lambda}_{(\text{B} - \text{Na}^+)} + \bar{\Lambda}_{(\text{c} - \text{Cl}^-)}$$

$$\bar{\Lambda}_s (S^\circ/\text{oo}, t^\circ\text{C}) = a_{00} + a_{01}t + a_{02}t^2 + (a_{10} + a_{11}t)S \pm \epsilon \text{ cm}^2/(\text{ohm eq})$$

Partial Equivalent Conductance	$a_{00}$	$a_{01}$	$a_{02} \times 10^3$	$a_{10}$	$a_{11} \times 10^3$	$\epsilon^{\text{a/}}$
$\bar{\Lambda}_{\text{NaCl}}$	51.36	1.73	6.37	-.200	-13.4	$\pm .18$
$\bar{\Lambda}_{(\text{K}^+ - \text{Na}^+)}$	10.80	.464	-.627	.119	-4.41	$\pm .07$
$\bar{\Lambda}_{(\text{Ca}^{++} - \text{Na}^+)}$	-6.11	-.225	-2.66	.0275	2.32	$\pm .06$
$\bar{\Lambda}_{(\text{Mg}^{++} - \text{Na}^+)}$	-5.15	-.391	-2.99	-.123	5.34	$\pm .02$
$\bar{\Lambda}_{(\text{SO}_4^{=} - \text{Cl}^-)}$	-18.65	-.445	-2.12	-.0235	-1.62	$\pm .10$
$\bar{\Lambda}_{(\text{HCO}_3^- - \text{Cl}^-)}$	-18.6	-.663	-4.27	-.112	5.02	$\pm .23$
$\bar{\Lambda}_{(\text{NO}_3^- - \text{Cl}^-)}$	-.0754	-.246	-1.65	-.108	3.89	$\pm .13$
$\bar{\Lambda}_{\text{sea salt}}$	48.61	1.62	5.53	-.221	-12.6	$\pm .18^{\text{b/}}$

a/  $\epsilon$  is the standard deviation between predicted and observed.

b/  $\epsilon$  is the square root of the sum of the squares of  $\epsilon_i / .60553$ .

available; as a result the residuals between the predicted and observed values are not zero.

Table IV is a comparison between observed and predicted  $\bar{\Lambda}_s$  from the equations in Table III for the eight salts. The differences between observed and predicted values is less than the experimental error. The examples given in Table IV were selected to illustrate the nature of the error over the temperature range studied at various salinities.

#### The Partial Specific Conductance of Water in Seawater

One dilution experiment was carried out on a seawater of 34.430‰ salinity and at 24.955°C. Approximately 10 grams of distilled water were added to 1.008 kg of seawater. The quantity  $\Delta K/K \Delta m$  was determined. It was shown from Weyl's (1964) treatment of specific conductance data that  $\Delta K/K \Delta m$  is approximately equal to minus the slope  $n$ . The value found, 0.888, compares favorably with the value, 0.892, calculated by Weyl.

#### Calculation of $\bar{\Lambda}_{\text{sea salt}}$

Seawater can be regarded as a two-component system made up of water and "sea salt." Each of these components will contribute to the conductance of a gram of seawater according to

Table IV. Comparison Between the Observed and Predicted Values of the Partial Equivalent Conductances.

