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No. 200

TITLE

THE TEMPERATURE VARIATION OF THE SOLUBILITY PRODUCT OF CALCIUM CARBONATE IN SEA WATER

AUTHORSHIP

William G. MacIntyre

Establishment

Atlantic Oceanographic Group

Dated August 16, 1965.

PROGRAMMED BY THE CANADIAN COMMITTEE ON OCEANOGRAPHY

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I acknowledge the financial support given by the Institute of Oceanography, Dalhousie University, and thank the Institute staff for their co-operation. Thanks are due to members of the Chemistry Department, Dalhousie University for free discussion and advice. I owe a particular debt to Dr. K. E. Hayes and Dr. D. E. Ryan for help with details of this study.

Mr. Carl Cunningham, a Fisheries Research Board technician, is singled out here as a friend and companion whose assistance with field work has been most welcome.

Finally, I thank my wife, Deanna, who contributed to all phases of this work. She acted as a laboratory technician and stenographer. I hope that this work may reflect a little of her effort.

ABSTRACT

Apparent solubility product determinations of calcium carbonate in sea water of Cl ‰ 19 over the range 0 - 40°C gave solubility product temperature coefficients:

$\Delta K'sp/\Delta T = 0.0063 \times 10^{-6}/°C$ for calcite

and $\Delta K'sp/\Delta T = 0.0078 \times 10^{-6}/°C$ for aragonite.

The solubility products found at 25°C were:

0.54×10^{-6} (calcite) and 0.90×10^{-6} (aragonite)

The temperature coefficients were only half as great as estimated by earlier workers. Previous attempts to evaluate the temperature coefficients have been hampered by a lack of solubility measurements below 15°C.

Analytical methods for calcium and carbonate were described and the errors in carbonate analysis by the pH-alkalinity method were discussed. A spectrophotometric titration for carbonate was tested and found unsatisfactory in sea water.

The significance of pH determinations in sea water has been considered. A pH measurement for sea water has been proposed in which high ionic strength buffers are used to estimate H^+ molarity.

Solubility products obtained in the temperature coefficient study were used to calculate saturation levels of St. Lawrence River and North West Atlantic Ocean water with respect to calcium carbonate.

DEFINITIONS OF SYMBOLS

A	Absorbance
A'	Constant used by Buch and Nynas (1939) in calculation of the pH temperature coefficient $\propto$
$\mathring{A}$	Ångström unit ($\simeq 10^{-8}$ cm.)
$\mathring{a}$	Quantity related to ionic radius in Debye-Huckel theory
A and B	Constants of the Debye-Huckel equation
c	Constant of extended Debye-Huckel equation
a_H	True activity of hydrogen ion
a'_H	Hydrogen ion activity as measured by the usual glass-calomel elec trode technique
Alk	Titration alkalinity; the excess of strong base over strong acid ions in a solution
Cl ‰	Chlorinity, parts chloride per thousand by weight in sea water
CO_3 Alk	The portion of the titration alkalinity contributed by carbonate and bicarbonate ions
E	Electromotive force (Volts)
E_j	Electromotive force at a liquid junction
F	The Faraday (96, 500 int. coulombs/equivalent)
H_2	Molar enthalpy of a pure substance
$\overline{H}_2^o$	Partial molar enthalpy of a substance at infinite dilution
K_1 H_2CO_3	Thermodynamic first dissociation constant of carbonic acid

$K_2\ H_2CO_3$	Thermodynamic second dissociation constant of carbonic acid
$K'_1\ H_2CO_3$	Apparent first dissociation constant of carbonic acid
$K'_2\ H_2CO_3$	Apparent second dissociation constant of carbonic acid
$Ksp\ CaCO_3$	Thermodynamic solubility product of calcium carbonate
$K'sp\ CaCO_3$	Apparent solubility product of calcium carbonate
L_2	Differential heat of solution of a substance in infinitely dilute solution
$\overline{L_2} - L_2$	Differential heat of solution of a substance in concentrated solution
M	Molarity of a solution
N	Normality of a solution
n_i	Number of moles of the ith component of a solution
pCO_2	Partial pressure of CO_2 (atmospheres)
pH	Negative logarithm of a'_H
pK	Negative logarithm of equilibrium constant
R	Gas constant, 8.31274 $\frac{\text{int. joules}}{\text{mole degree}}$
T	Absolute temperature, degrees Kelvin
t_i	Transference number of the ith ion of a solution
z	Ionic change
α	Constant in the temperature correction of pH according to Buch and Nynas

α_o	Henry's law coefficient of solubility of CO_2 in pure water
α_s	Henry's law coefficient of solubility of CO_2 in sea water
γ	Molar activity coefficient
$\gamma^{\pm}$	Molar activity coefficient product for a salt
Δ	Increment
ΔF	Change of free energy in a process
ΔH	Change of enthalpy in a process
$\Delta \bar{V}$	Change of molar volume when a substance dissolves
μ	Ionic strength which equals $1/2 \sum m_i z_i^2$ where m_i is the molarity of the ith ion in a solution
$\sum$	Summation
$\sum CO_2$	Total carbon dioxide concentration in solution

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CHAPTER I

INTRODUCTION

The geochemical and oceanographic significance of the calcium carbonate solubility product in natural waters has been clearly stated in the works of Wattenberg (1933), (1935), (1936). Predictions of degree of saturation of calcium carbonate in sea water, of re-solution and secondary precipitation of calcareous sediments, and of diagenetic transformations in sediments can only be made if the behaviour of the solubility product is known.

The calcium carbonate-sea water system has been reviewed at frequent intervals. Hindman (1942) has given an excellent account of the gradual application of physical chemistry to the system and a clear presentation of available data. Later reviews by Revelle and Fairbridge (1957) and by Cloud (1962) have added detail to the framework provided by Hindman. However, much of the information required to derive quantitative conclusions is still lacking.

Since the system consists of a slightly soluble salt in contact with sea water, the equilibrium is defined through knowledge of the variation of the solubility product with temperature and pressure, with crystal form, and with composition and ionic strength of the sea water. At present the last mentioned factor cannot be treated theoretically because the ionic strength of sea water is so high that ions do not behave as simple charges in a medium of constant dielectric constant. The

quantum mechanical effects of short range interaction can only be treated in a qualitative manner. Until a theory of concentrated ionic solutions is available, sea water must be studied analytically.

For calcium carbonate, the apparent solubility product can be obtained by experiment as:

$$[Ca^{++}] \cdot [CO_3^{=}] = K'sp$$

The thermodynamic solubility product is related to this by

$$[Ca^{++}]\gamma_{Ca^{++}} \times [CO_3^{=}]\gamma_{CO_3^{=}} = a_{Ca^{++}} \times a_{CO_3^{=}} = Ksp$$

The activity coefficients γ require evaluation for calculation of the activity product. There is no method available to evaluate the activity coefficients of these ions in sea water, and slight hope for development of a method unless reversible electrodes for Ca^{++} and $CO_3^{=}$ can be devised.

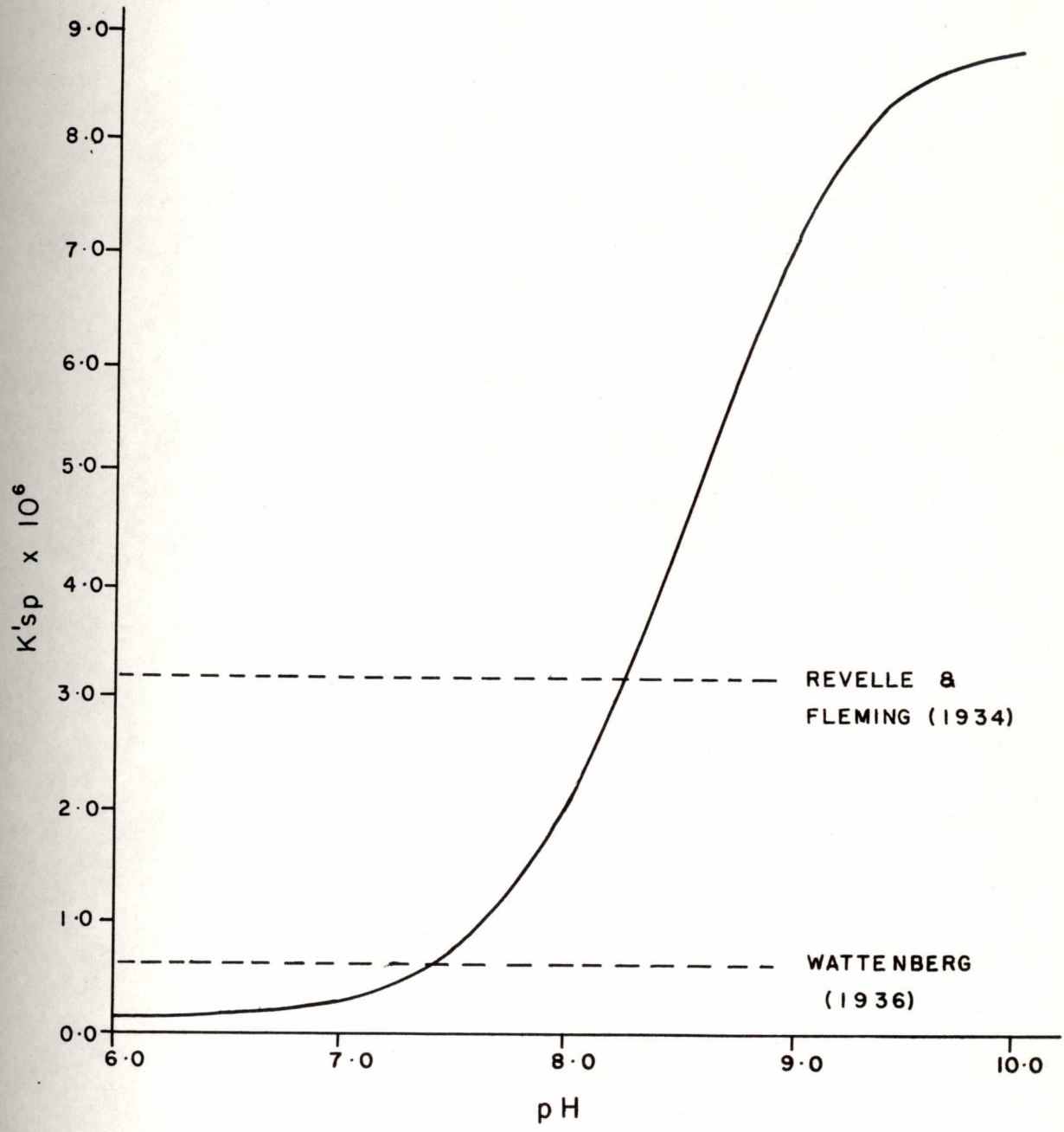
In the following work, apparent solubility products are used as in previous works by Wattenberg and Timmerman (1936), Smith (1941), Hindman (1942), and Kramer (1959). Many results can be obtained from apparent equilibrium constants, and these results serve as a basis for obtaining thermodynamic quantities as solution theory develops. The work of Garrels et al. (1959), on the stability of carbonate complexes in sea water is an attempt to get thermodynamic equilibrium constants from apparent equilibrium constants by approximating with the Debye-Huckel theory that has been surprisingly successful.

Studies of this nature are desirable in sea water if (as in Garrels' work) the limitations of the procedure are clearly understood.

Before going further a distinction should be realized between the ion product and the apparent solubility product in sea water. The ion product is simply the product of analytical concentrations of the ions in a system which is not necessarily at equilibrium, whereas apparent solubility product is the equilibrium ion product. Confusion on this point is apparent from discussions of Fig. 42 of Sverdrup, Johnson and Fleming (1942) by Garrels and Dreyer (1952), Cloud (1959), and Park (1961). The Figure is reproduced here as Fig. 1 and can be derived by the assumption of alkalinity as 2.3×10^{-3} and $[Ca^{++}]$ as 0.01 M, if $[CO_3^{=}]$ is calculated at each pH and multiplied by the $[Ca^{++}]$. The Figure thus shows the variation of the ion product with pH under the restricting conditions, but gives no indication that the solubility product varies with pH. The solubility products are shown as horizontal straight lines invariant with the pH. Experiments described below have shown that the solubility product is not a function of pH over the range 6 - 8.5, thus confirming the horizontal lines shown in Fig. 1.

Apparent solubility product measurements of calcium carbonate have been made over the past three decades, and widely divergent results have been produced by a number of workers. The deviations have resulted from failure to reach equilibrium, and equilibration with impure solid phases. Less serious deviations arise from the

Fig. 1



Reproduction of Fig. 42, Sverdrup et al. (1942)

random scatter of K'sp values caused by errors inherent in the pH-alkalinity method of $CO_3^{=}$ determination.

The deviations can be lessened by use of sufficient equilibration time and a better $CO_3^{=}$ determination. Undetected variation in solid sample composition is probably a secondary source of error. Park (1961) has used equilibration times as long as 200 days, and considered four partially independent measurements of $[CO_3^{=}]$. Another method of $[CO_3^{=}]$ determination is evaluated below.

Many measurements of K'sp for calcite and aragonite have been made near 25°C at 1 atmosphere total pressure but few K'sps have been determined at lower temperatures. A literature survey has shown that no K'sp measurements have been made at temperatures lower than 15°C.

The K'sp variation with pressure has received still less attention However, Pytkowicz (1963), (1964), (1965)a, and Broecker (personal communication) are now carrying out theoretical and experimental studies of this variation.

Study of the calcium carbonate equilibrium in sea water is complicated by the dependence of $[CO_3^{=}]$ on the dissociation constants K'_1 and K'_2 of carbonic acid and on the solubility of carbon dioxide in pure water and sea water. The K' values of Lyman (1956) are used in all work below, since these are most widely accepted at present. Carbon dioxide solubilities are taken from the tables of Buch (1951),

and Harned and Davis (1943), which Lyman has noted require recalculation to include specific salt effects.

Chave et al. (1962) have shown that magnesium impurities in the $CaCO_3$ lattice can cause changes in solubility, such that a high magnesian calcite is more soluble than aragonite. They also note that equilibrium is difficult to achieve because the solid contains more than one cation. For a complete understanding of the system, the solubility product as a function of composition of the solid and aqueous phases is required.

As is obvious from the above, complete resolution of the system is a formidable task. In the following study the composition variables are eliminated by using pure calcite or aragonite and Lyman and Fleming's (1940) synthetic sea water for $CaCO_3$ - water equilibrations. All equilibrations have been carried out at one atmosphere total pressure. The aim of the present work has been to determine the K'sp variation of calcite and aragonite over the temperature range 0-40°C, using various partial pressures of CO_2 in the equilibrations. The results can be applied to surface waters of the ocean, and in a subsequent chapter are related to field surveys carried out by the author.

Pytkowicz (1963) has noted the discrepancies in K'sp $CaCO_3$ values by various workers and states that further measurements are needed to determine the correct values for calcite and aragonite in sea water. The present work has been designed to fill this need and to provide

solubility products at low temperatures for use in calculation of saturation states. Low temperature values used previously by Wattenberg and Timmerman (1936) were extrapolations from higher temperatures. Direct measurement at low temperatures is a check on the extrapolation.

Emphasis is not placed here on solubilities in dilute sea water. Studies of the effect of ionic strength on solubility have been made by Frear and Johnston (1929), Wattenberg (1933), Hindman (1942), Shternina and Frolova (1952), Miller (1952), Levchencko and Bekman (1962), Park (1961), and Akin and Lagerwerff (1965).

In order to draw conclusions with the Debye-Huckel theory, measurements would be required in the region of extremely dilute solutions, and any Debye-Huckel type equation must become empirical at $\mu > 0.1$. Akin and Lagerwerff have found remarkable agreement with a Debye-Huckel equation containing reasonable parameters at $\mu > 0.1$ but this agreement seems somewhat fortuitous in relation to the general behaviour of divalent electrolytes.

K'sp variations with salinity can be accounted for in an approximate manner by the use of available data. Further data collection seems unjustified unless it is carried out carefully as a test for new solution theories.

CHAPTER II

CALCIUM CARBONATE SOLUBILITY PRODUCT VARIATION WITH TEMPERATURE

Buch et al. (1932), in their calculation of the carbonic acid dissociation constants in sea water, showed that the activity coefficients of carbonate and bicarbonate ions varied little with temperature. From this they were able to calculate the variation of the apparent dissociation constants with temperature by using the known variation of the thermodynamic dissociation constants to adjust the series of measurements they had made in sea water. The appreciable differences between Buch and Lyman's constants makes the above procedure seem somewhat questionable.

Wattenberg carried this argument further by assuming that the temperature coefficients of the apparent and thermodynamic solubility products of calcium carbonate are sufficiently similar that the known values for the thermodynamic constant by Backstrom (1921) could be used to derive the K'sp $CaCO_3$ variation with temperature. This was the basis of Wattenberg's (1933) extrapolation.

The thermodynamic solubility product of calcium carbonate varies with temperature according to:

$$\frac{\partial \ln Ksp}{\partial T} = \frac{\bar{H}_2^o - H_2}{RT^2} \qquad (1)$$

where $\bar{H}_2^o$ is the partial molar enthalpy of the dissolved $CaCO_3$ at

infinite dilution and H_2 is the molar enthalpy of the pure crystalline $CaCO_3$.

The quantity $(\bar{H}_2^o - H_2)$ is equal to the differential heat of solution in the infinitely dilute solution and is written:

$$- L_2 = \bar{H}_2^o - H_2 \qquad (2)$$

Thus, if a way could be found to evaluate L_2, a direct means of obtaining the Ksp vs. temperature variation would result.

When other salts are present in the solution the differential heat of solution at the given salt concentration is:

$$\left(\frac{\partial (\Delta H)}{\partial n_2}\right)_{n_1} = \bar{L}_2 - L_2 \qquad (3)$$

$\bar{L}_2 - L_2$ can be obtained from experiment, and if $\bar{L}_2$ is known L_2 can be evaluated. Simple calculations show that

$$L_2 = - RT^2\left(\frac{\partial \ln \gamma_\pm}{\partial T}\right) \qquad (4)$$

Unfortunately in sea water it is not possible to use the Debye-Huckel theory to get $\gamma_\pm$ and thus $\bar{L}_2$. The variation of the apparent solubility product with temperature is from equation (3):

$$\frac{\partial \ln K'sp}{\partial T} = \frac{\bar{L}_2 - L_2}{RT^2} \qquad (5)$$

and substituting from equation (1) and (4):

$$\frac{\partial \ln K'sp}{\partial T} = \frac{\partial \ln Ksp}{\partial T} - \frac{\partial \ln \gamma_\pm}{\partial T} \qquad (6)$$

From equation (5) it is obvious that if $\bar{L}_2 - L_2$ could be evaluated by calorimetry, an independent measure of K'sp as a

function of temperature would result. No investigations on this line have been carried out in the present work. The calorimetric measurements would not be easy as the heat changes are small.

Wattenberg (1933) assumed that:

$$\frac{\partial \ln Ksp}{\partial T} = \frac{\partial \ln K'sp}{\partial T} \qquad (7)$$

in order to carry out his extrapolation. Comparison with equation (6) shows that he neglected the variation of the mean ionic activity coefficients with temperature, although experimental studies by Hindman (1942) have roughly confirmed Wattenberg's assumption. Hindman used an empirical equation of the form:

$$pK'sp = pKsp + \log \gamma_{\pm} \qquad (8)$$

to express the dependence of pK'sp on ionic strength. He found from calcite equilibrations at 15-30°C that $\log \gamma_{\pm(CaCO_3)}$ was approximately temperature independent.

In the present work K'sp measurements are made from 0-40°C. The results are compared with the K'sp determinations of earlier workers. From equation (5), the data gives the differential heat of solution of calcium carbonate in sea water, but as previously noted, this is of limited use at present because activity coefficients are not available.

Wattenberg's assumption from equation (7) can be checked by a comparison of Ksp and K'sp variations with temperature for calcite.

The variation of Ksp $CaCO_3$ with temperature has been treated by Zavodnov (1964), Ghiringelli and Bianucci (1963), and can be calculated from the temperature coefficient of calcite solubility and Ksp at 25°C given by Frear and Johnston (1929).

Comparison can then be made with the K'sp calcite data given below. The low temperature values given by previous workers for sea water cannot be used here because they are obtained by Wattenberg's extrapolation.

Solubility products for both calcite and aragonite have been measured in sea water. From the equilibrium:

$$CaCO_3 \text{ calcite} \rightarrow Ca^{++} + CO_3^{=}$$

$$\Delta F = -RT \ln K'sp \text{ calcite} \qquad (9)$$

$$CaCO_3 \text{ aragonite} \rightarrow Ca^{++} + CO_3^{=}$$

$$\Delta F = -RT \ln K'sp \text{ aragonite} \qquad (10)$$

and subtracting equation (9) from (10) there results:

$$CaCO_3 \text{ aragonite} \rightarrow CaCO_3 \text{ calcite}$$

$$\Delta F = -RT \ln \frac{K'sp \text{ aragonite}}{K'sp \text{ calcite}} \qquad (11)$$

The ratio of the two solubility products thus gives a measure of the molar free energy difference between calcite and aragonite crystals. Thermodynamic properties of the calcite-aragonite transition can be obtained from ΔF and available heat capacity data. However the experimental accuracy of ΔF is not high enough to lend much significance to this procedure.