Salt	Salinity ‰	Temp. °C	Predicted $\kappa$ cm <sup>2</sup> /(ohm eq)	Observed cm <sup>2</sup> /(ohm eq)	Obs. - Pred.
NaCl	34.325	24.958	80.16 $\pm$ .18	80.13 $\pm$ .04	-.03
	30.126	24.958	82.41 $\pm$ .18	82.38 $\pm$ .03	-.03
	34.325	14.986	64.96 $\pm$ .18	64.96 $\pm$ .04	0.00
	34.325	0.00	44.49 $\pm$ .18	44.54 $\pm$ .12	+.05
	30.126	0.00	45.33 $\pm$ .18	45.36 $\pm$ .32	+.03
KCl	34.325	24.958	102.46 $\pm$ .19	102.64 $\pm$ 1.42	+.18
	30.126	24.958	104.66 $\pm$ .19	104.74 $\pm$ .02	+.08
	34.325	14.986	84.39 $\pm$ .19	84.36 $\pm$ .10	-.03
	34.325	0.00	59.38 $\pm$ .19	59.40 $\pm$ .12	+.02
	30.126	0.00	59.72 $\pm$ .19	59.86 $\pm$ .26	+.14
Na <sub>2</sub> SO <sub>4</sub>	34.325	24.958	46.89 $\pm$ .21	46.93 $\pm$ .33	+.04
	30.126	24.958	49.40 $\pm$ .21	49.33 $\pm$ .08	-.07
	34.325	14.986	37.52 $\pm$ .21	37.48 $\pm$ .02	-.04
	34.325	0.00	25.04 $\pm$ .21	25.04 $\pm$ .04	0.00
	30.126	0.00	25.98 $\pm$ .21	26.09 $\pm$ .25	+.11
K <sub>2</sub> SO <sub>4</sub>	34.325	24.958	69.19 $\pm$ .22	69.14 $\pm$ .40	-.05
	30.126	24.958	71.66 $\pm$ .22	71.62 $\pm$ .02	-.04
	34.325	14.986	56.95 $\pm$ .22	56.98 $\pm$ .02	+.03
	34.325	0.00	39.92 $\pm$ .22	39.86 $\pm$ .06	-.06
	30.126	0.00	40.36 $\pm$ .22	40.28	-.08
KHCO <sub>3</sub>	35.567	24.920	64.43 $\pm$ .30	64.25 $\pm$ .33	-.18
	30.180	24.920	67.18 $\pm$ .30	67.19	+.01
	33.953	14.950	53.73 $\pm$ .30	53.96 $\pm$ .14	+.23
	35.567	0.00	36.70 $\pm$ .30	36.68	-.02
	30.180	0.00	37.74 $\pm$ .30	37.92 $\pm$ .14	+.18
Ca(NO <sub>3</sub> ) <sub>2</sub>	35.567	24.920	61.48 $\pm$ .23	61.34 $\pm$ .42	-.14
	30.180	24.920	63.95 $\pm$ .23	63.86 $\pm$ .32	-.09
	33.953	14.950	51.28 $\pm$ .23	51.42 $\pm$ .09	+.14
	35.567	0.00	35.19 $\pm$ .23	35.18	-.01
	30.180	0.00	36.70 $\pm$ .23	36.70 $\pm$ .06	0.00
MgSO <sub>4</sub>	35.567	24.920	29.72 $\pm$ .21	29.79 $\pm$ .10	+.07
	30.180	24.920	32.88 $\pm$ .21	32.82 $\pm$ .18	-.06
	33.953	14.950	24.53 $\pm$ .21	24.46 $\pm$ .06	-.07
	35.567	0.00	15.24 $\pm$ .21	15.24	0.00
	30.180	0.00	17.10 $\pm$ .21	17.20 $\pm$ .07	+.10

Table IV. Continued.

Salt	Salinity ‰	Temp. °C	Predicted $\bar{\Lambda}$ / $\text{cm}^2/(\text{ohm eq})$	Observed $\text{cm}^2/(\text{ohm eq})$	Obs. - Pred.
$\text{NaNO}_3$	35.567	24.920	$71.81 \pm .22$	$71.64 \pm .38$	-.17
	30.180	24.920	$74.75 \pm .22$	$74.72 \pm .02$	-.03
	33.953	14.950	$59.24 \pm .22$	$59.47 \pm .17$	+.23
	35.567	0.00	$40.33 \pm .22$	40.28	-.05
	30.180	0.00	$41.99 \pm .22$	$42.02 \pm .15$	+.03

<sup>a/</sup> Error given is  $\pm$  the standard deviation of the standard deviations tabulated in Table III.

$$vK = c_{\text{sea salt}} \bar{\Lambda}_{\text{sea salt}} + (1 - c) \bar{\Lambda}_w \quad (11)$$

where  $v$  = specific volume

$c_{\text{sea salt}}$  = equivalents of "sea salt" per gram of seawater

$c$  = mass fraction of salt in seawater

"Sea salt" is defined as an anhydrous mixture of the salts contained in the artificial seawater formula of Kester et al. (1967). The number of equivalents of "sea salt," 0.60553, in a seawater of 35‰ salinity, was calculated from the anion equivalents in the artificial seawater formula.

The partial equivalent conductance of "sea salt,"  $\bar{\Lambda}_{\text{sea salt}}$ , can be calculated from specific conductance measurements or by summing the contributions of the partial equivalent conductances of the various salts. The  $\bar{\Lambda}_{\text{sea salt}}$  was calculated from the specific conductance at

0, 5, 10, 15, 20, and 25°C and at salinities of 30, 32.5, 35, and 37.5‰ with the equation

$$\bar{\Lambda}_{\text{sea salt}} = \frac{vK[1-(1-c)(\frac{\bar{v}_w}{v} - n)]}{c_{\text{sea salt}}} \quad (12)$$

(from Equations 11 and 5). Equation 7 was used to determine the specific conductance and  $n$ , the  $\log K$  vs.  $\log Cl‰$  slope. The specific volume was taken from Knudsen's (1901) Hydrographic Tables and the partial specific volume of water in seawater,  $\bar{v}_w$ , was calculated from the data and equations of Duedall and Weyl (1967). The data were fitted to Equation 9, giving the following coefficients:

$$\begin{aligned} a_{00} &= 46.66 \text{ cm}^2/(\text{ohm eq}) \\ a_{01} &= 1.447 \text{ cm}^2/(\text{ohm eq}^\circ\text{C}) \\ a_{02} &= 5.81 \times 10^{-3} \text{ cm}^2/(\text{ohm eq}^\circ\text{C}^2) \\ a_{10} &= -0.163 \text{ cm}^2/(\text{ohm eq}‰) \\ a_{11} &= -7.06 \times 10^{-3} \text{ cm}^2/(\text{ohm eq}^\circ\text{C}‰) \\ \epsilon &= \pm 0.03 \text{ cm}^2/(\text{ohm eq}) \end{aligned} \quad (13)$$

Included in Table III are the coefficients for the partial equivalent conductance of "sea salt" calculated by the second method from the results of this work. The equation used was

$$\bar{\Lambda}_{\text{sea salt}}(S‰, t^\circ\text{C}) = (\sum_{ij} a_{ij} S^{i,j})_{\text{NaCl}} + \sum_{\Delta i} \frac{x_i}{0.60553} (\sum_{ij} a_{ij} S^{i,j}) \quad (14)$$



where  $x_i$  equals the equivalents of cations or anions, other than  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{F}^-$ , contained in artificial seawater of 35‰ salinity. Due to a lack of data, the  $\text{H}_4\text{BO}_4^-$  in artificial seawater has been ignored;  $\text{F}^-$  and  $\text{Br}^-$  have been counted as  $\text{Cl}^-$ ; and  $\text{Sr}^{++}$  has been assumed to behave like  $\text{Ca}^{++}$ . The partial equivalent conductance differences,  $(\text{K}^+ - \text{Na}^+)$ ,  $(\text{Mg}^{++} - \text{Na}^+)$ ,  $(\text{Ca}^{++} - \text{Na}^+)$ ,  $(\text{HCO}_3^- - \text{Cl}^-)$ , and  $(\text{SO}_4^{--} - \text{Cl}^-)$ , are designated by  $\Delta_i$ . The approximations made with respect to  $\text{F}^-$ ,  $\text{Br}^-$ , and  $\text{Sr}^{++}$  will cause the  $\bar{\Lambda}_{\text{sea salt}}$  to be about 0.013% low. This relatively insignificant effect is due, in part, to the low concentrations of these ions in seawater and to the similarity in conductances of the substituted ions. The differences in the partial equivalent conductances of  $\text{KBr}$  and  $\text{SrCl}_2$  vs.  $\text{KCl}$  and  $\text{CaCl}_2$ , respectively, are only 2 to 3% (Park, 1964; revised Connors and Park, 1967).

The coefficients for  $\bar{\Lambda}_{\text{sea salt}}(S\text{‰}, t^\circ\text{C})$  for Equation 9 and the results of this work, Table III, are reasonably close. Table V shows a comparison between the two equations for selected temperatures and salinities. In Figure 4 comparisons are made at 35‰ from 0 to 25°C between the partial equivalent conductances of  $\text{NaCl}$ , "sea salt" (this work, Table III), and the "sea salt" determined from specific conductance and partial specific volume data. The similarity between  $\bar{\Lambda}_{\text{NaCl}}$  and the "sea salt" curves is evident and expected. The  $\bar{\Lambda}_{\text{sea salt}}$  curves are lower. This is due mainly to the presence of