There are unknown factors in the above consideration of the calcite-aragonite transition because all data gathered by the author has been obtained in a sea water solvent. Energies other than the lattice free energy in the calcium carbonate-sea water system, such as the crystal surface free energy, may be affected by the inert salts to different degrees for the different crystal structures. Account of these energies is not taken in the above, and there is no guarantee of cancellation. A better procedure is to work in dilute solutions with no foreign ions as Backstrom (1921) and Jamieson (1953) have done. The present author feels that errors in estimation of ΔF (aragonite -> calcite) resulting from the use of sea water as a solvent are quite small, and that the sea water result has the advantage of easier analysis because calcium carbonate is more soluble in sea water than distilled water.

From equation (5), it is apparent that since K'sp of both calcite and aragonite have been measured as a function of temperature, the differential heats of solution of calcite and aragonite in sea water can be compared.

CHAPTER III

EQUILIBRATION METHODS AND APPARATUS

Several methods have been used to bring calcium carbonate to equilibrium in water. Frear and Johnston (1929), and Weyl (1959) packed tubes with calcium carbonate and pumped water through this packing. Shternina and Frolova (1952), Wattenberg (1933), Hindman (1942), Park (1961), and most other workers stirred calcium carbonate suspensions. Revelle and Fleming (1934), Miller (1952), and Sharp and Kennedy (1965) allowed calcium carbonate to remain in contact with water without agitation. Miller, and Sharp and Kennedy avoided stirring because it could not be done easily in their high pressure bombs. Since stirring reduces equilibration time, and this has proven to be quite considerable for sea water, lack of stirring in the work of Revelle and Fleming makes their results questionable.

Akin and Lagerwerff (1965) and Shternina and Frolova (1952) have used flow systems in which gas with a known carbon dioxide content was continuously fed into the equilibration chamber. However, most workers have chosen the easier method of feeding a charge of gas of known (or approximately known) composition into the equilibration chamber, sealing it and allowing equilibrium to be reached. The convenience of the latter method exceeds the disadvantage that pCO_2 is then not a fixed variable. In the following work, both flow and closed systems have been used.

All solubility studies below have been carried out on stirred calcium carbonate suspensions. A reaction vessel mounted in a constant temperature bath was used for both flow and closed system measurements. Closed system measurements were also made in sealed flasks containing $CaCO_3$ suspended in a constant temperature bath. The flasks were charged with CO_2, and stirred by mechanical agitation.

(a) Reaction Flask Fixed in Constant Temperature Bath

The general arrangement is shown in Fig. 2. The reaction vessel was kept at the desired temperature by the combined action of refrigeration and heaters. Control over the range 0-40°C was within $\pm$0.02°C using a ballasting technique in which the refrigerator runs continuously and temperature is maintained by a 1500 watt immersion heater regulated with a Haake "Unitherm" thermostat. At temperatures greater than 15°C tap water can be used in the cooling coils.

Stirring in the reaction vessel was by a teflon coated iron bar driven by a magnetic stirrer mounted below the bath assembly. The bath was a 15 gallon aquarium with glass bottom to permit the magnetic stirring.

The reaction vessel was a pyrex bottle 10 inches high, 5 inches in diameter, and had a 71/60 standard taper female joint as the mouth.

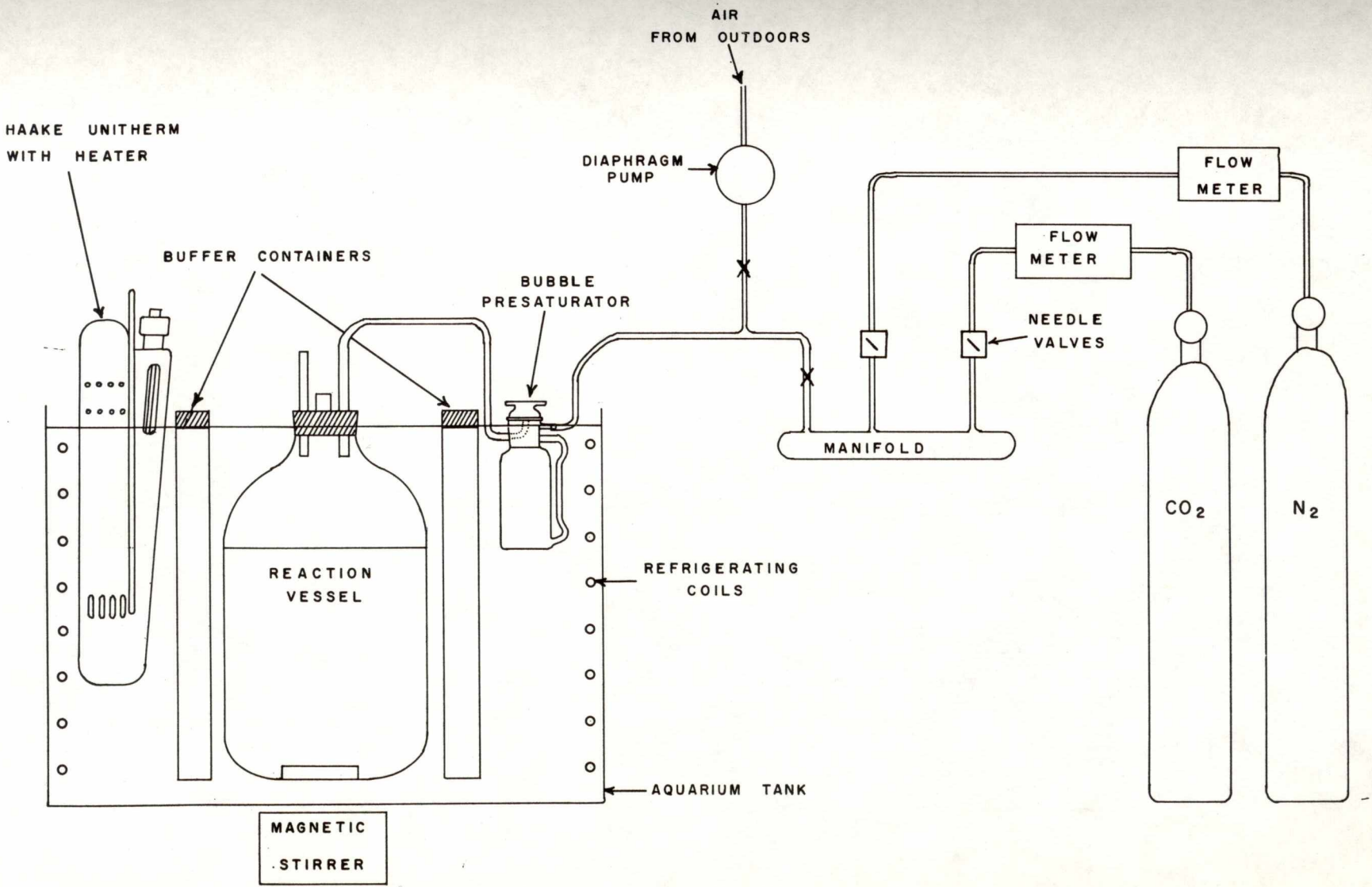


Fig. 2

Reaction Flask Fixed in Constant Temperature Bath

The vessel was closed with a rubber stopper perforated as required for solution analysis and gas admission and exhaust.

Cylindrical buffer containers were mounted in the bath so that pH determination of the solution in the reaction vessel could be standardized at the temperature of equilibration.

Gases of various composition were supplied by the gas feed-in system. A bubbler presaturator containing the solution to be measured was immersed in the bath, so that in experiments with continuous gas flow, there would be little loss of water from the reaction vessel.

Atmospheric air, CO_2-N_2 mixtures, or CO_2 at 1 atmosphere could be fed into the reaction flask. Capillary flow meters permitted regulation of gas flow to produce various CO_2-N_2 mixtures, and were constructed according to the specifications of Benton (1919). The use of this system for preparation of gas mixtures has been treated carefully by Troy (1955).

The reaction vessel was always filled to within 3 inches of the top with the $CaCO_3$-water mixture and contained about 1.5 liters of solution.

(b) Equilibration by Agitation in Sealed Containers

Some equilibrations were done with a paddle wheel arrangement similar to that devised by Wattenberg (1933) and later used by Hindman (1942) and Park (1961). These closed system solubility determinations

provided data that should be comparable to the results of the above workers. Also any difference due to equilibration method could be detected by comparison with results from the flow system method.

Fig. 3 shows the paddle wheel used to agitate bottles of $CaCO_3$-H_2O mixture in a constant temperature bath. This bath had no intrinsic temperature control. Water from the bath described in section (a) of this Chapter was pumped by the "Unitherm" into the paddle wheel bath, and was gravity fed back to the main bath.

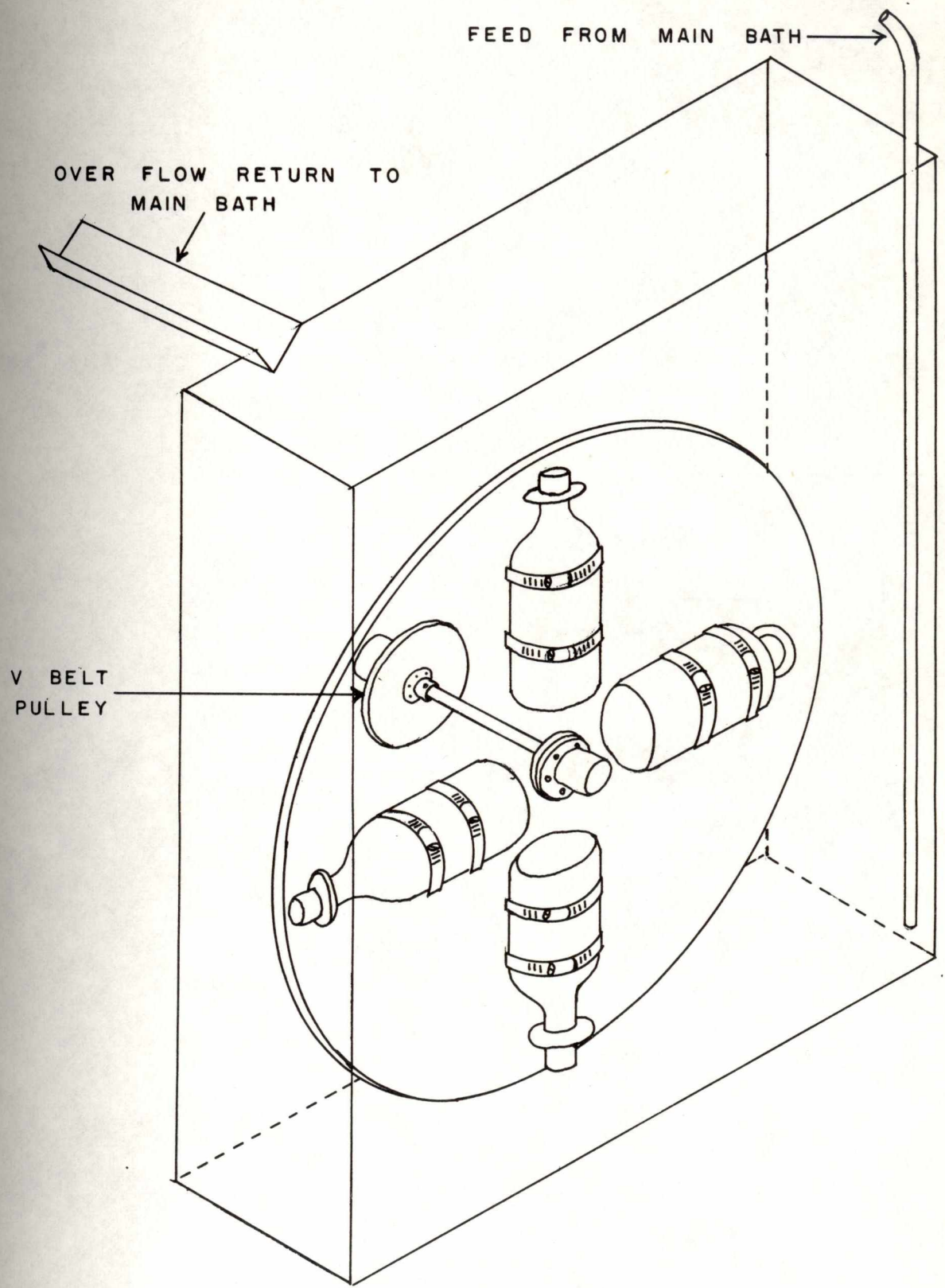
The paddle wheel bath was a brass tank, 16 inches long, 8 inches wide, and 18 inches high. The paddle wheel itself was a 15 inch diameter, 1/4 inch thick plastic disc. The disc was slotted and hose clamps passed through the slots to hold the bottles in place.

Stirring of the solutions in the bottles was effected by rotation of the paddle wheel at 80 rpm. A V-belt drive from a variable speed electric motor above the bath gave good control of rotation speed.

The high pumping rate of the "Unitherm" in the main bath and effective stirring by the paddle wheel kept the temperature of the paddle wheel bath constant to $\pm 0.05^{\circ}C$.

Bottles mounted on the wheel were standard 8 ounce narrow mouth with gas tight polythene caps. Both pyrex and polythene bottles were used in equilibrations to permit detection of a container effect from sources such as borate leaching from pyrex.

Fig. 3



Apparatus for Rotation of Sealed Flasks

(c) Equilibrium from Under and Super Saturation

With both equilibration methods, equilibrium of calcium carbonate with sea water could be approached from either under or super saturation. Calcium carbonate is more soluble at lower temperatures and higher partial pressures of carbon dioxide. Thus, an initial equilibration can be done at a low temperature, the bath temperature then raised and a new equilibrium reached from a supersaturated solution.

Approach from undersaturation is a result of the normal equilibration method, provided that the calcium carbonate ion product of the synthetic sea water is not greater than the final solubility product. A low ion product can be assured by the use of synthetic sea water in which calcium is omitted and replaced by magnesium. A better method is to carry out a preliminary equilibration at a higher temperature followed by re-equilibration of the solution undersaturated in calcium carbonate at the lower temperature.

In the present work temperature control of the saturation state was used, with the exception of a few solubility determinations from undersaturation in calcium free synthetic sea water.

Precipitation from supersaturation by charging a $CaCO_3$-H_2O mixture with CO_2, filtering out the excess $CaCO_3$, and lowering pCO_2 to obtain a calcium carbonate solid phase was not studied. Cloud (1962), Hindman (1942) and (inadvertently) Revelle and Fleming (1934) have

shown that the absence of crystallization nuclei produces inordinately long equilibration times. The recent work of Pytkowicz (1965)b confirms this long time before nucleation, and merits more detailed investigation.

(d) Calcium Carbonate for Solubility Determinations

The calcite used most frequently was Fisher certified reagent grade $CaCO_3$. Microscopic examination showed it to consist of calcite rhombs of 4 micron average size. The effect of particle size on solubility was not studied here. The author feels that this effect might be geochemically significant and might be a cause contributing to the wide range of solubility product values obtained by various workers. A work similar to that of May and Kolthoff (1948) for calcium carbonate would be most welcome. In the present work, the particle size has been kept, as far as possible, above the 2 micron limit at which Backstrom (1921) believes there should be no size effect. The control of size was done by microscopic examination. Simple filtration could not be used, as millipore filters retain many particles smaller than their nominal cutoff limit.

Natural calcite used was obtained from the Ward Scientific Company as 1 cubic inch rhombs of iceland spar (optical grade) from Chihuahua, Mexico. A few rhombs were ground to about 10 micron average size for comparison with the Fisher material.

Natural shell aragonite was provided by the Fisheries Laboratory at St. Andrews, N.B. and was identified as Polynices heros (Say) by D. Peer of the Fisheries Research Board of Canada. The shells were ground in an agate mortar to yield needle-like fragments of 20 micron average length.

Artificial aragonite was prepared with the directions of Kitano, Park, and Hood (1962). This interesting method involves precipitation of $CaCO_3$ from $CaHCO_3$ solution through loss of carbon dioxide. The presence of magnesium favors the formation of pure aragonite at room temperature.

X-ray diffraction studies on these materials were made by Dr. Loring of the Fisheries Research Board of Canada using a Norelco type 12045 diffraction unit with a type 52250 proportional counter. Both natural and artifical aragonite were found to be calcite free, although traces of calcite may have been present.

Grinding aragonite has been considered as a source of error, as some calcite might be produced by the grinding action. However diffraction analysis of Polynices heros aragonite gave no indication of a calcite peak after grinding. The calibration curve for diffraction analysis was prepared similarly to that of Turekian and Armstrong (1960).

CHAPTER IV

ANALYSIS OF EQUILIBRATED SOLUTIONS FOR DISSOLVED CALCIUM CARBONATE

Determination of the apparent solubility product

$$K'sp = [Ca^{++}] \cdot [CO_3^{=}] \qquad (1)$$

requires analysis for both calcium and carbonate ions because the carbonate ion is also involved in the carbonic acid equilibrium system. The sample to be analyzed must be filtered to remove particulate calcium carbonate before aliquots of the filtrate are taken. In the work below, calcium has been obtained by titration with ethylene-diaminetetraacetic acid. The only procedure available for carbonate analysis was the pH-alkalinity method.

(a) pH Determination

Immediately upon opening the equilibration vessel, the pH of the solution was measured by immersing a Radiometer model GK202-C combination glass electrode in the $CaCO_3$ solution. The output from the electrode was read with a Radiometer model pH M4 meter and was standardized with N.B.S. (U.S. National Bureau of Standards) buffers at the sample temperature. Temperature equality of buffer and sample was insured by mounting the buffer containers in the bath near the equilibration vessel. In some cases a separate calomel electrode of the re-formable junction type (Radiometer K-100) was used and the calomel lead of the GK202-C pair disconnected. This check

of calomel electrode performance was necessary because both Hindman (1942) and Lyman (1956) had found that calomel sleeve junction electrodes failed to give reproducible potentials.

In order to avoid any possible suspension effect, solid $CaCO_3$ was allowed to settle for 12 hours before the equilibration vessel was opened and the pH measured. The suspension effect of $CaCO_3$ is discussed in section (b), Chapter VI.

All measurements were made by first standardizing with N. B. S. 0.05M potassium phthalate buffer (pH $\simeq$ 4.00) and then checking the standardization with 0.025 M KH_2 phosphate - 0.025 M Na_2H phosphate and 0.01 M borax. Bates'(1964) pH values of N. B. S. buffers as a function of temperature were used in this check. Values obtained by the standardization check agreed within $\pm$ 0.005 pH units with those given by Bates. All buffer solutions were prepared in the laboratory following Bates' directions.

The electrodes were immersed in the $CaCO_3$ solution and the pH read, then returned to the low pH buffer as a check, again immersed in the $CaCO_3$ solution, and finally returned to the high pH buffer as a check.

The GK202-C glass electrode was found to have the same response as a hydrogen electrode over the pH range 4 - 9 within the required limits.

pH measurement by the direct immersion method, rather than after removal to a separate vessel as in Hindman's (1942) work, was

preferable because it minimized CO_2 exchange. Wattenberg (1933) was also forced to remove portions of solution to a quinhydrone electrode chamber, as glass electrodes were not available at that time. The necessity to remove the sample for pH determination and the lack of glass electrodes that had sufficiently low resistance prevented earlier workers from making accurate low temperature pH measurements. The ease with which measurements can now be made over the range 0-40°C is a tribute to the ingenuity of pH equipment manufacturers.

At low temperatures glass electrodes become sluggish because the electrode resistance increases with decreasing temperature and the species involved in the electrode equilibria are less mobile at low temperatures. With the GK202-C combination electrode an equilibration time of 5 minutes before measurement was required at 0°C, compared with only 30 seconds at 30°C. The combination electrode was fitted with a rubber cork to prevent leakage of gas from the CaCO3 equilibration vessel during pH measurements.

(b) Filtration of Samples for Analysis

After pH of the $CaCO_3$ solution had been measured, particulate $CaCO_3$ was removed by filtering the water in the equilibration vessel. A minimal exchange of CO_2 was desirable, but quite large exchanges could be tolerated if the filtration was done rapidly to prevent calcium carbonate from precipitating. If $CaCO_3$ does not

precipitate, the calcium concentration of the sample remains constant, and the alkalinity, defined as:

$$[\Sigma \text{cations}] - [\Sigma \text{anions}] = [OH^-] - [H^+] + [HCO_3^-] + 2[CO_3^{=}] \quad (2)$$

is then independent of pCO_2. A change in pCO_2 alters the relative concentrations on the right side of equation (2) but not the total.

Various methods of filtration were used, with varying precautions against CO_2 exchange. No loss of $CaCO_3$ through precipitation was detected in the filtration methods given below. Control analyses in which portions of the same equilibrium mixture were filtered by the following methods gave no differences in calcium concentration or alkalinity outside the experimental error.

Filtration under an atmosphere identical to that used in equilibration was done as shown in Fig. 4a.

The solution was siphoned from the reaction vessel, and gravity filtered under a head of 50 cm. of water through an HA Millipore filter. Aliquots from the collection flask were pipetted for analysis. This scheme was used only at room temperature (25°C) to avoid pCO_2 differences arising from temperature difference between reaction vessel and filtration apparatus.

Low temperature filtrations were carried out by siphoning the solution into the gravity filtration apparatus as above, sealing the reservoir and collection flask and placing the filtration apparatus in a refrigerator set at the equilibration temperature.