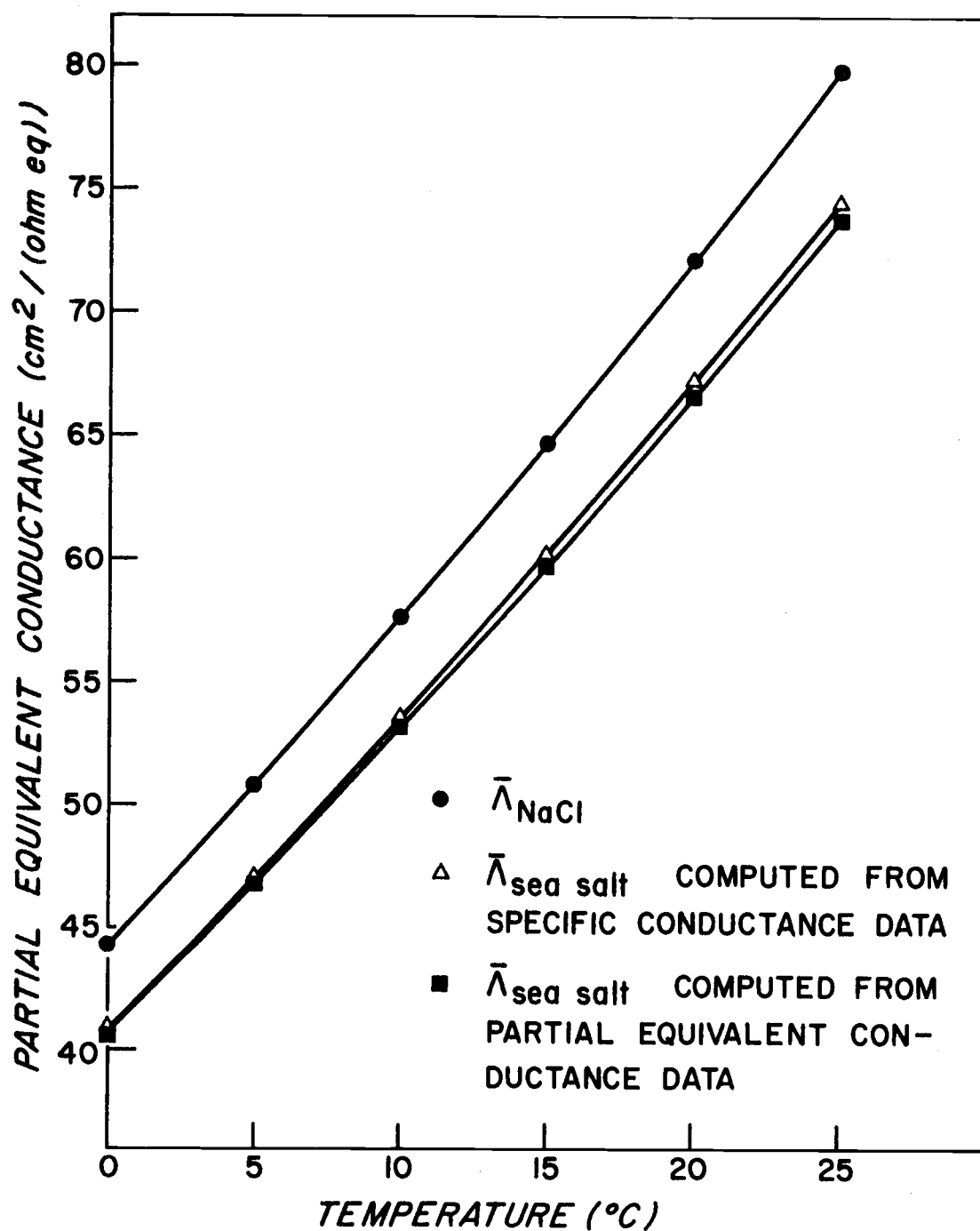


Figure 4. Temperature Dependency of the Partial Equivalent Conductance of NaCl and "Sea Salt" at 35‰ Salinity.

$\text{Mg}^{++}$  and  $\text{SO}_4^{--}$  ions in seawater. Their tendency to form ion pairs and more extensive hydration reduces the overall partial equivalent conductance of "sea salt." The maximum difference between the two  $\bar{\Lambda}_{\text{sea salt}}$  curves is about 1% at 25°C. A similar comparison at 30‰ has a smaller average error.

Table V. Partial Equivalent Conductance of "Sea Salt" ( $\text{cm}^2/(\text{ohm eq})$ ).

	35.04‰			30.00‰		
	23°C	15°C	0°C	25°C	15°C	0°C
Calculated Equation 9 and 13	71.61 $\pm$ .03	60.25 $\pm$ .03	40.95 $\pm$ .03	76.26 $\pm$ .03	61.59 $\pm$ .03	41.76 $\pm$ .03
This work Table III	70.90 $\pm$ .18	59.79 $\pm$ .18	40.87 $\pm$ .18	76.49 $\pm$ .18	61.81 $\pm$ .18	41.98 $\pm$ .18
Connors and Park (1967)	70.90	-----	-----	-----	-----	-----

## DISCUSSION

The partial equivalent conductance of "sea salt" can be determined from the results of Park (1964), as revised by Connors and Park (1967). The equation used is

$$\bar{\Lambda}_{\text{sea salt}}(35.04\text{‰}, 23^{\circ}\text{C}) = \sum_i \bar{\Lambda}_i \frac{n_i}{0.60553}$$

where  $n_i$  is the number of equivalents of salt  $i$  contained in seawater of salinity 35‰ (Kester et al. 1967). The results are included in Table V.  $\bar{\Lambda}_{\text{sea salt}}$  calculated from the work of Connors and Park (1967) is  $70.90 \text{ cm}^2/(\text{ohm eq})$ , and it agrees with the results of this work (Table III).

Park's revised values of the  $\bar{\Lambda}_s$ 's are compared, in Table VI, with those determined from Table III of this work. In general, the agreement between the two sets of partial equivalent conductances is good, with an average difference of less than 1%. Park determined the  $\bar{\Lambda}_s$ 's at only one temperature and salinity. However, the results of this work can be applied to a range of temperatures and salinities.

Table VI. Comparison of the Partial Equivalent Conductances of Salts in Seawater at a Salinity of 35.04‰ and at 23°C ( $\text{cm}^2/(\text{ohm eq})$ ).

Salt	This work Table III	Park (1964) as reevaluated by Connors and Park (1967)
NaCl	76.71 $\pm$ .18	76.8
KCl	98.47 $\pm$ .22	99.2
Na <sub>2</sub> SO <sub>4</sub>	44.58 $\pm$ .23	45.1
K <sub>2</sub> SO <sub>4</sub>	66.34 $\pm$ .27	67.0
KHCO <sub>3</sub>	62.48 $\pm$ .32	62.3
NaHCO <sub>3</sub>	40.73 $\pm$ .29	40.4
MgSO <sub>4</sub>	28.85 $\pm$ .24	29.2
MgCl <sub>2</sub>	60.98 $\pm$ .18	61.5
CaCl <sub>2</sub>	66.85 $\pm$ .19	66.6