All these precautions were found unnecessary, as the same results were obtained if the solution from the reaction vessel was millipore filtered at room temperature in the conventional manner.

The method finally adopted was to pipette the solutions directly from the reaction vessel using a filter stick of fine sintered glass (Corning, type F) to remove solid particles as shown in Fig. 4b.

(c) Carbonate Analysis

From the dissociation constants of carbonic acid in sea water, and the pH and alkalinity of the water in equilibrium with calcium carbonate, the carbonate ion concentration can be calculated. The method for calculating concentrations of carbon dioxide species in sea water has been treated thoroughly by Harvey (1957).

The carbonate concentration follows from the definitions of carbonate alkalinity and K'_2 H_2CO_3.

$$CO_3Alk = [HCO_3^-] + 2[CO_3^{=}] \qquad (3)$$

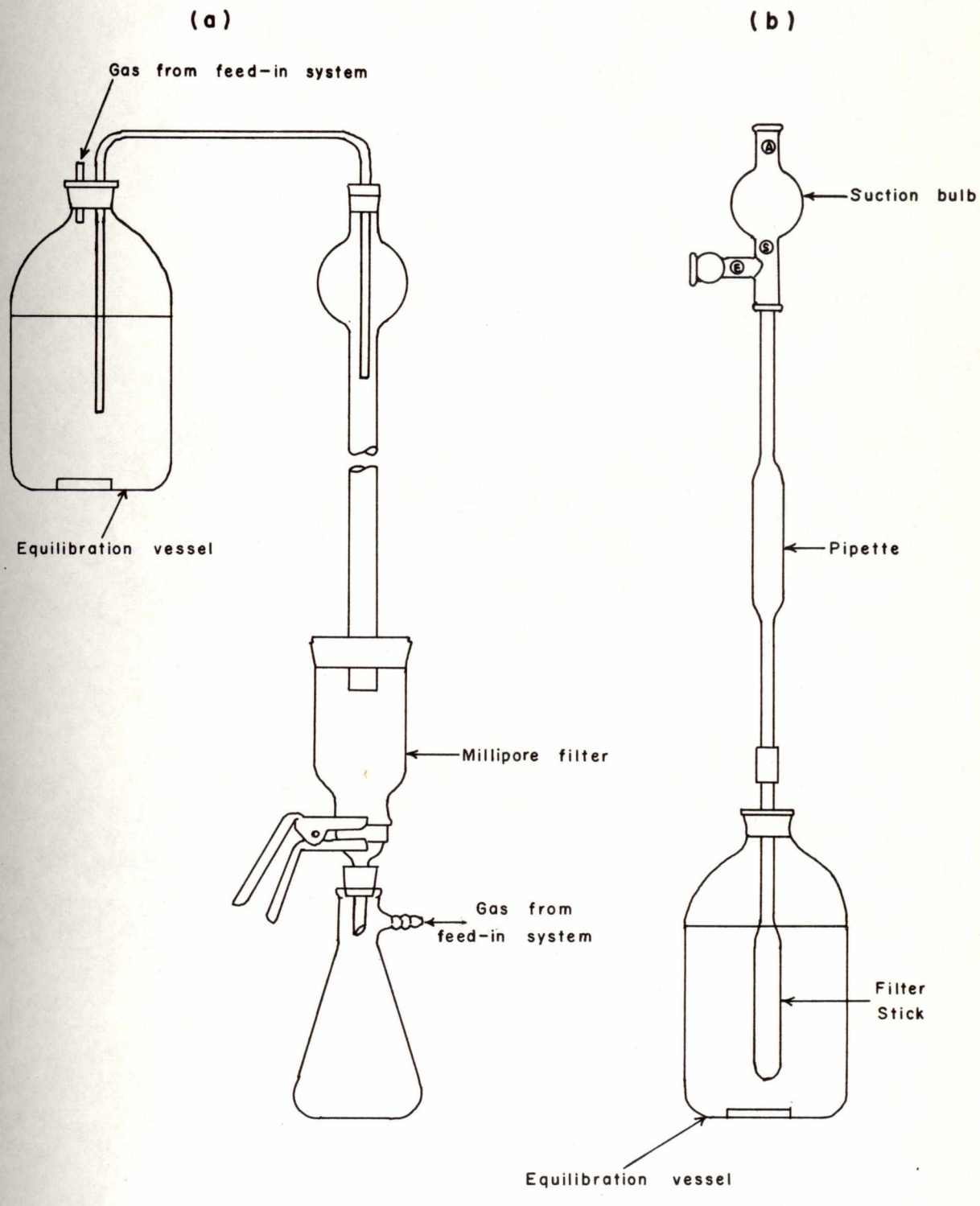
$$K'_2 = \frac{a'_H [CO_3^{=}]}{[HCO_3^-]} \qquad (4)$$

By substituting equation (4) in (3):

$$[CO_3^{=}] = \frac{CO_3\ Alk \times K'_2}{(a'_H + 2K'_2)} \qquad (5)$$

The significance of alkalinity and its determination has been discussed by Lyman (1956). The object of an alkalinity measurement is to obtain an estimate of $[HCO_3^-] + 2[CO_3^{=}]$, the portion of the alkalinity contributed by carbonate species and referred to as

Fig. 4



Filtration Apparatus for Equilibrated Solutions

carbonate alkalinity (CO_3Alk). Compensation for other weak acids (as boric acid) in sea water is made according to tables resulting from Buch's (1933) determination of the first dissociation constant of boric acid in sea water.

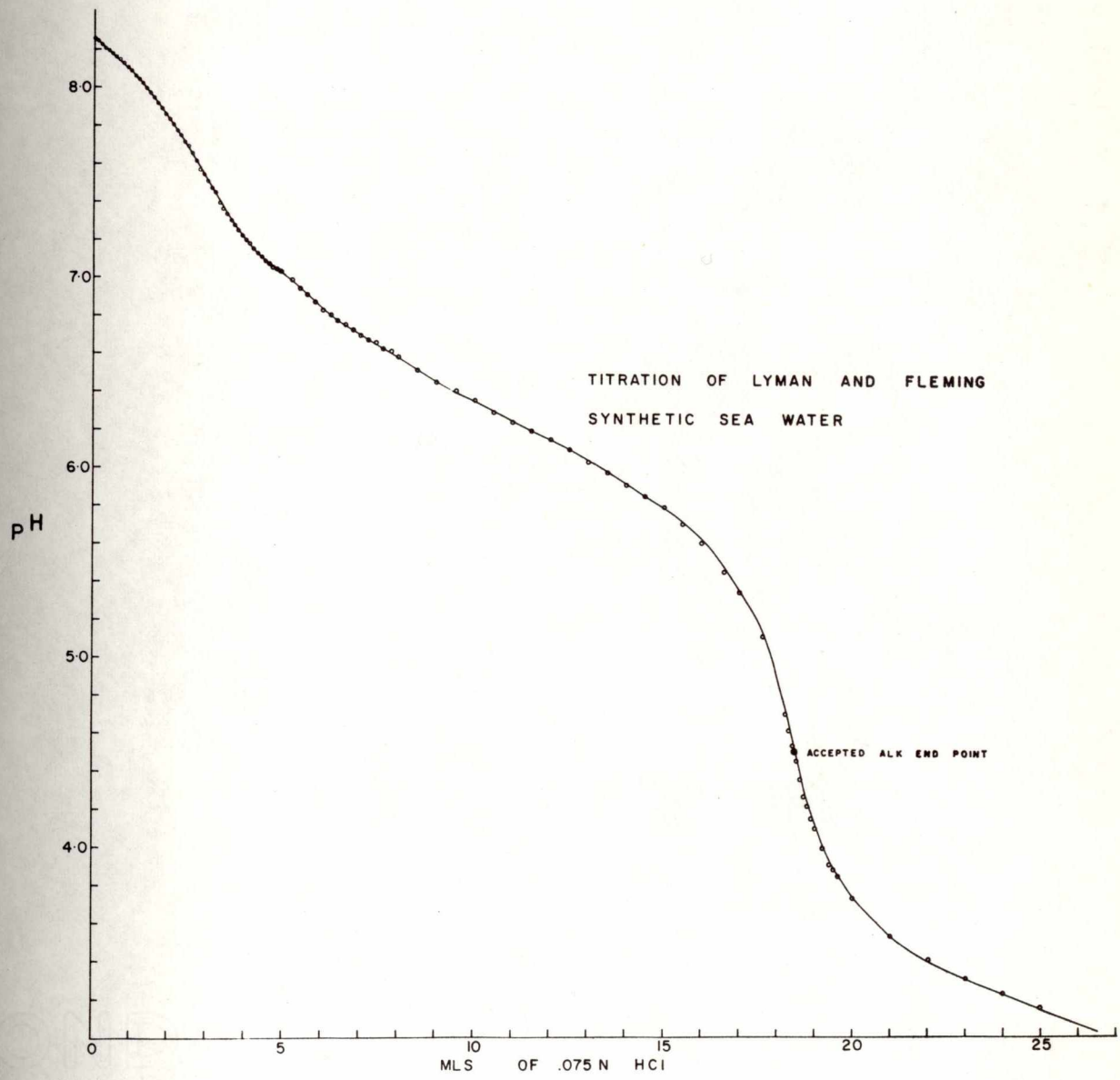
Alkalinity is usually determined by a potentiometric titration of the water sample to a pH of about 4.5 with HCl. Fig. 5 shows the sharp break in the titration curve at the alkalinity end point. It is possible, by a procedure given in Chapter VII, to calculate the exact pH of the alkalinity end point, and then to do a direct titration. However, this is a tedious undertaking. Anderson and Robinson (1946) have devised a technique in which HCl is added to overshoot the end point giving a final pH between 3 and 4. The titrant volume is then corrected to the end point from a knowledge of the dissociation constants of carbonic acid and the activity coefficient of the hydrogen ion. Lyman (1956) was able to obtain estimates of hydrogen ion activity coefficients at pH $<$ 4 from buffer capacity studies, and in comparing his coefficients with those of Anderson and Robinson (1946), he gave an excellent account of the theory underlying their method. The alkalinity is back corrected to the end point by the second term of:

$$\text{Alk} \times 10^{-3} = \frac{1000}{V} \left(N \times v + (v + V) \cdot \frac{a'_H}{f_H} \right) \qquad (6)$$

where

N is the normality of acid (equivs/liter)

Fig. 5



Alkalinity Titration Curve

v is the volume of acid used in titration (ml)

V is the volume of water sample (ml)

a'_H is calculated from final pH of titration

f_H is approximate H^+ activity coefficient from Anderson and Robinson's tables

Park et al. (1963) have recently developed a conductometric alkalinity titration, but the method is quite cumbersome because separate samples must be used to establish each successive point on the titration curve.

The choice of dissociation constant values of H_2CO_3 in sea water is a major problem. Somewhat arbitrarily, Lyman's (1956) values for K'_1 and K'_2 H_2CO_3 were used throughout this work. Buch's (1951) values were also carefully determined, but he worked only at one temperature (20°C) and extrapolated to all other temperatures under the assumption that the thermodynamic K values should vary with temperature in a manner similar to that for the apparent K' values. He then assembled the available data on K_1 and K_2 at various temperatures and computed the K'_1 and K'_2 variation with temperature. The assumption above may not be justifiable. Also, as Lyman notes, Buch's K' values resulted from use of several analytically unrelated methods, i.e. pCO_2, pH, ΣCO_2, and alkalinity determination.

Lyman's values have the advantage that the dissociation constants were calculated directly from titration curves, and depend only on pH determination and volumetric technique. No assumption was made as to the similarity of variation of K and K' with temperature. Titrations were carried out at 7.5°C, 20°C, and 32.5°C, with sea waters of different chlorinities. Unfortunately, few titrations were carried out at 7.5°C and 32.5°C.

For example, in Lyman's K'_2 determinations, titrations were made at:

7.5°C for Cl‰ - 18.03, 36.66, and 52.71

20.0°C for Cl‰ - 1.03, 4.00, 9.73, 18.03, 18.33
26.50, 34.18, 53.06

32.5°C for Cl‰ - 18.11, 37.48, 47.84

There accordingly was extensive interpolation and extrapolation to obtain the K'_2 tables from 0-35°C at 5°C intervals and Cl‰ 1.0, 4.0, 9.0, 16.0, 17.0, 18.0, 19.0, 20.0, 21.1, 25.0, 36.0, 49.0, and 64.0.

Lyman's values were chosen because no better values were available, and the work done appeared sound. Redetermination of the dissociation constants of carbonic acid in sea water is necessary, by the most accurate methods possible. Keeling (personal communication) is now beginning this difficult but important task.

(d) Calcium Analysis

The calcium concentration of sea water has often been determined in the effort to detect small deviations in the calcium to chlorinity ratio. Gripenberg (1937) used the calcium oxalate precipitation technique, a slow method with inherent errors due to coprecipitation of other alkaline earths. Gripenberg considered her results to be accurate to 0.7%. Chow and Thompson (1955) determined calcium in sea water by flame photometry. Corrections for interference of salts in sea water are necessary and the system must be recalibrated at each chlorinity. The accuracy of the method is 0.1 mg. atoms/liter at $[Ca^{++}]$ = 10mg. atoms/liter.

Complexing agents developed in the last decade have greatly simplified the determination of calcium in sea water, and careful technique has given very precise results.

Ethylenediaminetetraacetic acid (EDTA) forms a 1:1 complex with calcium ion that is extremely stable. If proper conditions are maintained the calcium content of sea water can be measured without interference from Mg^{++} and the other cations. This is referred to here as the direct calcium titration of sea water. It is based on the sea water calcium method of Pate and Robinson (1958).

Another method, referred to in the following as calcium titration after ion exchange separation, has been developed by

Carpenter (1957) and Tsubota and Kitano (1960). The sea water sample is run over a Dowex 50-x-8 ion exchange column and magnesium, calcium, and strontium are removed by buffer or complexing eluting agents. The separations have been shown to be quantitative The calcium containing effluent from the column is freed of elutant by decomposing it on heating. Water is then added and the resultant calcium solution titrated with EDTA. In this method there are no interfering ions. The method is also the most accurate available for determining calcium in sea water. Carpenter, using photometric end point detection, claims a precision of 0.1%.

In the present work however, Tsubota and Kitano's method has been used exclusively. This selection was made because the eluting agent used by Carpenter, the complexing agent ammonium acetylacetonate, is extremely unstable and must be prepared within 15 minutes of use. Carpenter's photometric methods were not needed as the precision available with visual titration was sufficient for purposes of this work.

Tsubota and Kitano used an ammonium formate-formic acid buffer solution as the eluting agent. The formate buffer is stable indefinitely, easily decomposed on heating, and as Park (1961) has shown, gives sharp separation of the alkaline earths in sea water. Park checked the strontium separation by adding Sr^{90} to the sea water and counting portions of the effluent solution.

Many indicators have been used to detect the end point of the calcium-EDTA titration. They are all complexing agents that form weaker complexes with calcium than does EDTA. When EDTA equivalent to the calcium content has been added, the indicator cannot compete with EDTA for the calcium ions, and thus goes to free indicator in solution. A suitable indicator for the titration must have the appropriate strength as a complexing agent, and the complexed and uncomplexed forms must be quite different in color so the end point may be easily detected.

Calcein has often been used, but was rejected here, because u.v. light was required to observe a sharp color change. Ammonium purpurate gave a better color change but this was not sharp.

A commercial indicator "Calver II" (Hach Chemical Co., Ames, Iowa) gave a sharp color change from red to blue at the end point of calcium - EDTA titrations for both the direct and ion exchange separation methods of sea water analysis, and was used exclusively in the work below. Requests that the manufacturer divulge the composition of Calver II were refused.

1) The direct calcium titration of sea water - Twenty five mls of the sea water to be analyzed was pipetted into a 125 ml erlenmeyer flask containing a teflon coated magnetic stirrer bar. Sodium hydroxide (1.0 N) was added from a dropper to bring the water to pH 12.15. Trials at various pH's have shown that for pH less

than 12, the Calver II indicator remains red at the calcium end point, and for pH greater than 12. 3 the color change of the indicator becomes less distinct. Magnesium hydroxide is precipitated from sea water at this high pH and is present as a suspension in the flask.

One tenth of a gram of Calver II indicator powder was then added, and the solution titrated with 0. 0150M EDTA (disodium salt). The end point was taken when no trace of pink from the calcium form of the indicator remained.

The EDTA was standardized with a calcium solution prepared by dissolving an accurately weighed amount of $CaCO_3$ (calcite) crystal in 0. 01N HCl and diluting to one liter.

Strontium is titrated along with calcium in this method. The calcium content of a sea water sample is obtained by subtracting the equivalents of strontium in the sample (assuming the Sr/Cl‰ ratio = 0. 00041 mg/Kg as given by Hummel and Smales (1956)) from the total calcium plus strontium obtained by titration. Lyman and Fleming (1940) synthetic sea water used in this work has been corrected in strontium concentration to the value obtained by Smales by altering the amount of $SrCl_2$ added. The strontium correction was then applicable for synthetic as well as natural sea water.

The end point is somewhat sharper, according to Pate and Robinson (1958), if most of the calcium is titrated with EDTA before sodium hydroxide is added. Calcium is complexed, and the

amount coprecipitated with magnesium hydroxide thereby reduced. No difference in the final end point resulted from addition of NaOH at various stages in titration, but stirring time for stabilization of the indicator color was greatly reduced when NaOH was not added until late in the titration. Perhaps this time reduction depends on the rate at which calcium is removed from the magnesium hydroxide by EDTA.

Addition of KCN to the sodium hydroxide solution, as suggested by Pate and Robinson, had no effect on the titration. Thus no trace metals were present in sufficient concentrations to block the indicator function.

The direct titration method was used by MacIntyre and Platford (1964) in calcium analysis of open ocean water. Precision of better than ±1% could not be attained. The analysis for calcium in calcium carbonate solubility studies and in sea water samples described in Chapter VII were done with ion exchange separation, as a precision of ±0.5% was sought.

2) Calcium titration after ion exchange separation - Park's (1961) adaptation of Tsubota and Kitano's (1960) alkaline earth separation was used, and the scheme given below is directly according to Park. However, Park's analysis of the calcium effluent with EDTA containing magnesium ions and Eriochrome black T indicator gave calcium

concentrations that were about 3% lower than the expected values for synthetic sea water with accurately known calcium content.

Park also observed this discrepancy in runs on sea water samples, in which he found low calcium to chlorinity ratios. The proposed explanation was that $CaCO_3$ had precipitated from the water during storage.

The present author felt that the discrepancy originated in the method of titration. Accordingly, Calver II indicator was used in the EDTA titration of effluent for calcium. Calcium concentration was then found to be within 1/2% of the known value. The analytical procedure and some trial analyses are now given.

Ion exchange separation was carried out on an exchange column similar to that used by Park. The resin-filled column was a standard Fischer and Porter (Westminster, Pa.) model. Eluting agents were stored in a 125 ml separatory funnel and fed through a polyethylene capillary tube to the column. The flow was regulated to 0.4 ml/min.

The DOWEX 50-x-8 resin (100-200 mesh) was converted to the hydrogen form by running 100 mls of 4N HCl followed by 100 mls of 1.5N HCl through the column. Distilled water (50 mls) was run through to wash out excess HCl.

Five mls of sea water sample was run over the column, which was again washed with 25 mls distilled water. Magnesium was

eluted with 90 mls of 1M formic acid - 1M ammonium formate buffer (in the ratio required to give pH 4.00. A further 5 ml of buffer was run through and tested by addition of EDTA with Eriochrome black T (EBT) indicator to prove the absence of calcium and magnesium. The pH of this test was controlled by adding an excess of NH_4OH-NH_4Cl buffer prepared by adding 67.5 gms NH_4Cl to 570 mls 15N NH_4OH and diluting to one liter. The condition for a satisfactory calcium titration was that there be no color change of the EBT indicator. Sensitivity trials showed the test responsive for $[Mg^{++}] + [Ca^{++}]$ equivalent to 0.01 mls sea water.

Ninety mls of 1M formic acid - 1M ammonium formate buffer of pH 4.10 was then run through the column to elute the calcium. This volume was found sufficient to remove calcium as indicated by testing as above on a following 5 ml portion of effluent.

The receiving beaker containing the calcium effluent was placed under an infrared lamp and heated until vapours of formate were no longer visible. Dilute HCl was added, completely dissolving the calcium containing residue.

Sodium hydroxide (1.0N) was used to bring the calcium solution to pH 12.15 with the standard potentiometric pH technique. One tenth gram of Calver II powder was added and the calcium titrated with 0.0150M EDTA.

Analysis of standard calcium solutions and of Lyman and Fleming (1940) synthetic sea water were done to test the precision of the method. The results for synthetic sea water are given in Table 1. Magnesium contents were also determined by the standard EBT method.

Table 1

Replicate EDTA Titration of Lyman and Fleming Sea Water

Sample	mls EDTA Calcium effluent	mls EDTA Magnesium effluent
1	3.38	17.91
2	3.40	17.90
3	3.40	17.95
4	3.42	17.91
Average	3.40±.02 mls	17.91±.03 mls

Since Lyman and Fleming synthetic sea water is 0.01024M in calcium and 0.05357M in magnesium, 3.41 mls EDTA should be required in the titration of calcium and 17.86 mls EDTA in the titration of magnesium. It is doubtful if the above agreement could be improved without recourse to the more involved procedures of Carpenter (1957).

Test runs with 10 mls of synthetic sea water failed to give agreement, presumably because the column was overloaded.

A sample elution curve for the titration of calcium after ion exchange separation is given in Fig. 6. Titrations were done on successive 10 ml portions of effluent from the column loaded with 5 mls of Lyman and Fleming sea water.

(e) The Relation Between Calcium Concentration and Alkalinity

Since calcium carbonate and carbon dioxide approach equilibrium in sea water, some relation between calcium content and alkalinity is to be expected. Wattenberg (1933) has derived a relation by considering that the calcium of sea water has had two origins: the dissolving of calcium carbonate in sea water; and the addition of calcium to sea water from weathering of primordial rock. Dissolved calcium carbonate is assumed to give a calcium carbonate-bicarbonate solution, while primary calcium is paired with the other anions of sea water. According to Wattenberg,

$$\left[Ca^{++}\right] = \left[Ca^{++}\right] \text{ from } CaCO_3 + \left[Ca^{++}\right]' \text{ from primary weathering.} \qquad (7)$$

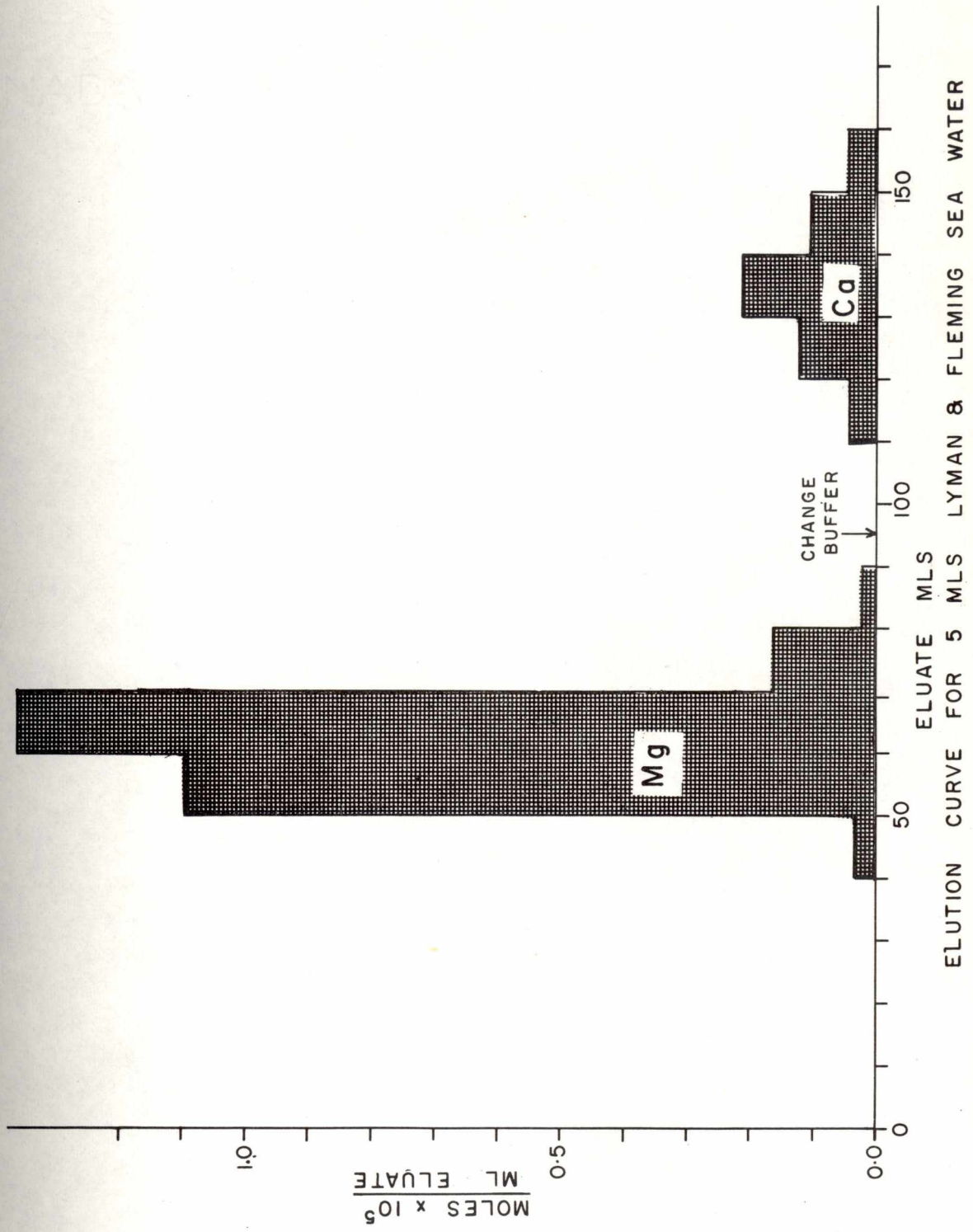
This, as Hindman (1942) points out, amounts to a consideration that if $CaCO_3$ were dissolved in a water initially containing no calcium

$$\left[Ca^{++}\right] = \frac{CO_3 \text{ Alk}}{2} \qquad (8)$$

If there was additional $\left[Ca^{++}\right]'$ from the calcium content of water before equilibration then

$$\left[Ca^{++}\right] = \frac{CO_3 \text{ Alk}}{2} + \left[Ca^{++}\right]' \qquad (9)$$

Fig. 6



Ion Exchange Separation of Calcium and Magnesium

Wattenberg's relation was calculated using the $[Ca^{++}]$ /Cl‰ and CO_3 Alk/Cl‰ ratios of sea water. Substitution of:

$$\frac{[Ca^{++}]}{Cl‰} = 0.5389 \times 10^{-3} \frac{\text{moles}}{\text{liter}} \times \frac{\text{kg}}{\text{gm}}$$

and

$$\frac{CO_3Alk}{Cl‰} = 0.615 \times 10^{-4} \frac{\text{moles}}{\text{liter}} \times \frac{\text{kg}}{\text{gm}}$$

in equation (9) gives:

$$[Ca^{++}] = \frac{CO_3Alk}{2} + 0.477\ Cl‰ \frac{\text{millimoles}}{\text{liter}} \qquad (10)$$

Equation (10) is the well-known Wattenberg relation. It is far more useful than the $[Ca^{++}]$ /Cl‰ ratio because it applies to any solution in which calcium carbonate is dissolved, regardless of original calcium content, while the ratio refers only to the conditions of natural sea water.

The Wattenberg relation is therefore applicable to studies of $CaCO_3$ solubility in synthetic sea waters, as well as to oceanic calcium concentrations. At several places in the following work, the calcium concentration has been determined by both calculation from the Wattenberg relation and direct EDTA titration. The agreement was always good.

CHAPTER V

EARLIER STUDIES OF THE SOLUBILITY PRODUCT OF CALCIUM CARBONATE IN SEA WATER

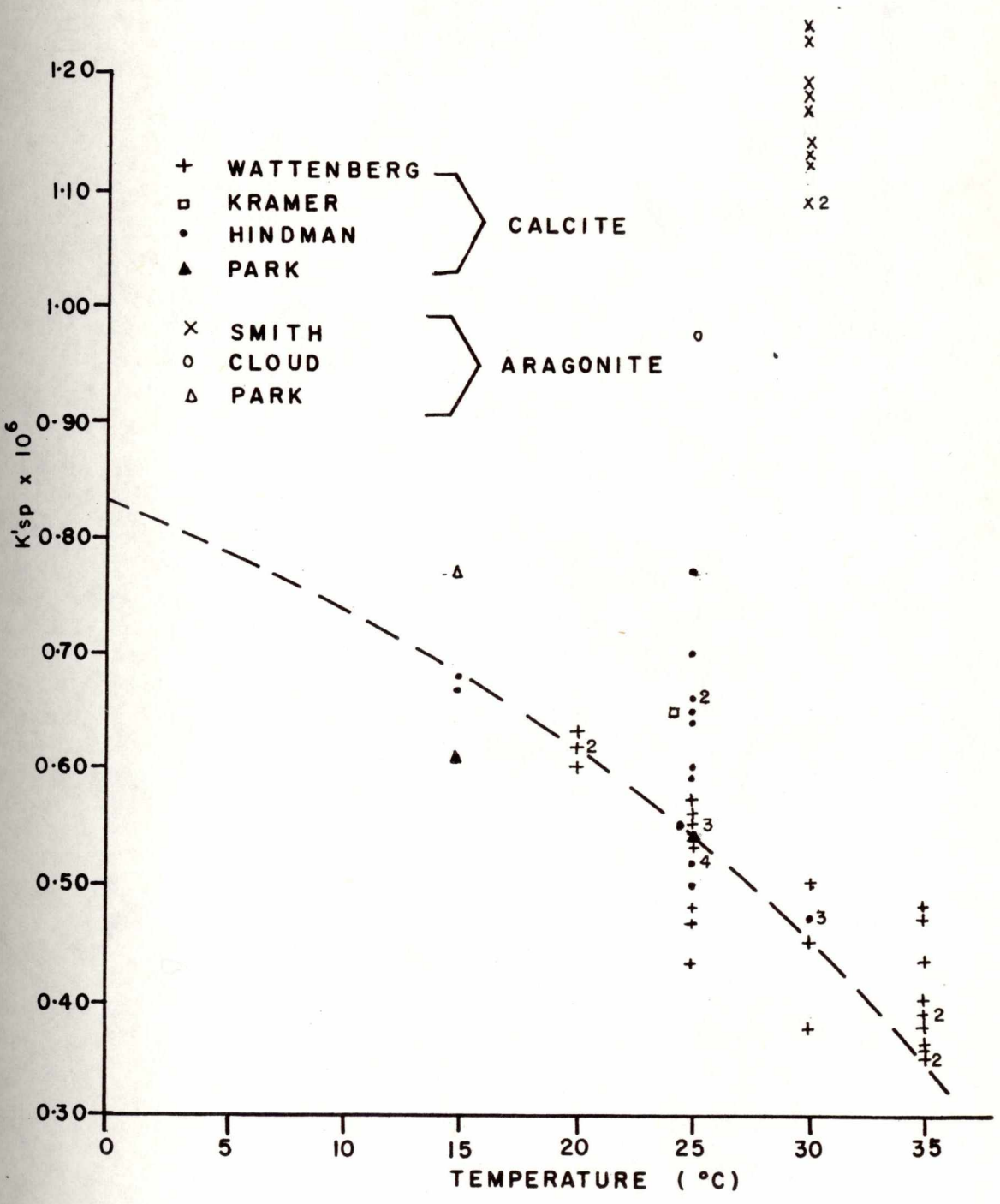
In order to interpret results of the present work, calcium carbonate solubility product data by earlier investigators has been assembled. Conditions under which the data was obtained, equilibration procedures, analytical methods and calculation techniques are given below. The author knows of no other determinations of calcium carbonate solubility product in sea water.

Tabulation of K'sp $CaCO_3$ in sea water of Cl‰ 19 was not possible because statements of the wide variety of techniques could not be compressed into a suitable table. Accordingly, the experimental details of each work have been listed in chronological order of publication. Following this, the corresponding K'sp $CaCO_3$ values have been listed. These K'sp values are shown as a function of temperature in Fig. 7. It is apparent from the figure that the temperature coefficient of K'sp $CaCO_3$ in sea water cannot be estimated with any certainty from available information.

Discussion of these results has been included in the discussion of the present results to permit critical comparison.

The K'sp information of Revelle and Fleming (1934), Wattenberg and Timmerman (1936), Smith (1941), Hindman (1942), Kramer (1959), Park (1961), and Cloud (1962) follows.

Fig. 7



Earlier K'sp $CaCO_3$ Values at Cl‰ 19

Revelle and Fleming

Method of Equilibration - filtered samples of Pacific Ocean sea water made basic by bubbling in dry CO_2 free air; $CaCO_3$ precipitated from homogeneous solution without stirring

pH Determination - colorimetric, Sorensen scale

Carbonic Acid Dissociation Constants - values of Moberg et al. (1934)

Calcium Analysis - calcium oxalate precipitation

Total Carbon Dioxide - gasometric, Greenberg (1932)

Alkalinity Titration - with indicator

Equilibration Time - 30 days

Crystal Modification of $CaCO_3$ - aragonite

Wattenberg

Method of Equilibration- sea water and $CaCO_3$ shaken in sealed flask

pH Determination - quinhydrone electrode, Sorensen buffer system

Carbonic Acid Dissociation Constants - Buch's (1932 and 1933) values

Calcium Analysis - calculated from Wattenberg relation

Alkalinity Titration - with indicator as in Wattenberg (1933)

Equilibration Time - 50 hours

Crystal Modification of $CaCO_3$ - calcite

Smith

Method of Equilibration - Bahama Bank sea water and $CaCO_3$ shaken in sealed bottles

pH Determination - colorimetric, Sorensen scale

Carbonic Acid Dissociation Constants - Buch's (1932 and 1933) values

Calcium Analysis - calcium oxalate precipitation

Alkalinity Titration - with indicator

Equilibration Time - 11 to 38 days

Crystal Modification of $CaCO_3$ - aragonite

Hindman

Method of Equilibration - sea water and $CaCO_3$ shaken in sealed flasks

pH Determination - glass electrode, N. B. S. buffers

Carbonic Acid Dissociation Constants - Buch's (1938), corrected from Sorensen pH scale

Calcium Analysis - calculated from Wattenberg relation

Alkalinity Titration - potentiometric end point detection

Equilibration Time - 80 to 160 hours

Crystal Modification of $CaCO_3$ - calcite

Kramer

Method of Equilibration - not given

Crystal Modification of $CaCO_3$ - calcite

Park (a)

Method of Equilibration - sea water and calcium carbonate shaken in sealed flasks

pH Determination - glass electrode, N. B. S. buffers

Carbonic Acid Dissociation Constants - Lyman's (1956) values

Calcium Analysis - EDTA titration of Tsubota and Kitano (1960)

Alkalinity Titration - potentiometric end point detection

Equilibration Time - 240 days

Crystal Modification of $CaCO_3$ - calcite

Park (b)

Method of Equilibration - water previously saturated with calcite placed in contact with aragonite in Weyl's (1961) carbonate saturometer. Difference of K'sp aragonite-calcite calculated from pH of saturometer. K'sp calcite data from (a) used in calculation

Equilibration Time - 30 minutes

Crystal Modification of $CaCO_3$ - aragonite

Cloud

Method of Equilibration - analyzed Bahama Bank water near Andros Island, and took $[Ca^{++}] \cdot [CO_3^{=}]$ as K'sp; ion product evaluated from field data.

pH Determination - glass electrode, N. B. S. buffers

Carbonic Acid Dissociation Constants - Buch's (1938) values, corrected from Sorensen pH scale

Calcium Analysis - by Carpenter's (1957) EDTA titration and by calcium oxalate precipitation

Alkalinity Titration - potentiometric end point detection

Crystal Modification of $CaCO_3$ - aragonite

Revelle and Fleming Cl‰ 20*

K'sp $CaCO_3$ (aragonite) at 30°C

	2.11
	2.55
	2.44
Average	2.37×10^{-6}

*All values from supersaturation

Wattenberg Cl‰ 17.56*

K'sp $CaCO_3$ (calcite) at equilibration temperature

Temp.	20°C	25°C	30°C	35°C
	0.62	0.55	0.50	0.48
	0.63	0.56	0.45	0.47
	0.62	0.57	0.38	0.43
	0.60	0.55	AV. 0.44×10^{-6}	0.39
AV.	0.62×10^{-6}	0.53		0.40
		0.43		0.35
		0.48		0.38
		0.47		0.39
		0.51		0.37
	AV.	0.52×10^{-6}		0.35
				0.36
			AV.	0.40×10^{-6}

At 19.0 Cl‰ Wattenberg estimates:

T°C	K'sp x 10^{+6}
20	0.62
25	0.55
30	0.47
35	0.38

Smith Cl‰ 20*

K'sp $CaCO_3$ (aragonite) at 30°C

1.24
1.09
1.13
1.09
1.18
1.19
1.23
1.14
1.12
1.17

AV. 1.16×10^{-6}

*All values from supersaturation

Hindman Cl‰ 18 - 20*

K'sp $CaCO_3$ (calcite) at equilibration temperature and chlorinity

Temp.	15°C	25°C	30°C
	18.5 0.47u	19.0 0.65u	18.5 0.67u
	18.5 0.47u	19.0 0.59u	18.5 0.67u
	18.5 0.47u	19.0 0.60s	AV. 0.67×10^{-6}
	AV. 0.47×10^{-6}	19.0 0.52u	
		18.5 0.52u	
		18.5 0.52u	
		19.0 0.70s	
		19.0 0.55u	
		18.5 0.66s	
		18.5 0.66s	
		18.5 0.52u	
		19.8 0.77s	
		18.5 0.60s	
		18.5 0.60s	
		18.5 0.50u	
		18.5 0.52u	
		19.0 0.64u	
	Value taken	0.52×10^{-6}	

*Values marked "u" from under saturation and "s" from supersaturation

Kramer (1958) (1959) Cl‰ 19

K'sp $CaCO_3$ (calcite) at equilibration temperature

Temp.	5°C	25°C
	2.8×10^{-6}	0.86×10^{-6}

In the latter of the above papers, these data were rejected by Kramer for unknown reasons. His final choice is:

25°C
0.65×10^{-6}

Park Cl‰ 20.0

K'sp (calcite) at equilibration temperature

15°C	25°C
0.61×10^{-6}	0.54×10^{-6}

K'sp (aragonite) at 15°C = 0.77×10^{-6} from undersaturation.

Cloud

K'sp $CaCO_3$ (aragonite) at 30°C

$$\text{Value taken } \frac{0.98}{0.99}\ 0.98 \times 10^{-6}$$

CHAPTER VI

EXPERIMENTAL RESULTS

(a) Solubility Products of Calcite and Aragonite in Sea Water

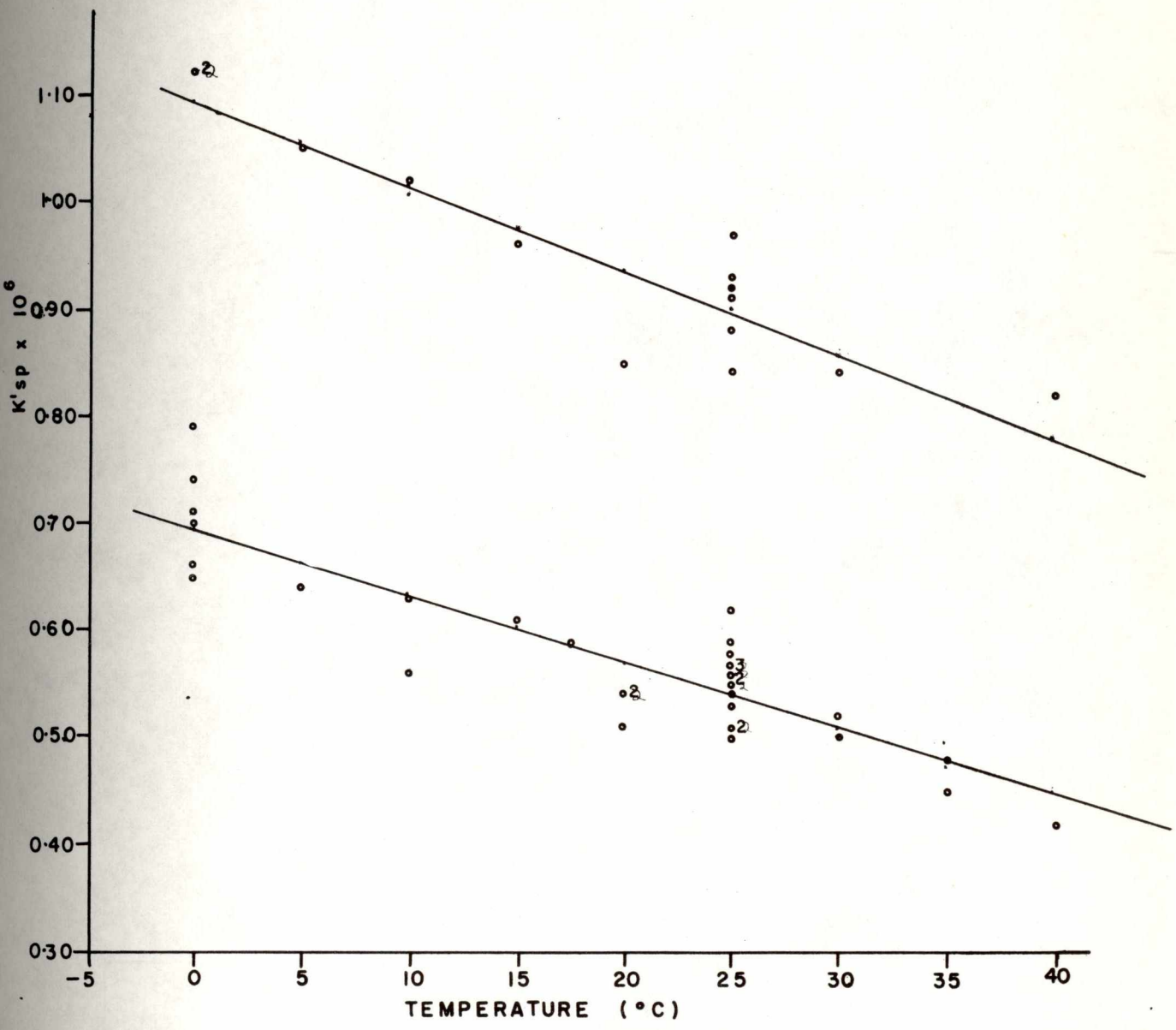
Apparent solubility product determinations of calcium carbonate in sea water of Cl‰ 19 were made using the apparatus and analytical methods described in Chapters III and IV. The results are given in Tables 2 and 3, and the temperature dependence of K'sp calcite and K'sp aragonite indicated by the data is shown in Fig. 8.