#### pH and the Partial Equivalent Conductance

The partial equivalent conductance is defined, in the limit, for zero salt addition. Therefore, there will be no change in the pH of the solution for a true partial equivalent conductance measurement. The addition of finite amounts of NaCl, KCl, K<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, or NaNO<sub>3</sub> caused no detectable change in the pH; so, the change in conductance was due only to the salt added. The addition of the salts of strong acids/weaker bases, Ca(NO<sub>3</sub>)<sub>2</sub> and MgSO<sub>4</sub>, caused the pH to drop 0.02(5) units. The decrease in pH is due mostly to a shift in the second apparent dissociation constant of carbonic acid by complex

formation between divalent cations and the carbonate ion. The changes in the stoichiometric concentrations of  $\text{HCO}_3^-$ ,  $\text{CO}_3^{=}$ ,  $\text{H}_4\text{BO}_4^-$ , and  $\text{H}_3\text{O}^+$  are approximately  $+2 \times 10^{-5}$ ,  $-2 \times 10^{-5}$ ,  $-7 \times 10^{-6}$  and  $+4 \times 10^{-10}$  equivalents/liter, respectively, for an addition of 0.0172 eq/kg  $\text{MgSO}_4$  to seawater of 35.5‰ salinity at 23°C. The change in the second apparent dissociation constant of carbonic acid was calculated from the data and equations of Weyl (1961), Garrels, Thompson, and Siever (1961), and Thompson (1966). The effect that these changes will have on  $\bar{\Lambda}_{\text{MgSO}_4}$  can be estimated from the partial ionic conductances given by Park (1964) from the following:

$$\% \text{ Error} = \frac{100 \sum_i \bar{l}_i \Delta n_i}{\bar{\Lambda}_{\text{MgSO}_4} \Delta n_{\text{MgSO}_4}} \quad (15)$$

The partial equivalent conductance of  $\text{MgSO}_4$  was calculated from Table III. The  $\bar{l}_i$ 's are the partial ionic conductances of the changing species. The  $\text{H}_3\text{O}^+$  has been excluded (and also  $\text{OH}^-$ ) due to the negligible change in its concentration and  $\bar{l}_{\text{SO}_4^{=}}/2$  substituted for  $\bar{l}_{\text{H}_4\text{BO}_4^-}$ . The error estimated from the above for  $\text{MgSO}_4$  is +0.08%, and it is negligible when compared to experimental error. The same analysis applied to  $\text{Ca}(\text{NO}_3)_2$  would give similar results.

The addition of 0.005 eq/kg of  $\text{KHCO}_3$  to a seawater of 35.5‰ at 23°C causes a drop in pH of 0.3 units. The changes in concentration of the buffering species are approximately +0.00467 eq  $\text{HCO}_3^-$ ,

+ 0.0005 eq  $\text{CO}_3^{--}$ , - 0.00004 eq  $\text{H}_4\text{BO}_4^-$ , and +  $6 \times 10^{-9}$  eq  $\text{H}_3\text{O}^+$ . The error introduced in determining  $\bar{\Lambda}_{\text{KHCO}_3}$  from Equation 4 can be approximately evaluated by the argument used for  $\text{MgSO}_4$  addition.

$$\begin{aligned} \bar{\Lambda}_{\text{KHCO}_3} \Delta n_{\text{KHCO}_3} = & \bar{\Lambda}'_{\text{KHCO}_3} \Delta n'_{\text{KHCO}_3} + \bar{\Lambda}_{\text{K}_2\text{CO}_3} \Delta n_{\text{K}_2\text{CO}_3} \\ & + \bar{\Lambda}_{\text{H}_4\text{BO}_4^-} \Delta n_{\text{H}_4\text{BO}_4^-} \end{aligned} \quad (16)$$

where  $\bar{\Lambda}_{\text{KHCO}_3}$  is taken from Table III,  $\Delta n_{\text{KHCO}_3} = 0.005$  eq,  $\Delta n'_{\text{KHCO}_3} = 0.00467$  eq,  $\bar{\Lambda}'_{\text{KHCO}_3}$  is the corrected partial equivalent conductance, and  $\bar{\Lambda}_{\text{K}_2\text{CO}_3}$  is taken from the revision of Park's (1964) work. Again  $\text{H}_3\text{O}^+$  is not considered due to the small change in concentration, and  $\text{H}_4\text{BO}_4^-$  is regarded as behaving like a monovalent sulfate ion. The error amounts to -0.2%.

### Conductivity-Density Correlation

The use of temperature and conductivity data to determine the density of seawater is being investigated by Cox et al. (1962). To investigate the alteration in the conductivity-density correlation for slight changes in the relative composition of seawater, we consider the density change produced if 1 gm of a particular salt is added to 1 kg of seawater at 35‰ salinity and at temperatures of 0 and 25°C. We can then compare three quantities: a) the actual change in density given as a change in  $\sigma_t$ ; b) the change in density that would

be inferred from conductance measurements, assuming that "sea salt" had been added; and c) the change in density from a chloride titration.