Alkalinities averaged from three titrations and pH's verified by restandardization and remeasurement have been used in all K'sp calculations. Alkalinity values not reproducible to $\pm$ 1%, or pH's not consistent to 0.01 units were rejected and analysis repeated. If the agreement was still poor, the sample was discarded.

In solubility runs with $pCO_2 \simeq 3 \times 10^{-4}$ atm, the titration alkalinity was corrected for borate according to Buch (1933). At $pCO_2 = 1$ atm, the solution was sufficiently acidic for all borate to be present as boric acid molecules which do not contribute to the alkalinity. Carbonate alkalinity was then taken as equal to titration alkalinity.

Duplicate solubility runs with pyrex and polyethylene bottles in the paddle wheel bath (section (b), Chapter III) gave similar results, indicating that leaching of pyrex in these equilibrations is not significant from pH 6 to 8.5.

Fig. 8



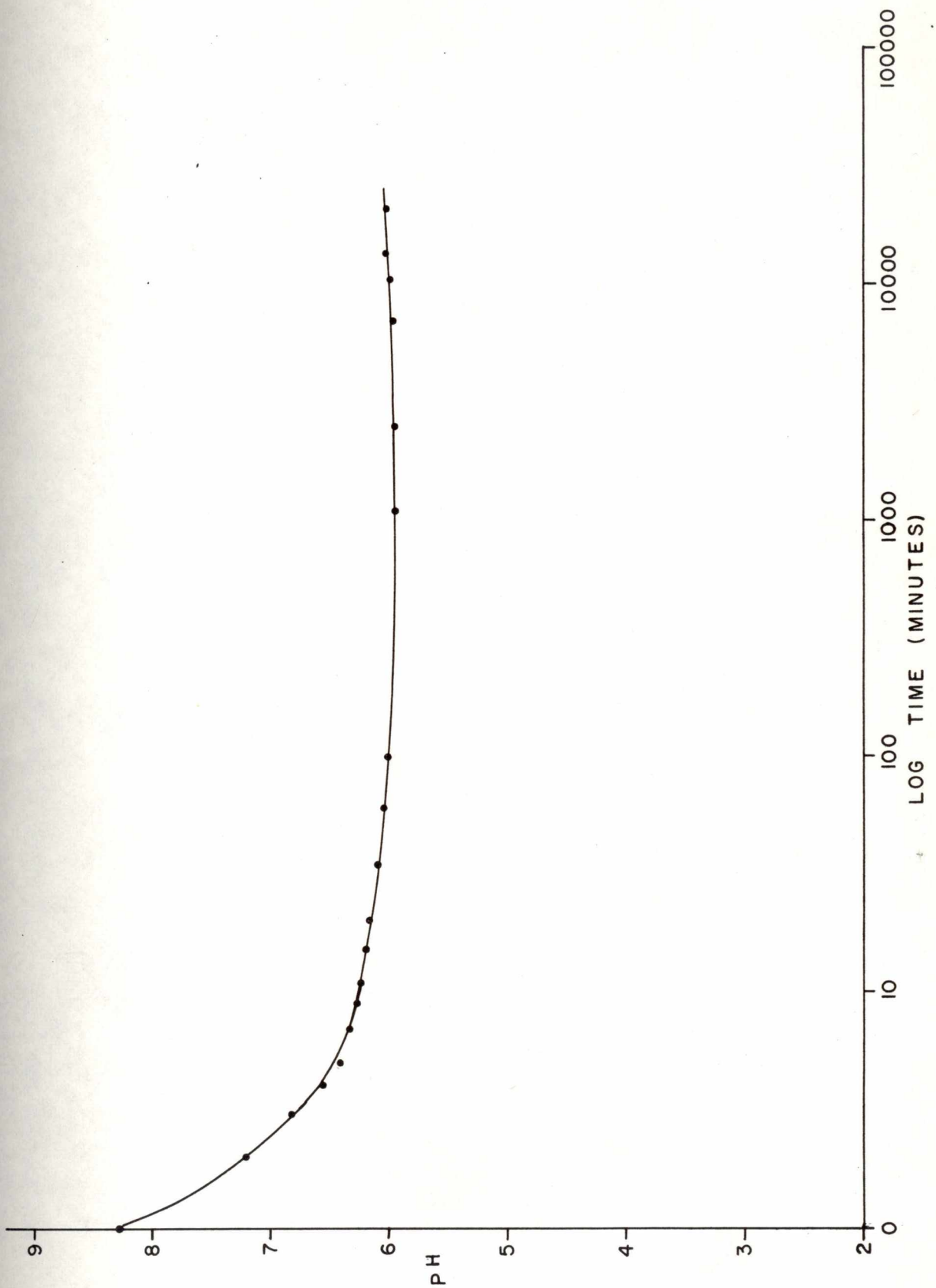
K'sp $CaCO_3$ as a Function of Temperature at Cl‰ 19

(b) Equilibration Time

Some solubility runs were monitored to determine the time required to reach equilibrium. The combination electrode was inserted in the fixed reaction vessel, its signal amplified with a Radiometer model pH M 22 pH meter and registered on a chart recorder. Stability was so high that the electrode, standardized at 24 hour intervals, showed no drift. Leakage of KCl from the calomel electrode was not a problem, due to the slow flow rate of the porous pin liquid junction. It was feared that the pH electrode system, when in contact with the stirred, finely divided calcium carbonate solution might show a "suspension effect", as defined by Pallmann (1930). Tests proved that the effect was easily observed with clays, but not with calcium carbonate. Garrels (personal communication) reached the same conclusion.

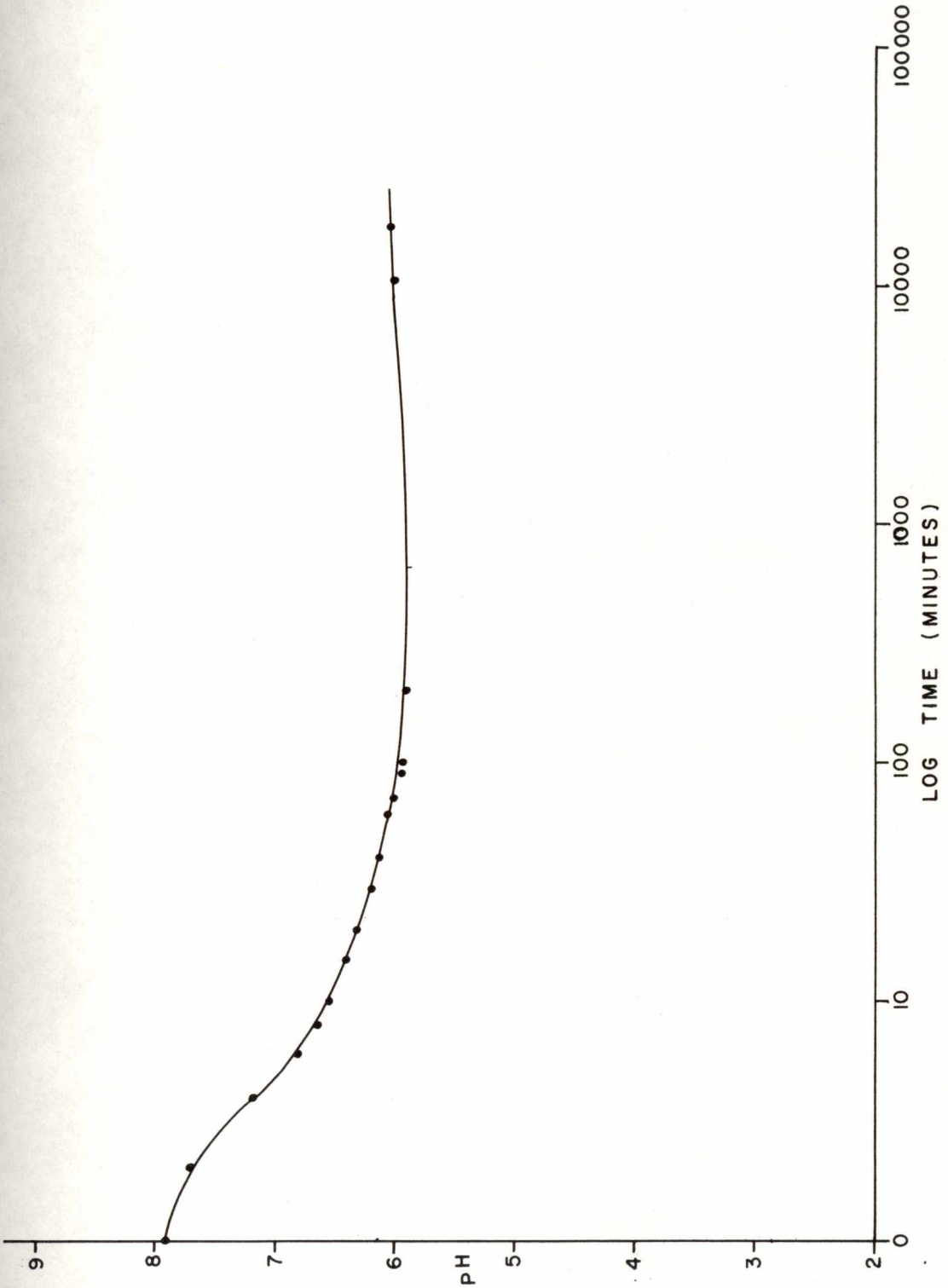
The time required for continuous passage of pure CO_2 to change pH from the value with $pCO_2 = 3 \times 10^{-4}$ atmospheres to the value at $pCO_2 = 1$ atmosphere was taken as the time to reach calcium carbonate equilibrium. Figures 9 and 10 are monitored solubility runs on powdered calcium carbonate, while Fig. 11 is the result of attempting equilibration of a one cubic inch rhomb of calcite with sea water. The crystal was mounted on a teflon stand above the stirrer bar so there would be no grinding action. In the figures,

Fig. 9



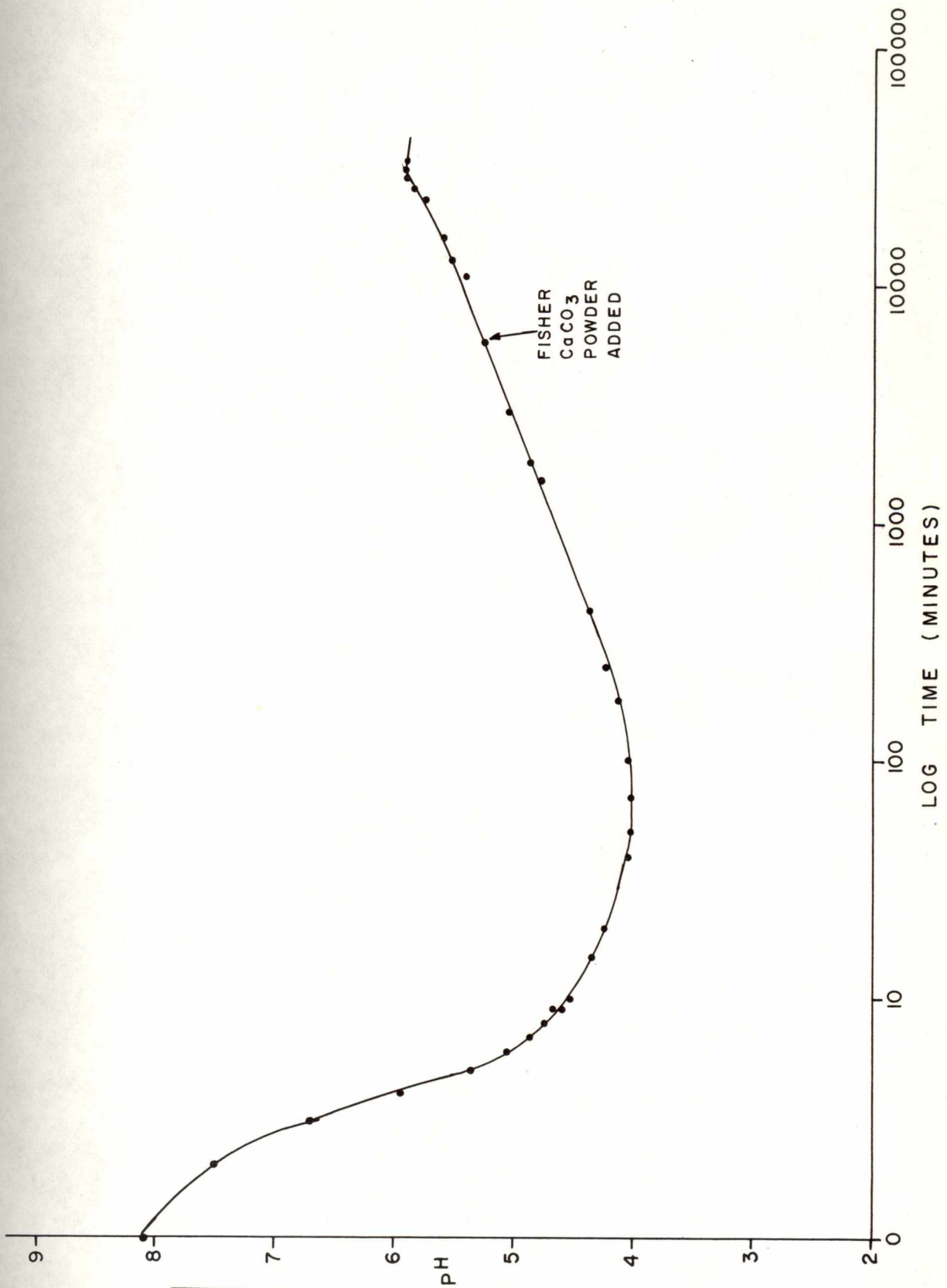
pH Change in Equilibration of Calcite Powder with Sea Water

Fig. 10



pH Change in Equilibration of Calcite Powder with Sea Water

Fig. 11



pH Change in Equilibration of Single Calcite Crystal with Sea Water

time 1 minute is the instant when the $CaCO_3$ - sea water system initially in equilibrium with the laboratory atmosphere was disturbed by the introduction of pure carbon dioxide. The monitored runs of Figures 9 and 10 were carried out under similar conditions, and gave similar results, to those of Shternina and Frolova (1952) for calcite in NaCl with pCO_2 = 1 atm and equilibration from under-saturation. As is obvious from Fig. 11, carbon dioxide did not react rapidly with the single calcite crystal and the pH dropped much lower than in the first two cases because unreacted carbonic acid was in excess. Later in the run, powdered $CaCO_3$ was added. The optimum equilibration time (10-20 days) found from Figures 9 and 10 is of the same magnitude as suggested by Shternina and Frolova. Longer equilibration periods are certainly desirable (if the system is undisturbed over the interval) but a four day equilibration should be sufficient to bring the pH to within the experimental error limit of the equilibrium pH.

Kinetic calculations similar to those of Shternina and Frolova were not made, but there is agreement indicating that for calcium carbonate powder, the reaction rate depends on the rate of the bicarbonate formation reaction, if one accepts Shternina and Frolova's interpretation. For the single calcite crystal the diffusion limited reaction obtained by Gortikov and Panteleeva (1937) seems suitable.

(c) Effect of Dissolved Calcium Carbonate on Ionic Strength

Chlorinities were not exactly 19‰ as given in the heading of Tables 2 and 3, because some calcium carbonate dissolved, increasing the ionic strength.

For sea water of original chlorinity 19‰ , brought to pH = 6 by CO_2 addition, a titration alkalinity of about 40×10^{-3} moles/liter is produced. The ionic strength and the chlorinity must be increased by the amount of dissolved calcium carbonate corresponding to the alkalinity. At pH 6 the dissolved calcium carbonate is almost entirely present as calcium and bicarbonate ions. Thus:

$$[Ca^{++}] = 1/2 \times 40 \times 10^{-3} = 20 \times 10^{-3} \text{ M}$$

$$[HCO_3^-] = 40 \times 10^{-3} \text{ M}$$

These concentrations may be substituted in the ionic strength expression of equation (1)

$$\mu = 1/2 \sum m_i z_i^2 \qquad (1)$$

to give

$$\mu = 1/2 (80 \times 10^{-3} + 40 \times 10^{-3}) = .06$$

From Lyman and Fleming's (1940) equation,

$$\mu = .00147 + .03592 \text{ Cl} + .000068 \text{ Cl}^2 \qquad (2)$$

at Cl‰ 19 ,

$$\mu = 0.708$$

The total ionic strength of the equilibrated $CaCO_3$ solution is:

$$\mu = 0.708 + 0.06 = 0.768 \qquad (3)$$

Substitution of this ionic strength in equation (2) shows the final chlorinity to be $\simeq$ 20.2% .

As shown in Fig. 25, Chapter VII, K'sp $CaCO_3$ increases by 0.041×10^{-6} per unit increase of chlorinity. Solubility runs at pH = 6 with a synthetic sea water of original Cl‰ 19 will have a true chlorinity of about 20‰ so that the K'sp values obtained would be 0.04×10^{-6} too high. A correction can be made by using slightly more dilute sea water in the equilibration, that is, the synthetic sea water can be diluted to original Cl‰ 18. This procedure was used for the low pH runs. By a calculation similar to the above, it can be seen that no salinity correction is required at pH 8, so undiluted synthetic sea water can be used.

Control of chlorinity is not critical in the equilibrations as an error of Cl‰ 0.25 causes a change of 0.01×10^{-6} in K'sp $CaCO_3$ which lies with the experimental error of the analytical methods.

Table 2

Conditions and Results for Solubility Product Determinations of Calcite in Sea Water of Cl‰ 19

Run No.	Temp °C	pCO_2 (Atm)	Crystal Form (1)	Days Equil.	Equil. System (2)	Sat. (3)	pH	Alk. $x10^3$	$[Ca^{++}]$ $x10^2$	$[CO_3^{=}]$ $x10^4$	K'sp $x10^6$	Sea Water (4)
1	0	$3x10^{-4}$	C	8	FFS	u	8.58	3.13	0.176	3.66	0.65	Ca Free
2	0	1.0	C	19	FCS	u	6.20	37.24	2.77	0.253	0.70	L + F
3	0	1.0	C	11	FFS	u	6.15	48.07	2.43	0.270	0.66	Ca Free
4	0	1.0	C	20	FFS	u	6.15	39.83	3.15	0.224	0.71	L + F
5	0	1.0	C	5	FFS	u	6.16	44.62	3.08	0.250	0.79	L + F
6	0	1.0	C	29	FCS	u	6.16	42.15	3.03	0.245	0.74	L + F
7	5	$3x10^{-4}$	C	3	FFS	u	8.48	3.43	0.163	3.73	0.64	Ca Free
8	10	1.0	C	34	FCS	u	6.15	33.22	2.57	0.244	0.63	L + F
9	10	$3x10^{-4}$	C	10	FFS	u	8.48	3.07	0.148	3.72	0.56	Ca Free
10	15	$3x10^{-4}$	C	4	FFS	u	8.42	3.32	0.153	3.98	0.61	Ca Free
11	17.5	1.0	C	36	FCS	s	6.07	31.66	2.49	0.235	0.59	L + F
12	20	0.5	C	5	FFS	u	6.27	28.86	1.48	0.364	0.54	Ca Free
13	20	1.0	C	23	FCS	u	6.09	28.19	2.31	0.235	0.54	L + F
14	20	$3x10^{-4}$	C	7	FFS	u	8.39	2.92	0.139	3.66	0.51	Ca Free
15	25	1.0	C	28	FCS	s	6.23	20.66	1.94	0.279	0.54	L + F
16	25	1.0	IS	8	FCS	u	6.04	26.09	2.20	0.227	0.51	L + F
17	25	1.0	IS	8	R	s	6.25	21.90	2.07	0.309	0.62	L + F
18	25	1.0	C	17	R	u	6.22	20.75	1.94	0.273	0.53	L + F
19	25	1.0	C	17	R	u	6.21	22.42	2.03	0.289	0.59	L + F
20	25	1.0	C	17	R	u	6.26	20.28	1.92	0.286	0.55	L + F
21	25	1.0	C	17	R	u	6.22	21.99	2.00	0.289	0.58	L + F

22	25	$3x10^{-4}$	C	6	FFS	u	8.38	2.84	0.132	3.80	0.50	Ca Free
23	25	1.0	C	7	FCS	u	6.09	24.85	2.15	0.240	0.51	L + F
24	25	1.0	C	7	R	s	6.14	23.87	2.10	0.260	0.55	L + F
25	25	1.0	C	7	R	s	6.16	23.77	2.09	0.270	0.57	L + F
26	25	1.0	C	7	R	s	6.15	23.82	2.10	0.270	0.57	L + F
27	25	1.0	C	7	R	s	6.15	23.71	2.09	0.270	0.56	L + F
28	25	1.0	IS	10	R	s	6.15	24.18	2.12	0.271	0.57	L + F
29	25	1.0	C	10	R	s	6.14	24.28	2.12	0.266	0.56	L + F
30	30	$3x10^{-4}$	C	11	FFS	u	8.33	2.82	0.129	4.02	0.52	Ca Free
31	30	0.5	C	4	FFS	u	6.24	25.10	1.27	0.395	0.50	Ca Free
32	35	$3x10^{-4}$	C	7	FFS	u	8.33	2.48	0.116	3.99	0.45	Ca Free
33	35	1.0	C	27	FCS	s	5.96	23.39	2.07	0.234	0.48	L + F
34	40	1.0	C	29	FCS	u	6.13	14.70	1.64	0.254	0.42	L + F

(1) C - Reagent calcite
IS - Ground iceland spar
SA - Shell aragonite
A - Artificial aragonite

(2) FFS - Fixed, flow system
FCS - Fixed, closed system
R - Rotating flask, closed system

(3) u - Equilibrium from undersaturation
s - Equilibrium from supersaturation

(4) L + F - Lyman and Fleming sea water
Ca Free - Lyman and Fleming sea water without calcium

Table 3

Conditions and Results for Solubility Product Determinations of Aragonite in Sea Water of Cl‰ 19

Run No.	Temp °C	pCO_2 (Atm)	Crystal Form (1)	Days Equil.	Equil. System (2)	Sat. (3)	pH	Alk. $\times 10^3$	$[Ca^{++}]$ $\times 10^2$	$[CO_3^{=}]$ $\times 10^4$	K'sp $\times 10^6$	Sea Water (4)
1	0	1.0	SA	34	FCS	u	6.19	51.38	3.50	0.320	1.12	L + F
2	0	1.0	SA	19	FCS	u	6.24	48.48	3.33	0.336	1.12	L + F
3	5	1.0	SA	23	FCS	u	6.25	42.78	3.04	0.350	1.05	L + F
4	10	1.0	SA	28	FCS	s	6.16	43.44	3.08	0.330	1.02	L + F
5	15	1.0	SA	23	FCS	u	6.15	39.80	2.90	0.331	0.96	L + F
6	20	1.0	SA	6	FCS	s	6.07	37.65	2.83	0.299	0.85	L + F
7	25	1.0	SA	10	R	u	6.29	26.50	2.23	0.410	0.91	L + F
8	25	1.0	SA	10	R	u	6.30	26.39	2.23	0.418	0.93	L + F
9	25	1.0	SA	10	R	u	6.25	27.42	2.28	0.387	0.88	L + F
10	25	1.0	SA	10	R	u	6.29	26.30	2.22	0.415	0.92	L + F
11	25	1.0	A	10	R	s	6.29	27.44	2.28	0.425	0.97	L + F
12	25	1.0	SA	10	FCS	u	6.11	32.88	2.55	0.329	0.84	L + F
13	30	1.0	SA	23	FCS	u	6.11	29.18	2.36	0.359	0.84	L + F
14	40	1.0	SA	34	FCS	s	6.25	19.37	1.87	0.441	0.82	L + F

(1), (2), (3), and (4) are described in Table 2.

(d) Discussion

In geological-geochemical investigations such as those of Cloud (1962) and Revelle and Emery (1957), K'sp $CaCO_3$ values have been adjusted with the temperature coefficient given by Wattenberg and Timmerman (1936). Wattenberg's temperature dependence is shown as a dashed line in Fig. 7. His K'sp data demonstrates the extent and large uncertainty of K'sp extrapolation. Wattenberg's extrapolation gains some support from comparison with results in dilute solution (see Chapter II), but it is better to measure K'sp $CaCO_3$ directly.

Direct measurements of K'sp at various temperatures are given in Fig. 8. Solid lines drawn on the Figure represent the author's estimate of the temperature coefficient of K'sp $CaCO_3$.

Wattenberg's temperature dependence of K'sp is non-linear, giving:

$$\frac{\Delta K'sp}{\Delta T} = \frac{0.011 \times 10^{-6}}{^{o}C} \quad \text{for temperatures } 0\text{-}20^{o}C$$

and

$$\frac{\Delta K'sp}{\Delta T} = \frac{0.018 \times 10^{-6}}{^{o}C} \quad \text{for temperatures } 20\text{-}35^{o}C.$$

In view of the uncertain K'sp data, it appears that Wattenberg's extrapolated line could be taken as straight instead of curved, and that there is no fundamental reason for curvature.

From Fig. 8,

$$\frac{\Delta \text{ K'sp calcite}}{\Delta T} = \frac{0.0063 \times 10^{-6}}{^{o}C}$$

and

$$\frac{\Delta \text{ K'sp aragonite}}{\Delta T} = \frac{0.0078 \times 10^{-6}}{^{o}C}$$

The temperature dependence of K'sp has been regarded as linear, because the points given in Fig. 8 do not permit detection of small deviations from linearity. The lines were fitted by the method of least squares, as calculated on the IBM 1620 computer. All points were given equal statistical weights.

Reproducibility of the determinations limits the precision of the K'sp $CaCO_3$ temperature coefficient. Values for a given temperature have a spread only slightly less than that found by previous workers. However, determinations at many temperatures give a better basis for establishing a temperature coefficient because widely separated temperatures make it easier to assign a slope to the K'sp vs. temperature plot.

From the above measurements, the temperature coefficient of K'sp $CaCO_3$ is $\pm \frac{0.0070 \times 10^{-6}}{^{o}C}$. The significance of the small temperature coefficient difference between calcite and aragonite is doubtful.

Scatter of the points shown in Fig. 8 is not appreciably reduced by eliminating points where equilibration was from supersaturation.

Hindman (1942) found that K'sp $CaCO_3$ values from supersaturated solutions were erratic, and accepted his more consistent values from undersaturation as correct. He proposed that the higher K'sp $CaCO_3$ values from supersaturation were caused by hinderance of precipitation by dissolved organic material. There is some basis for the proposal in that his K'sp determinations from under and super saturation were more in agreement for artificial than for natural sea water. Recent works on the effect of organic material on calcium carbonate by Alekin and Moricheva (1958), Chave (1965), and Simkiss (1964) have rendered the proposal plausible.

The effect of organic substances has been avoided as far as possible here by using artificial sea water. Some organic substances must still be present in chemicals and distilled water used in equilibration. Some workers, notably Gee et al. (1932), have taken precautions to exclude living organisms from calcium carbonate - water solutions, but many and more elaborate precautions would be needed to eliminate organic material to the extent that it could no longer form a monolayer on calcium carbonate.

Most of the scatter of K'sp $CaCO_3$ values is a consequence of the analytical method for $[CO_3^{=}]$ determination. Park (1961) compared carbonate concentrations by the pH-alkalinity method and by a less precise method based on graphical analysis of the alkalinity titration curve. A difference of 7% was found which

was within his accepted experimental error for the pH-alkalinity method. Assuming a 1% error in the calcium determination, an error of 8% in K'sp $CaCO_3$ is then possible. If K'sp calcite is 0.50×10^{-6}, the error from analysis could be 0.04×10^{-6}.

Major sources of error in carbonate analysis are apparent from the expression:

$$[CO_3^{=}] = \frac{CO_3 \text{ Alk} \times K'_2}{(a'_H + 2K'_2)} \qquad (4)$$

There are fundamental errors arising from inaccurate K'_2 values, and both random and systematic errors in the experimental measurement of CO_3 Alk and a'_H. Errors in the former category do not affect the reproducibility of runs at a given temperature but will lead to incorrect values of the temperature coefficient of K'sp $CaCO_3$, while errors in the latter category contribute to the scatter of K'sp values at constant temperature.

In the present work pH measurement is accurate to $\pm$ 0.01 units, and alkalinity to within 2%. With a sample of $a'_H = 0.631 \times 10^{-6}$, CO_3 Alk = 23.00×10^{-3} M, and $K'_2 = 0.800 \times 10^{-9}$, $[CO_3^{=}]$ is 2.92×10^{-5}M. With the above errors, a'_H and CO_3 Alk could be read as 0.603×10^{-6} and 23.46×10^{-3} M respectively, giving $[CO_3^{=}] = 3.11 \times 10^{-5}$M. The error in carbonate concentration is about 7%, in agreement with Park's estimate.

Few criteria are available for checking the temperature coefficient of calcite and aragonite solubility products in sea water.

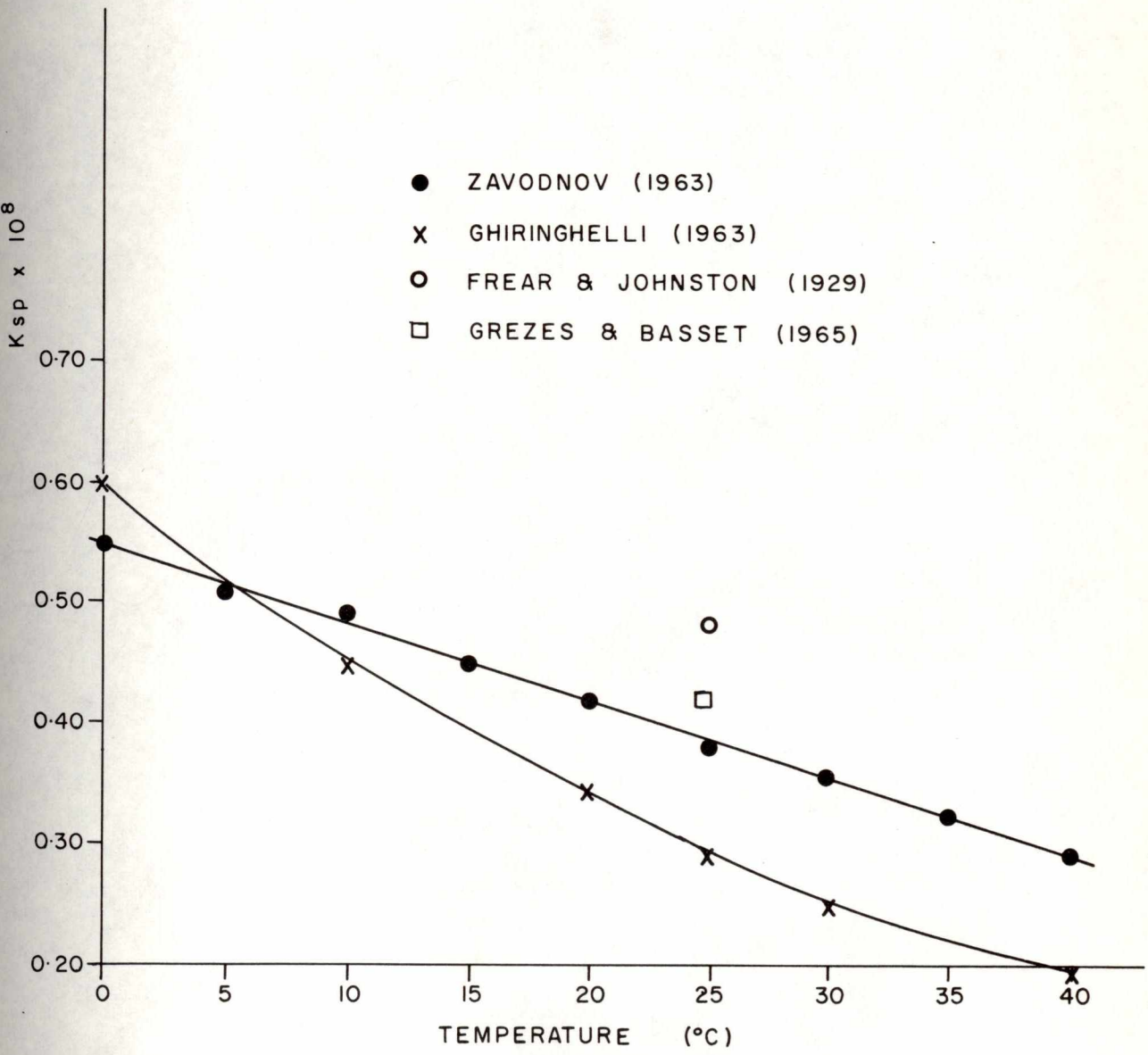
The variation found in the present study is not in agreement with Wattenberg's extrapolation, as may be seen by comparing Figures 7 and 8. Either the low temperature Ksp $CaCO_3$ values used in Wattenberg's extrapolation are incorrect, or the assumption that Ksp and K'sp of calcium carbonate have similar temperature coefficients is invalid.

When the $\frac{\Delta K'sp\ CaCO_3}{\Delta T}$ values found from Fig. 8 are compared with $\frac{\Delta Ksp}{\Delta T}$ values found by other workers and shown in Fig. 12, it is apparent that the present temperature coefficient is in good agreement with the coefficient given by Zavodnov (1964). The author feels that agreement with the work of Ghiringhelli and Bianucci (1963) is not to be expected, since their method of calculation was indirect and based only on a single solubility product measurement at 25°C. Zavodnov's study was based on a compilation of all previous calcite solubility determinations for dilute solutions over the range 0°-70°C at known pCO_2. The K H_2CO_3 values of Harned and Davis (1943) and Harned and Scholes (1941) were used in the calculations. Zavodnov's method of Ksp $CaCO_3$ calculation is rigorous and based on a large number of measurements.

Zavodnov gives $\frac{\Delta Ksp\ calcite}{\Delta T} = 0.0065 \times 10^{-6}/°C$ as compared with

$$\frac{\Delta K'sp\ calcite}{\Delta T} = \frac{0.0063 \times 10^{-6}}{°C}$$

Fig. 12



Variation of Ksp (calcite) with Temperature

and

$$\frac{\Delta K'sp\ aragonite}{\Delta T} = \frac{0.0078 \times 10^{-6}}{^{o}C}$$

from the present work.

These results indicate that the extrapolation method used by Wattenberg is correct and that his extrapolated K'sp values do not agree with those measured here, because his Ksp calcite and K H_2CO_3 data were not adequate.

Since there is no basis for a statement that Δ Ksp calcite $/\Delta T$ should equal $\Delta K'sp$ calcite $/\Delta T$, the variation of K'sp with temperature found here for sea water cannot be regarded as confirmed by comparison with Zavodnov's (1964) work. However, the agreement of Δ Ksp$/\Delta$ T and $\Delta K'sp/\Delta T$ indicate that $\gamma_{\pm}(CaCO_3)$ varies little with temperature. Most salts for which data are available (Harned and Owen (1958)) have small γ temperature coefficients, and $CaCO_3$ probably has a similar behaviour.

A test of the assumed negligibility of $\frac{\partial \gamma_{\pm}(CaCO_3)}{\partial T}$ for $\mu = 0.0$ to $\mu = 0.7$ must await development of a method for experimental $\gamma_{\pm}(CaCO_3)$ determination.

As noted in Chapter II, it is possible to calculate thermochemical quantities from the data of Tables 2 and 3. In the following columns these quantities are given for calcite and aragonite in sea water of Cl‰ 19. Calculation methods and equations are those described in Chapter II.

△ F aragonite → calcite		Differential Heat of Solution	
T °C	△F cal/mole		$(\bar{L}_2 - L_2)$
0	-245 ± 25	calcite	-1900 ± 500 cal/mole
25	-302 ± 25		
40	-350 ± 25	aragonite	-1410 ± 500 cal/mole

Other thermochemical quantities can be derived from the △F data, but the works of Jamieson (1953), Kelley and Anderson (1935) and Kobayashi (1951), in dilute solution might be of slightly higher accuracy. The values found by these authors are listed below and indicate the present uncertainty of △F aragonite --> calcite.

Kobayashi	△F (298.1°C) -311 cal/mole
Kelley and Anderson	△F (298.1°C) -273 cal/mole
Jamieson	△F (302.1°C) -278 cal/mole
	△F (311.2°C) -288 cal/mole
	△F (325.6°C) -305 cal/mole

Agreement between these △F values and those found from the above solubility measurements is fair. Jamieson's △F vs. temperature variation is appreciably less than in the present work. The difference is probably due to errors in the solubility measurements.

The heat of solution values are simply mathematical representations based on the slopes shown in Fig. 8. A negative value is to be expected, and high uncertainty must result because calculation of $\bar{L}_2 - L_2$ magnifies errors in the slopes.

The measurements made here of calcite and aragonite solubility products in sea water are not intended to provide thermochemical data. Rather, data was calculated and compared with the literature to provide evidence that the sea water - $CaCO_3$ system was near equilibrium.

Fair agreement of ΔF aragonite --> calcite means that either calcite and aragonite solubility runs were both reaching equilibrium, or both deviating from equilibrium by a constant factor. It is probable that equilibrium was reached, because K'sp calcite values for Cl‰ 19 agreed very well with those of previous workers (see Chapter V) at 25°C. For example, K'sp calcite found here is 0.54×10^{-6}, while Wattenberg (1936) found 0.52×10^{-6}, Hindman (1942) concurred, and Park (1961) found 0.54×10^{-6}. Unfortunately, there are few other temperatures at which the calcite data can be checked, and previous aragonite solubility measurements were not made below 25°C.

Heat of solution calculations further support the assumption of equilibrium. If Zavodnov's data is used to obtain a heat of solution one finds $L_2 = -2830$ cal/mole

and since

$$\bar{L}_2 - L_2 = -1900 \text{ cal/mole for calcite,}$$

and

$$\bar{L}_2 - L_2 = -1410 \text{ cal/mole for aragonite,}$$

then

$$\bar{L}_2 \text{ calcite} = +930 \text{ cal/mole}$$

and

$$\bar{L}_2 \text{ aragonite} = +1420 \text{ cal/mole}$$

Substituting the $\bar{L}_2$ value in equation (4), Chapter II:

$$\frac{\partial \ln \gamma_{\pm}}{\partial T} \text{ calcite} = 5.26 \times 10^{-3}$$

$$\frac{\partial \ln \gamma_{\pm}}{\partial T} \text{ aragonite} = 8.04 \times 10^{-3}$$

at 25°C. The temperature dependence of $\ln \gamma_{\pm}$ is small as is expected.

The fact that Hindman's (1942) and the present K'sp calcite values are in agreement and are not greatly dependent on the direction of approach to saturation is the most definite indication that equilibrium has been reached. It is unfortunate that other workers did not approach equilibrium from both under and super saturation.

Results of the solubility measurements given above differ significantly from Wattenberg's (1936) values, and the temperature coefficient of K'sp $CaCO_3$ is only half as great as Wattenberg calculated. Temperature is therefore not as important in controlling the carbonate system as was previously assumed.

According to Hindman a change from atmospheric pressure to 1000 atmospheres increases K'sp $CaCO_3$ in sea water about

seven times. From the present work a decrease of temperature from 40°C to 0°C changes K'sp by a factor of about 0.4. From Fig. 25 , Chapter VII, a change of chlorinity from 10‰ to 19‰ changes K'sp by a factor of about 0.5.

With this information, it appears that pressure is the main variable controlling K'sp $CaCO_3$ in sea water, while temperature and salinity are secondary variables of about equal importance.

At a given depth, pressure is constant, so temperature and salinity become the main variables. In most surface water of the open ocean, temperature is the controlling variable because salinity is nearly constant. All three factors (i.e. decrease in pressure, increase in temperature, and salinity) combine to produce high supersaturations as on the Bahama Banks.

It has been assumed in this discussion that the effects of pressure, temperature and salinity can be treated separately. This would only be possible if, in the equations:

$$\frac{\partial \ln K'sp\ CaCO_3}{\partial T} = \frac{\bar{L}_2 - L_2}{RT^2} \qquad (5)$$

$$\frac{\partial \ln K'sp\ CaCO_3}{\partial P} = \frac{\Delta \bar{V}}{RT} \qquad (6)$$

$$\ln K'sp\ CaCO_3 + \ln \gamma_{\pm}^{2}(CaCO_3) = \ln Ksp\ CaCO_3 \qquad (7)$$

where

$\ln \gamma_{\pm}^{2}(CaCO_3)$ is given by some function such as

$$\ln \gamma_{\pm}^{2}(CaCO_3) = -\frac{A\, z_+ z_- \sqrt{u}}{1 + \mathring{a}B\sqrt{u}} + cu + \ldots \qquad (8)$$

the partial molar volumes, partial molar heat contents, and the activity coefficient term were mutually independent of all but the main variable to which they related. The author believes the variables are nearly independent. Experimental K'sp's as a function of pressure should aid in resolving the problem in the future.

In Chapter VII, K'sp values measured here are used to calculate the saturation state of sea water in field studies. The K'sp values are simple thermodynamic limiting quantities. Any calcareous organism present in undersatudated sea water must expend metabolic energy in maintaining its shell or skeleton. In supersaturated sea water the organism may be forced to use energy to prevent excess calcium carbonate uptake. Calcium carbonate deposition probably requires an enzyme catalyst, because few if any areas of the oceans are sufficiently supersaturated for inorganic precipitation. Inorganic solution of $CaCO_3$ in the depths undoubtedly takes place after the organism dies. The work of Neuberg et al. (1957) on the carbamate reaction is indicative of the line of investigation that should be followed to elucidate organic transport of $CaCO_3$.