For small additions of "sea salt" to seawater, a linear relationship exists between  $\Delta K$  (calculated from Equation 7) and  $\Delta \rho$  (calculated from Knudsen's Hydrographical Tables, 1901). The inferred density change,  $\Delta \rho_{\text{inf}}$ , can be calculated for conductance measurements from

$$\Delta \rho_{\text{inf}} (S\text{‰}, t^{\circ}\text{C}) = \frac{\bar{A}_i \Delta n_i \times 10^{-3} \rho (S\text{‰}, t^{\circ}\text{C})}{B(S\text{‰}, t^{\circ}\text{C})} \quad (17)$$

where  $\Delta n_i$  is the equivalent of salt added/kilogram of seawater, and  $B(S\text{‰}, t^{\circ}\text{C})$  is the slope  $\Delta K/\Delta \rho$  for "sea salt" addition. The actual change in density,  $\Delta \rho_{\text{act}}$ , can be calculated from the partial equivalent volume data of Duedall and Weyl (1967).

$$\Delta \rho_{\text{act}} (S\text{‰}, t^{\circ}\text{C}) = \frac{1 + m_i}{\bar{v}_i \Delta n_i \times 10^{-3} + 1/\rho (S\text{‰}, t^{\circ}\text{C})} - \rho (S\text{‰}, t^{\circ}\text{C}) \quad (18)$$

where  $m_i$  is the weight of salt added per gram of seawater. The results are presented in Table VII for the salts investigated in this work, at 35‰ salinity and at 0 and 25°C. The results of adding other cation-anion pairs can be evaluated from the conductance differences given in Table III and from the volume differences of Duedall and Weyl (1967).



Table VII. Comparison Between the Actual Density Change and the Inferred Density Changes for the Addition of One gm of Salt to a kg of Seawater of 35‰ Salinity (gm/cm<sup>3</sup>).

Salt	t °C	$\Delta \rho_{\text{act}} \times 10^3$	$\Delta \rho_{\text{inf}} \times 10^3$ (conductance measurement)	$(\Delta \rho_{\text{act}} - \Delta \rho_{\text{inf}}) \times 10^3$ (conductance measurement)	$\Delta \rho_{\text{inf}} \times 10^3$ (chloride titration)	$(\Delta \rho_{\text{act}} - \Delta \rho_{\text{inf}}) \times 10^3$ (chloride titration)
NaCl	25	0.68	0.78	-0.10	0.80	-0.12
	0	0.76	0.83	-0.07	0.85	-0.09
KCl	25	0.61	0.78	-0.17	0.62	-0.01
	0	0.65	0.87	-0.22	0.66	-0.01
K <sub>2</sub> SO <sub>4</sub>	25	0.77	0.45	+0.32	0.00	+0.77
	0	0.81	0.50	+0.31	0.00	+0.81
Na <sub>2</sub> SO <sub>4</sub>	25	0.87	0.38	+0.49	0.00	+0.87
	0	0.78	0.38	+0.40	0.00	+0.78
KHCO <sub>3</sub>	25	0.63	0.37	+0.26	0.00	+0.67
	0	0.67	0.40	+0.27	0.00	+0.67
NaNO <sub>3</sub>	25	0.65	0.49	+0.16	0.00	+0.65
	0	0.71	0.52	+0.19	0.00	+0.71
Ca(NO <sub>3</sub> ) <sub>2</sub>	25	0.73	0.43	+0.30	0.00	+0.73
	0	0.78	0.47	+0.31	0.00	+0.76
MgSO <sub>4</sub>	25	1.00	0.29	+0.71	0.00	+1.00
	0	1.13	0.28	+0.85	0.00	+1.13

The greatest differences in the conductance-density relationship occur in  $\text{MgSO}_4$  addition because of both its small partial equivalent conductance and its partial equivalent volume relative to "sea salt." The smallest error in the relationship occurs when  $\text{NaCl}$  is added, since "sea salt" is mostly  $\text{NaCl}$ .

As an application of  $\bar{\Lambda}_s$  and  $\bar{v}_s$  data to an oceanographic problem, we consider two typical seawaters from the Mid-Pacific Ocean (Lyman, 1959). One is from the surface and the other is from a depth of 2000 meters; both seawaters have a chlorinity of 19.00‰. As a result of chemical and biological processes in the sea, water from 2000 m will contain more  $\text{HCO}_3^-$  (0.144 meq),  $\text{Ca}^{++}$  (0.1758 meq),  $\text{NO}_3^-$  (0.0293 meq),  $\text{H}_2\text{PO}_4^-$  (0.00244 meq), and dissolved silica (9 mgm) per kilogram of seawater than the surface water. The density anomaly in  $\sigma_t$  units,  $(\Delta\rho_{\text{act}} - \Delta\rho_{\text{inf}}) \times 10^3$ , has been calculated for the addition of  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Ca}(\text{NO}_3)_2$  to a seawater of 34.325‰ salinity at temperatures of 0 and 25°C with Equations 17 and 18. The silica has been disregarded since it has a negligible effect on conductivity and since partial molar volume data does not exist. The small amount of  $\text{H}_2\text{PO}_4^-$  has been treated as  $\text{NO}_3^-$ . The density anomaly for the surface sample is zero. For the 2000 m sample it is 0.008  $\sigma_t$  for conductivity measurements and 0.012  $\sigma_t$  for chloride determination at both temperatures.