Finally, it has been assumed here that dissolved calcium carbonate is present in sea water as calcium, bicarbonate and carbonate ions. If some of these ions are in reality complexed, as has been proposed by Greenwald (1941) and Garrels et al. (1959), the above conclusions will not be affected. Total calcium in solution

by EDTA titration and total carbonate by alkalinity titration could only be affected by complexing if the calcium was held so strongly by sea water anions that EDTA could not compete, or carbonate was held by cations so tightly that it could not react with HCl. This seems unlikely. Knowledge of the actual species present as a function of salinity, temperature, pH, and pressure will eventually be needed to follow the course of calcium carbonate in organisms. However, it must await the further development of solution theory, or direct measurement of ionic activity coefficients, to replace the rough Debye-Huckel approximations used by Garrels et al.

CHAPTER VII

A FIELD STUDY OF DISSOLVED CALCIUM CARBONATE IN RIVER AND OCEAN WATER

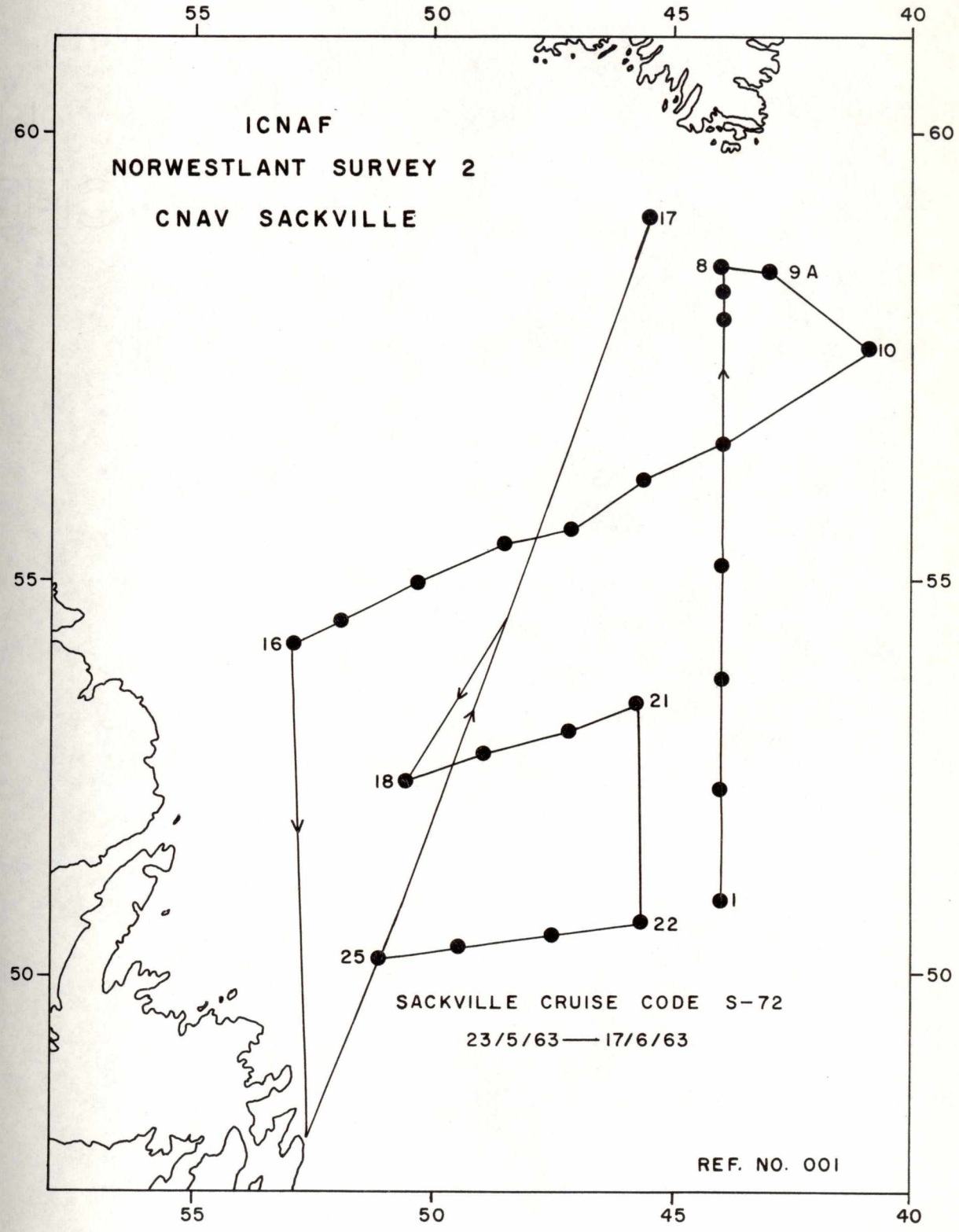
Measurements of dissolved calcium carbonate have been made by the author on cruise 10-29-64 of C.S.S. Hudson in the Gulf of St. Lawrence and by MacIntyre and Platford (1964) on cruise S-72 of CNAV Sackville in the Labrador Sea. The station positions are shown in Figs. 13 and 14. Labrador Sea stations were occupied May 21 to June 17, 1963, and the Gulf of St. Lawrence stations from November 16 to November 25, 1964.

(a) Experimental

Carbonate concentrations were measured by the standard pH-alkalinity method for both cruises. Some alkalinity measurements were made by direct titration to the inflection point and compared with those determined by the procedure of Anderson and Robinson (1946). All pH measurements were made with a Radiometer pH meter model pH M 4 using the Radiometer Type C glass electrode paired with a porous plug Radiometer calomel electrode.

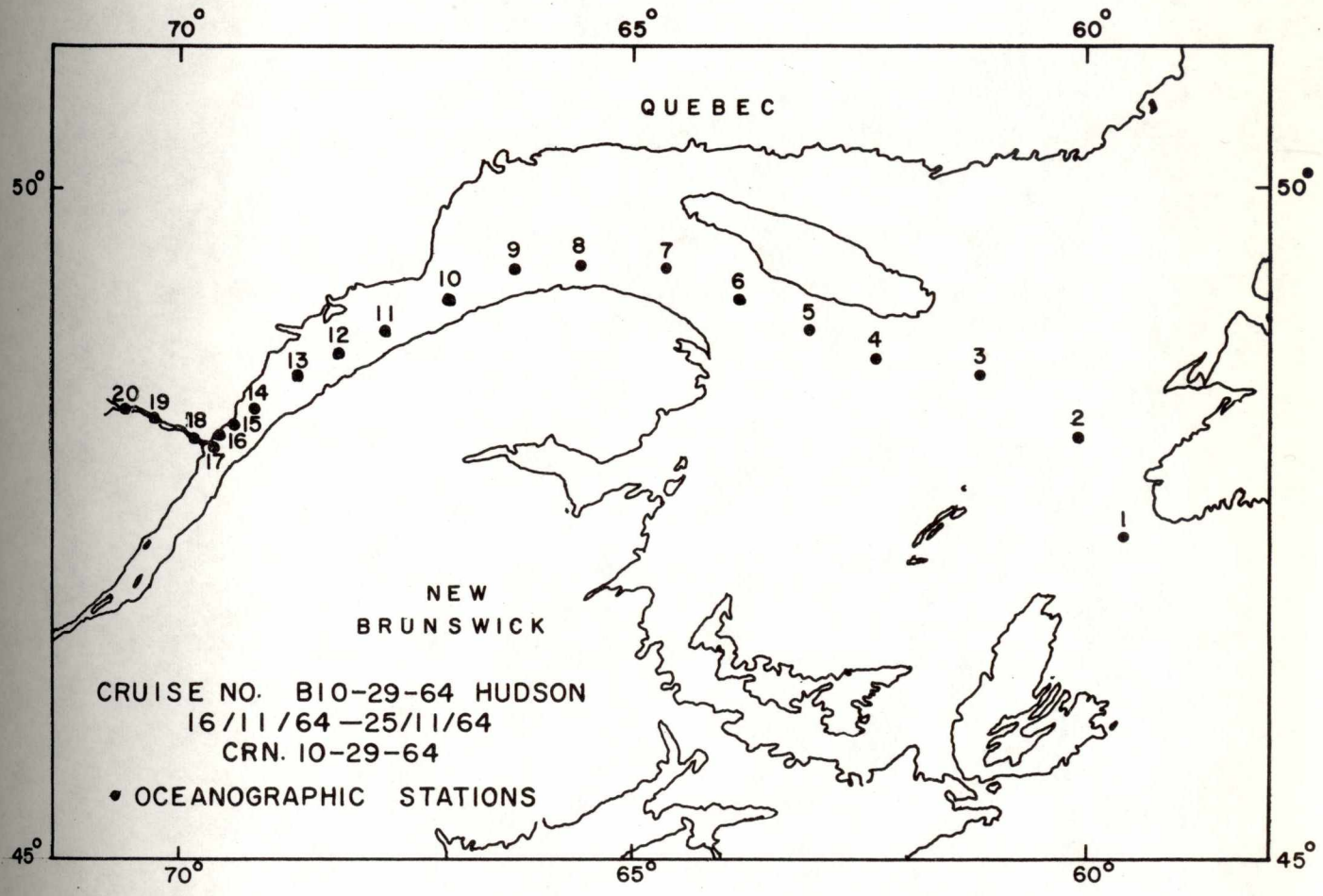
The apparatus was standardized at shipboard temperature before each station using the buffers 0.05M K H phthalate, 0.025M K H_2 phosphate and 0.025M Na_2H phosphate, and 0.05M borax.

Fig. 13



Positions of Labrador Sea Stations

Fig. 14



Positions of St. Lawrence River Stations

Water samples from the Labrador cruise were returned to the laboratory for determination of calcium. Twenty-five ml aliquots were brought to pH 12 with 1N NaOH and titrated with 0.0150 M EDTA, using Calver II indicator.

Results of the calcium titrations were applied in conjunction with alkalinity data to test the Wattenberg (1933) relation:

$$[Ca^{++}] = \frac{Alk}{2} + .477\ Cl‰ \qquad (1)$$

This was found to hold within 1% over the region. Accordingly, all calcium concentrations from the St. Lawrence cruise were calculated from the alkalinity and chlorinity. St. Lawrence samples with $Cl‰ < 15$ were returned to the laboratory in polyethylene bottles for determination of calcium by EDTA titration with prior ion exchange separation of magnesium and strontium (as described in Chapter IV) to obtain a comparison with the Wattenberg $[Ca^{++}]$ at lower chlorinities.

Water samples were taken in Knudsen bottles with teflon inner coating and fitted with reversing thermometers. Salinities from the Labrador Sea were measured on an NIO conductivity salinometer. Samples from the St. Lawrence were determined at sea with an Autolab inductively coupled salinometer.

(b) Results

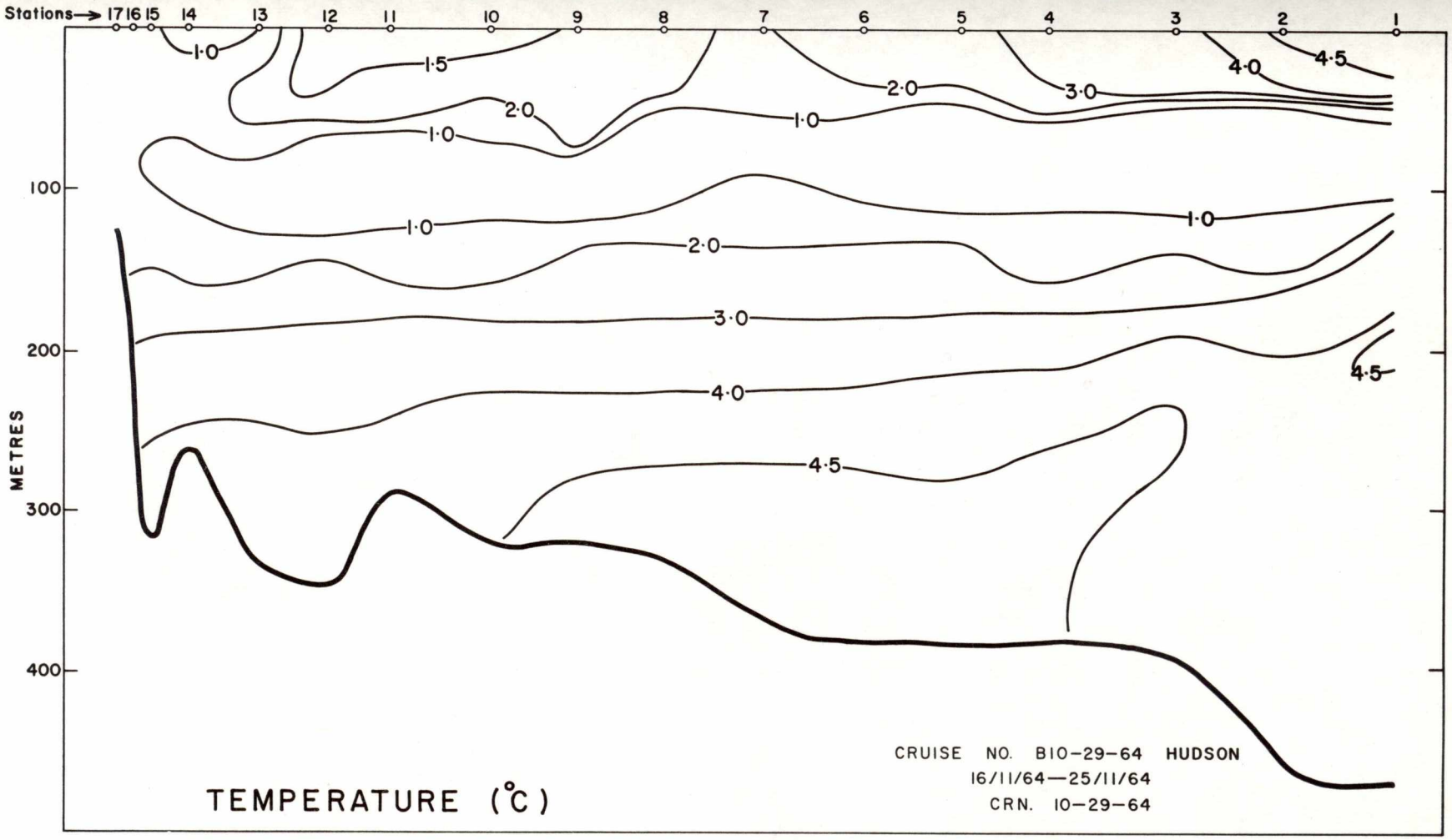
Figures 15 to 19 inclusive show the distribution of T, Cl‰ , pH, Alk, and $[Ca^{++}] \cdot [CO_3^{=}]$ respectively in a vertical section of the St. Lawrence River, while Figures 20 to 24 inclusive show the distribution of the same quantities in the Saguenay River. Only three stations were taken in the Saguenay, and sharp changes in water properties were found in the top twenty meters. Thus the contouring of Figures 20 to 24 inclusive is approximate, and contour lines had to be omitted near the surface where changes were too great to be conveniently plotted.

Tables 4 to 10 inclusive show the data corresponding to Figures 15 to 24 inclusive. Sample depths are indicated by the dots in the chlorinity distribution figures.

Table 11 is a presentation of the average results from the Labrador Sea taken from MacIntyre and Platford (1964). The results are assumed to be representative of North West Atlantic open ocean water.

(c) Discussion

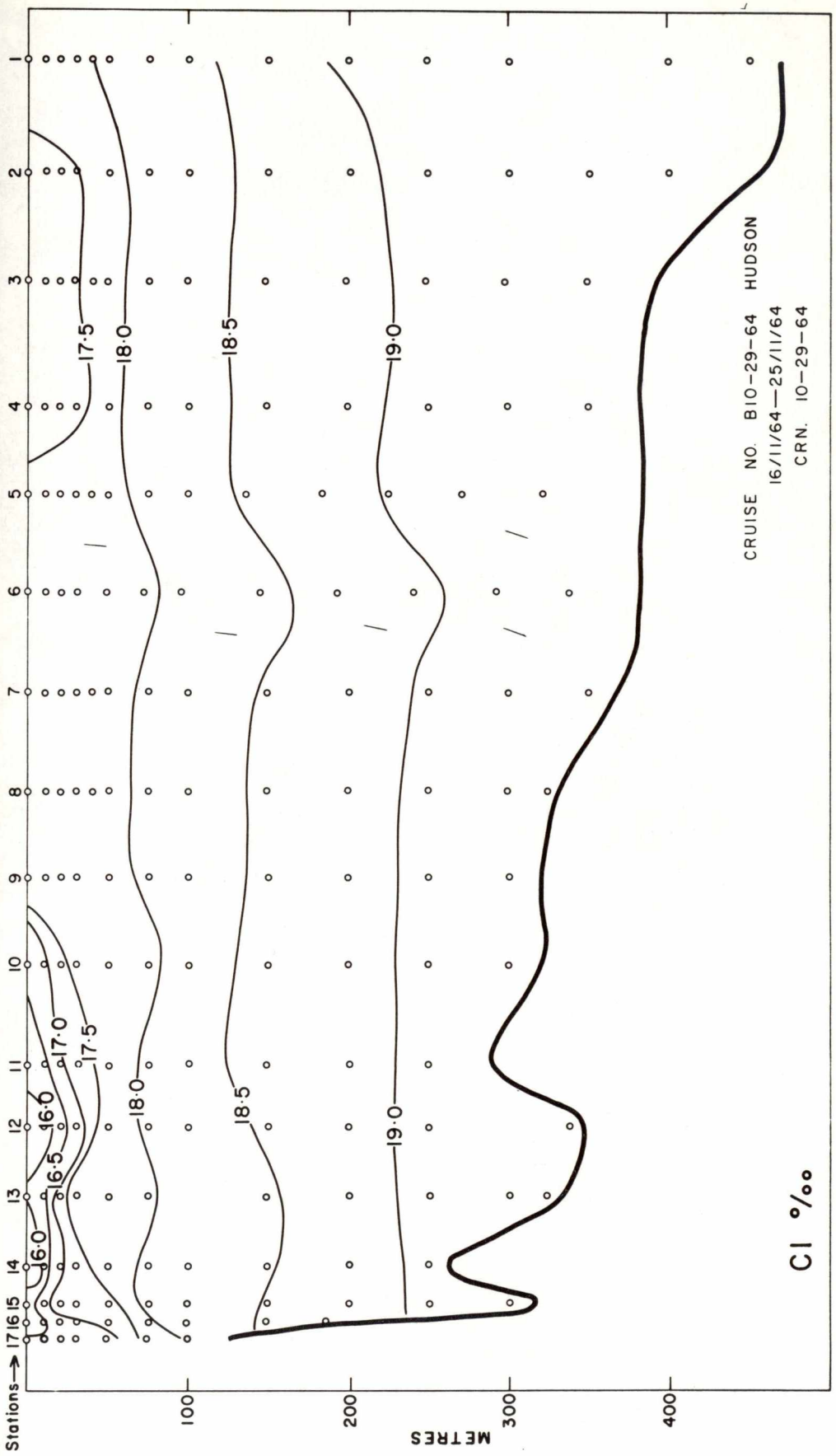
The water temperatures for the entire St. Lawrence region varied within the limits 1-4°C. This is essentially a constant temperature for the present purpose, because the temperature variation of the solubility product of calcite over this range is less than 5% of the solubility product.