## SUMMARY AND CONCLUSIONS

The partial equivalent conductances have been measured for NaCl, KCl,  $K_2SO_4$ ,  $Na_2SO_4$ ,  $KHCO_3$ ,  $NaNO_3$ ,  $Ca(NO_3)_2$ , and  $MgSO_4$  at various temperatures and salinities. The data presented as differences between salts of similar anions or cations can be expressed as a power series valid between 0 and 25°C and between 30 and 35.6‰ salinity.

$$\bar{\Lambda}_s (S\text{‰}, t^{\circ}C) = a_{00} + a_{01}t + a_{02}t^2 + (a_{10} + a_{11}t)S$$

The coefficients are evaluated and given in Table III.

Using these data, one can evaluate  $\bar{\Lambda}_{\text{sea salt}}$  by summing the contributions of the individual salts making up "sea salt." A comparison shows that the results obtained are in agreement, within experimental error, with the value of  $\bar{\Lambda}_{\text{sea salt}}$  obtained from specific conductance data.

The results of this investigation, together with published data on partial equivalent volumes, can be used to evaluate changes in the conductivity-density correlation resulting from changes in the relative composition of seawater.

## BIBLIOGRAPHY

- Chemical Rubber Company. 1965. Handbook of Chemistry and Physics. 46th ed. Cleveland. Various paging.
- Connors, D. N. and K. Park. 1967. The partial equivalent conductances of electrolytes in seawater: A revision, Deep-Sea Research. (In press)
- Cox, R. A., F. Culkin, R. Greenhalgh and J. P. Riley. 1962. Chlorinity, conductivity, and density of sea-water. Nature 193: 518-520.
- Duedall, I. W. and P. K. Weyl. 1967. The partial equivalent volumes of salts in seawater. Limnology and Oceanography 12: 52-59.
- Garrels, R. M., M. E. Thompson and R. Siever. 1961. Control of carbonate solubility by carbonate complexes. American Journal of Science 259:24-45.
- Jones, G. and G. M. Bollinger. 1931. The measurement of the conductance of electrolytes. III. The design of cells. Journal of the American Chemical Society 53:411-451.
- Jones, G. and D. M. Bollinger. 1935. The measurement of the conductance of electrolytes. VII. On platinization. Journal of the American Chemical Society 57:280-284.
- Kester, D. R., I. W. Duedall, D. N. Connors and R. M. Pytkowicz. 1967. Preparation of artificial seawater. Limnology and Oceanography 12:176-179.
- Knudsen, M. (ed.) 1901. Hydrographical tables. Copenhagen, G. E. C. Gad. 63 p.
- Lyman, J. 1959. Chemical considerations. In: Physical and chemical properties of sea water. Washington, D. C. p. 87-97. (National Research Council. Publication 600)
- Lyman, J. and R. H. Fleming. 1940. Composition of sea water. Journal of Marine Research 3:134-146.

- Park, K. 1964. Partial equivalent conductance of electrolytes in sea water. *Deep-Sea Research* 11:729-736.
- Pytkowicz, R. M. 1965. Rates of inorganic calcium carbonate nucleation. *Journal of Geology* 73:196-199.
- Sundheim, B. R. 1957. Electrical conductance in molten salt mixtures. *Journal of Physical Chemistry* 61:116-117.
- Thomas, B. D., T. G. Thompson and C. L. Utterback. 1934. The electrical conductivity of sea water. *Journal du Conseil International Pour L'Exploration de la Mer* 9:28-35.
- Thompson, M. E. 1966. Magnesium in sea water: An electrode measurement. *Science* 153:866-867.
- Weyl, P. K. 1961. The carbonate saturometer. *Journal of Geology* 69:32-44.
- \_\_\_\_\_. 1964. On the change in electrical conductance of sea water with temperature. *Limnology and Oceanography* 9:75-78.

## APPENDICES

## APPENDIX I

Sample calculation of the partial equivalent conductance of  $\text{NaNO}_3$  at 33.953‰ salinity and  $14.907^\circ\text{C}$ .

Salt weighed out on a piece of glassine powder paper, temperature and pressure noted and humidity estimated. Weight in vacuum = 0.71098 grams.

Temperature and humidity in the wet box were  $30.2^\circ\text{C}$  and 92% respectively at the time of mixing.

Total volume of seawater in the seawater plus salt solution:

1000 ml	
<u>-2.52 ml</u>	Volume of the magnetic stirring bar.
997.48 ml	
<u>+ .26 ml</u>	Increase in volume due to thermal expansion of the volumetric flask from $20^\circ\text{C}$ to $30.2^\circ\text{C}$ (Chemical Rubber Company, 1965).
997.74 ml	
<u>-0.26 ml</u>	Decrease in volume due to the volume occupied by 0.71098 gms of $\text{NaNO}_3$ in seawater of 33.953‰ at $30.2^\circ\text{C}$ . Calculated from the equations of Duedall and Weyl (1967).
997.48 ml	$\bar{v}_{\text{NaNO}_3} = 24.98 + 0.1645t - 0.00034t^2 + 0.0235S + 0.00086tS.$
$997.48 \text{ ml} \times 1.000027 \text{ cm}^3/\text{ml} = 997.50 \text{ cm}^3 \pm 0.32$	

Total weight of seawater added:

$997.50 \text{ cm}^3 \times 1.02089 \text{ gms}/\text{cm}^3 \times 10^{-3} \text{ kg/gm} = 1.01834 \text{ kg} \pm 0.00032$   
 where  $1.02089 \text{ gms}/\text{cm}^3$  is the density of seawater at 33.953‰ and  $30.2^\circ\text{C}$  (Knudsen, 1901).

Equivalents of salt added per kilogram of seawater:

$$\Delta c = \frac{0.71098}{1.01834 \times 85.01} = 0.0082129 \text{ eq/kg} \pm 0.000003$$

where 85.01 is the equivalent weight of  $\text{NaNO}_3$  (Chemical Rubber Company, 1965).

Determination of  $\Delta K/K$ :

Temperature of the oil bath  $14.907^\circ\text{C}$ .

Cell 1 (standard side of the bridge) filled with seawater.

Cell 3 (unknown side of the bridge) filled with seawater.

$$\text{Ratio} = 0.99647(5) \pm 0.00001$$

Cell 1 filled with seawater.

Cell 3 filled with seawater plus salt solution.

$$\text{Ratio} = 0.98492 \pm 0.00001$$

Cell 1 filled with seawater.

Cell 3 filled with seawater.

$$\text{Ratio} = 0.99648(5) \pm 0.00001$$

$$\frac{\Delta K}{K} = \frac{\text{Ratio (seawater vs. seawater) ave.}}{\text{Ratio (seawater vs. seawater plus salt)}} - 1 = 0.011737 \pm 0.00002$$

$$\bar{\Lambda}_{\text{NaNO}_3} = \frac{1000 v \Delta K}{\Delta c} + \bar{v}_{\text{NaNO}_3} K$$

$$\bar{\Lambda}_{\text{NaNO}_3} = (1394 \pm 3 + 28.6 \pm 0.2) K$$

$$\rho = 1.0252 \text{ gm/cm}^3 \text{ at } 33.953\% \text{ salinity and } 14.907^\circ\text{C}$$

$$\bar{v}_{\text{NaNO}_3} = 28.6 \text{ ml/eq at } 33.953\% \text{ salinity and } 14.907^\circ\text{C}$$

$$K = 0.041651 \text{ (ohm cm)}^{-1} \text{ from Weyl's (1964) equation.}$$

$$\bar{\Lambda}_{\text{NaNO}_3} = 59.25 \text{ cm}^2 / (\text{ohm eq})$$



## APPENDIX II

Listed below are the coefficients for the power series, in  $t^{\circ}\text{C}$  and  $S\%$ , used to normalize the  $\bar{\Lambda}_s$ 's to a common set of salinities and temperatures.

Table VIII. The Partial Equivalent Conductance of the  $i^{\text{th}}$  Salt for the Temperature Range 0 to  $25^{\circ}\text{C}$  and Salinity Range 30 to 35.6 ( $\text{cm}^2/(\text{ohm eq})$ ).

$\bar{\Lambda}_i$	$a_{00}$	$a_{01}t$	$a_{02}t^2 \times 10^3$	$a_{10}S$	$a_{11}tS \times 10^3$	$\epsilon$
$\bar{\Lambda}_{\text{NaCl}}$	51.361	1.7318	6.3684	-0.20014	-13.447	$\pm 0.18$
$\bar{\Lambda}_{\text{KCl}}$	63.116	2.1160	6.5508	-0.10678	-16.083	$\pm 0.14$
$\bar{\Lambda}_{\text{K}_2\text{SO}_4}$	43.722	1.7420	3.6031	-0.10972	-19.241	$\pm 0.20$
$\bar{\Lambda}_{\text{Na}_2\text{SO}_4}$	33.492	1.1871	5.1557	-0.24474	-12.766	$\pm 0.12$
$\bar{\Lambda}_{\text{KHCO}_3}$	44.050	1.4756	2.4997	-0.20468	-11.873	$\pm 0.30$
$\bar{\Lambda}_{\text{Ca}(\text{NO}_3)_2}$	45.319	1.2536	1.9580	-0.28558	-6.9606	$\pm 0.26$
$\bar{\Lambda}_{\text{MgSO}_4}$	27.480	0.8474	1.9000	-0.34397	-8.7366	$\pm 0.09$
$\bar{\Lambda}_{\text{NaNO}_3}$	51.303	1.4849	4.6186	-0.30861	-9.5389	$\pm 0.24$