Distribution of Temperature for St. Lawrence River Section

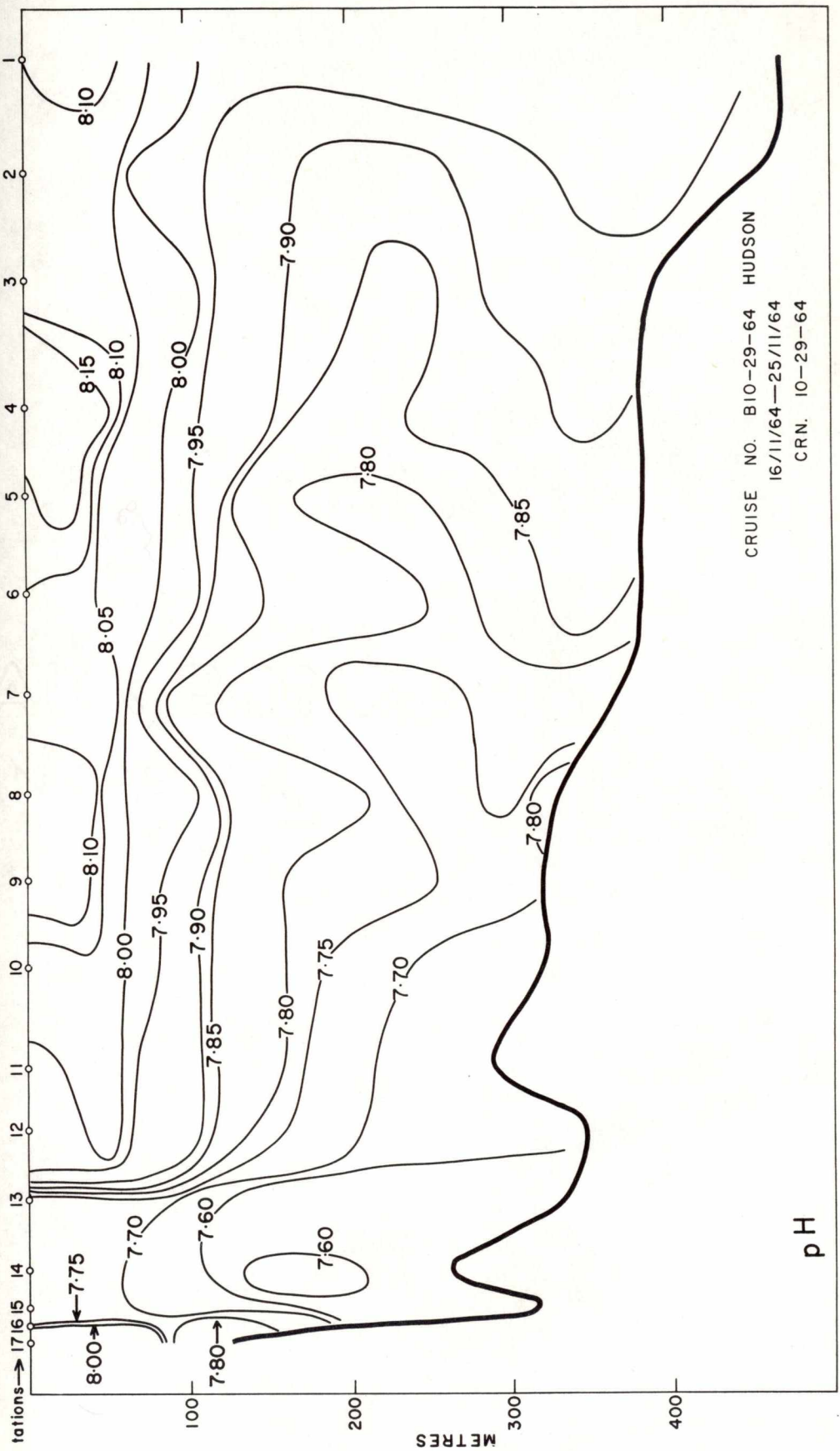
Fig. 15

Fig. 16



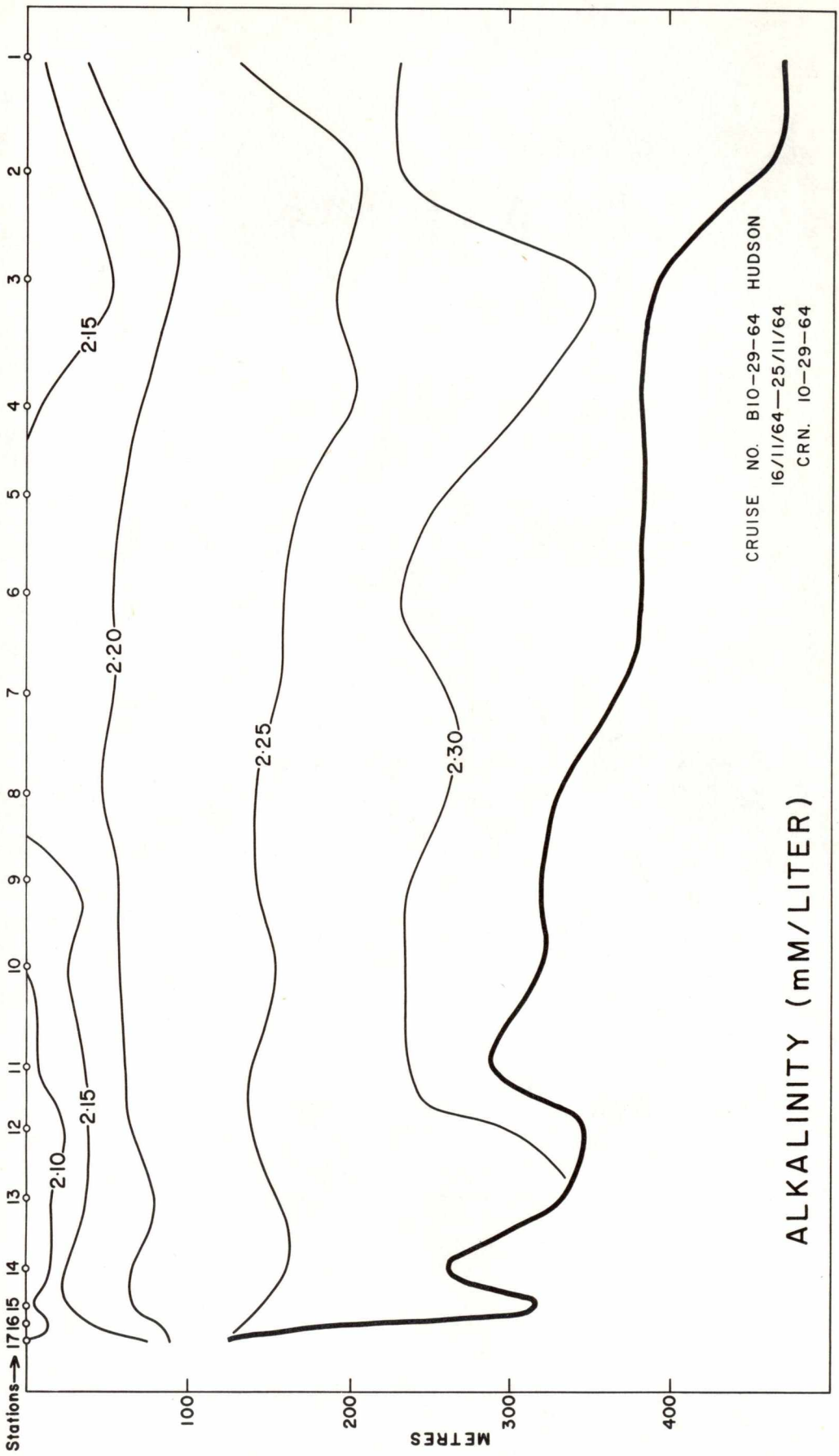
Distribution of Chlorinity for St. Lawrence River Section

Fig. 17



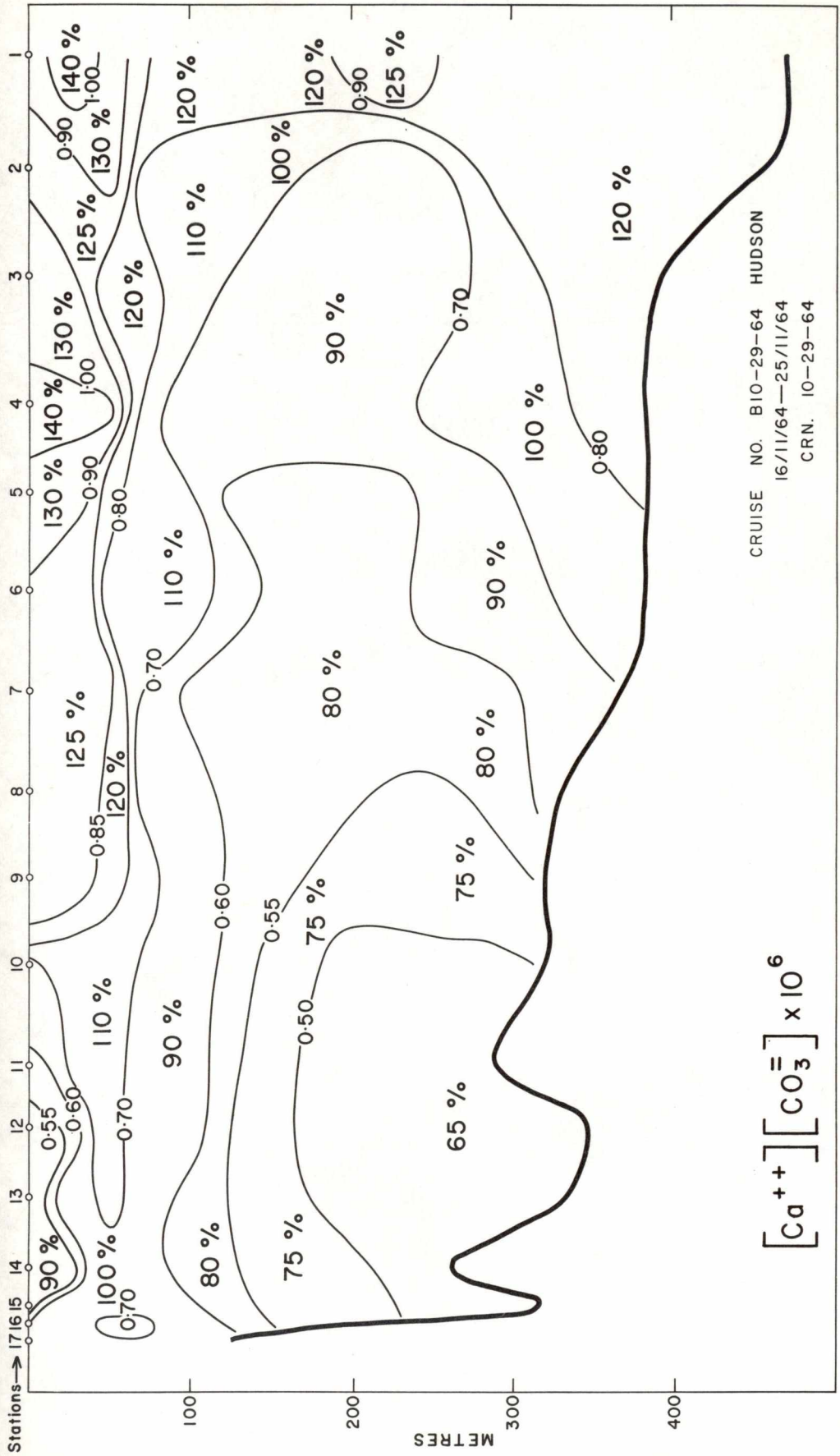
Distribution of pH for St. Lawrence River Section

Fig. 18



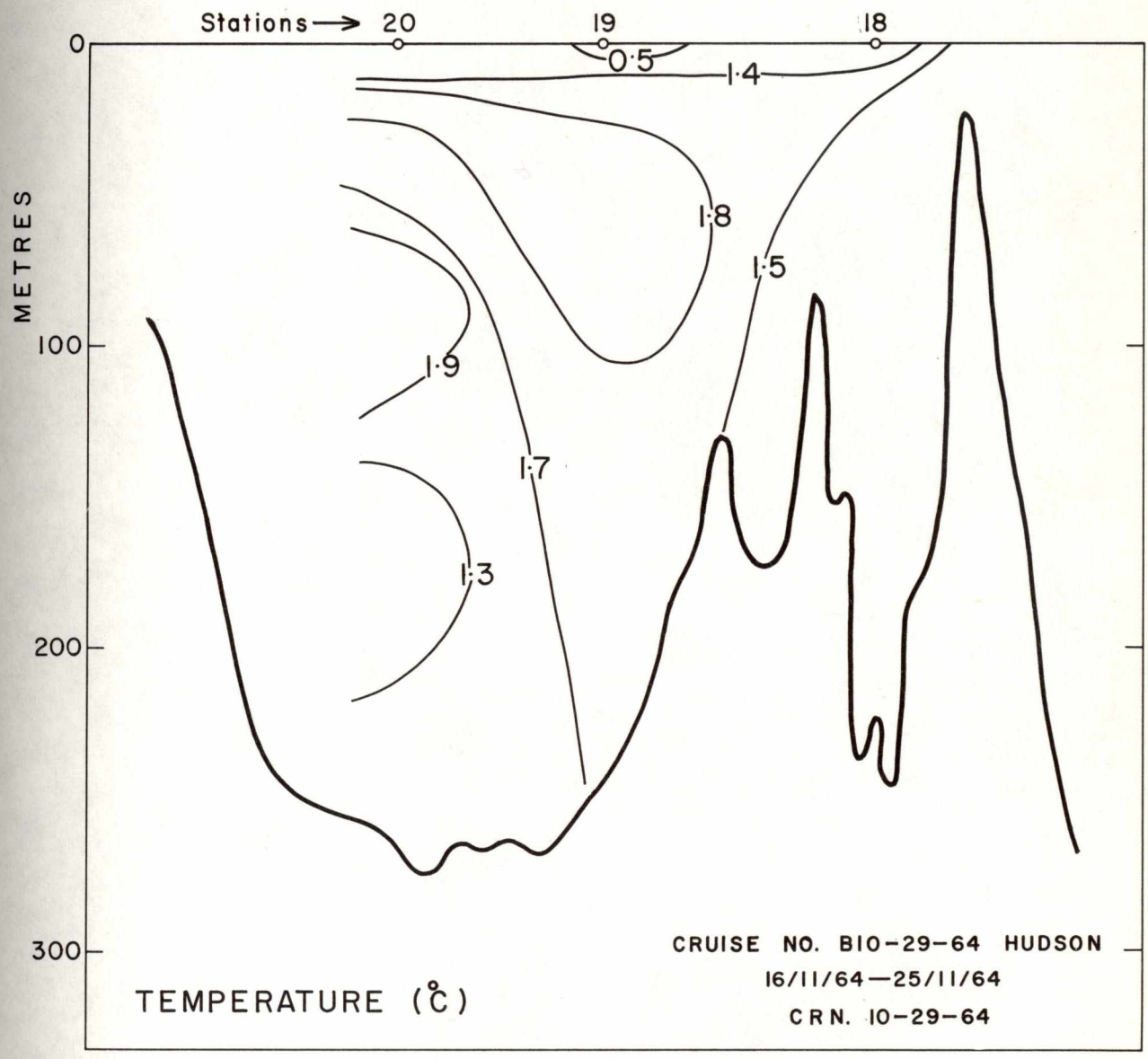
Distribution of Alkalinity for St. Lawrence River Section

Fig. 19



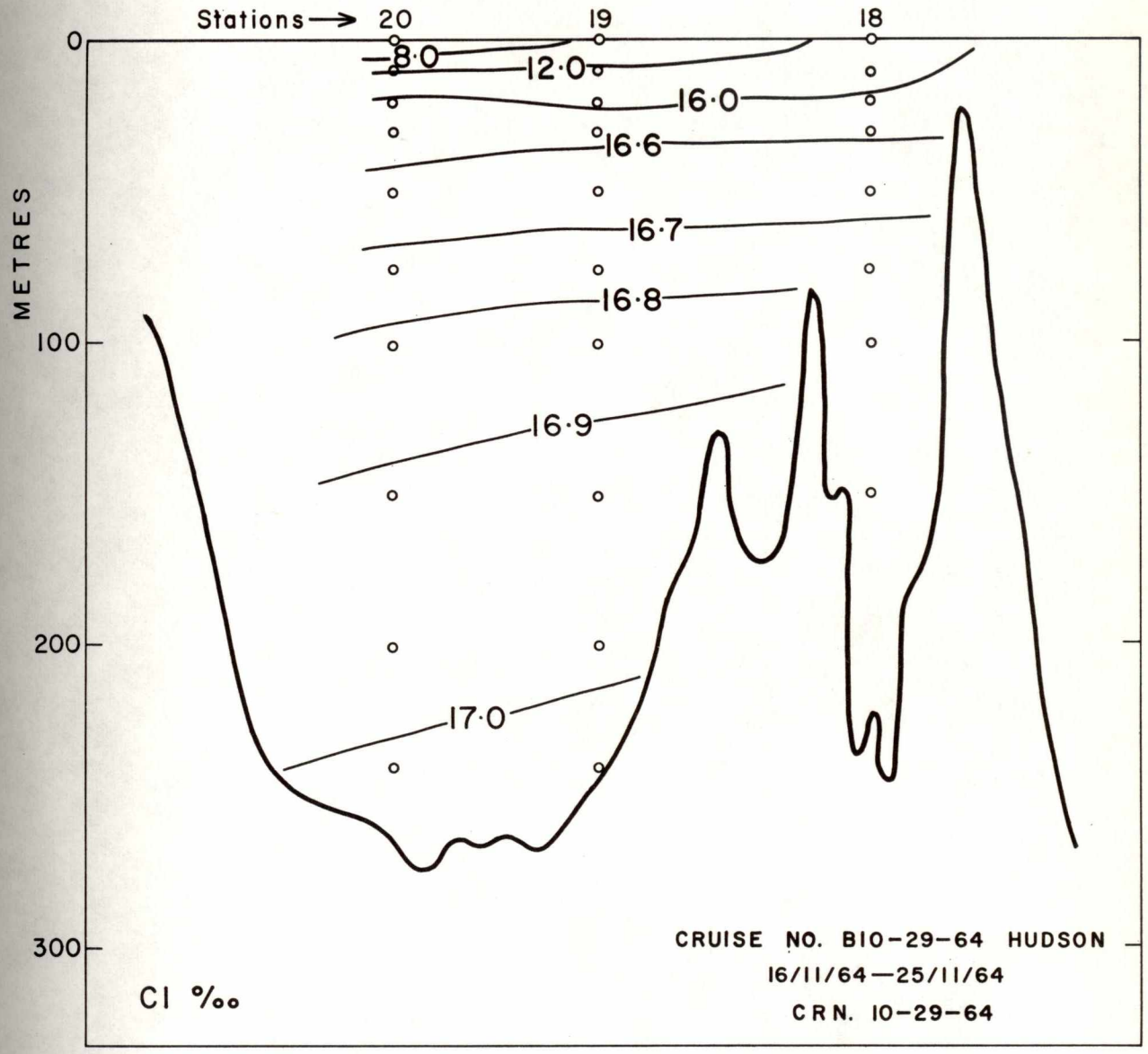
Distribution of Dissolved $CaCO_3$ for St. Lawrence River Section

Fig. 20



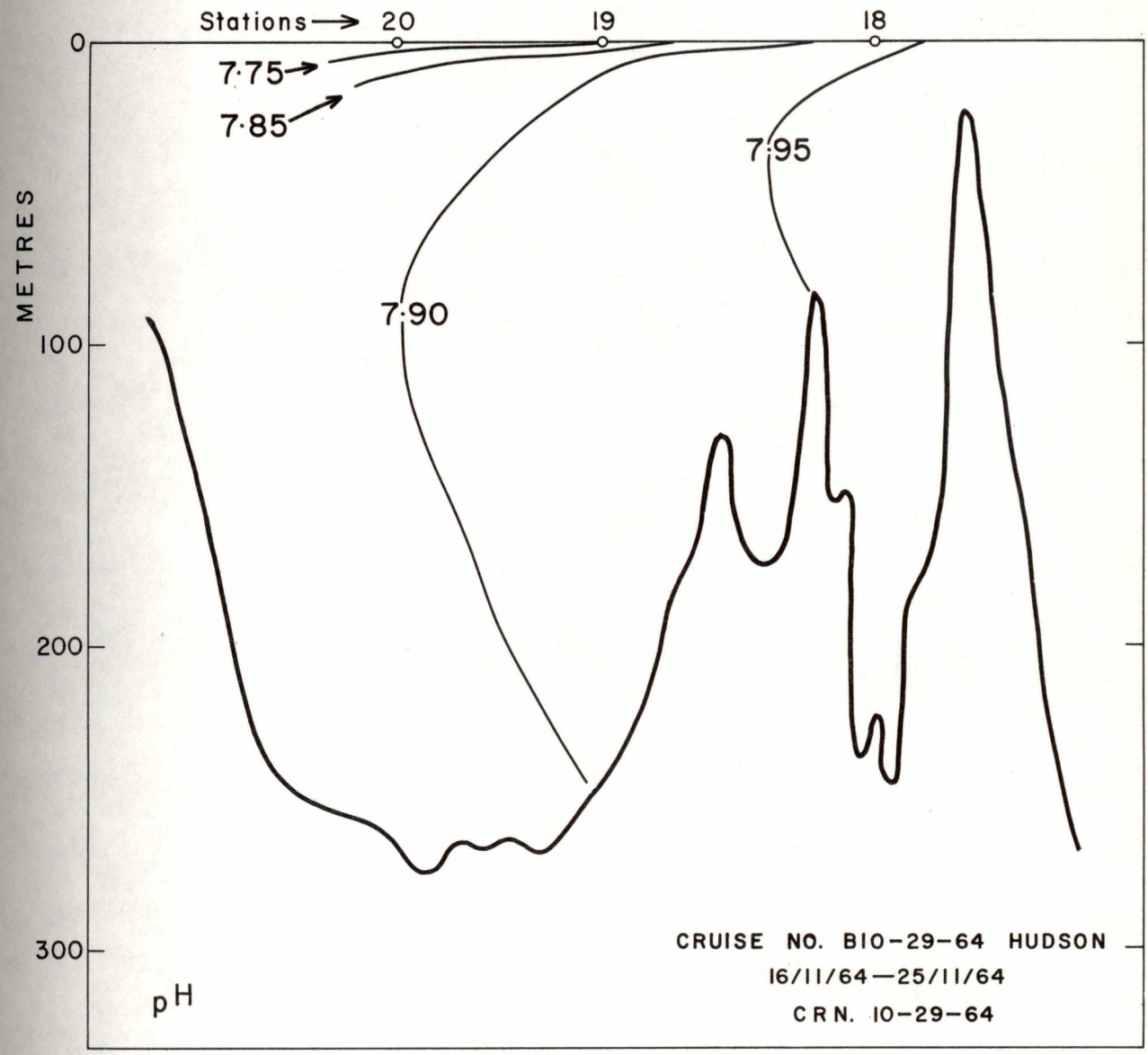
Distribution of Temperature for Saguenay River Section

Fig. 21



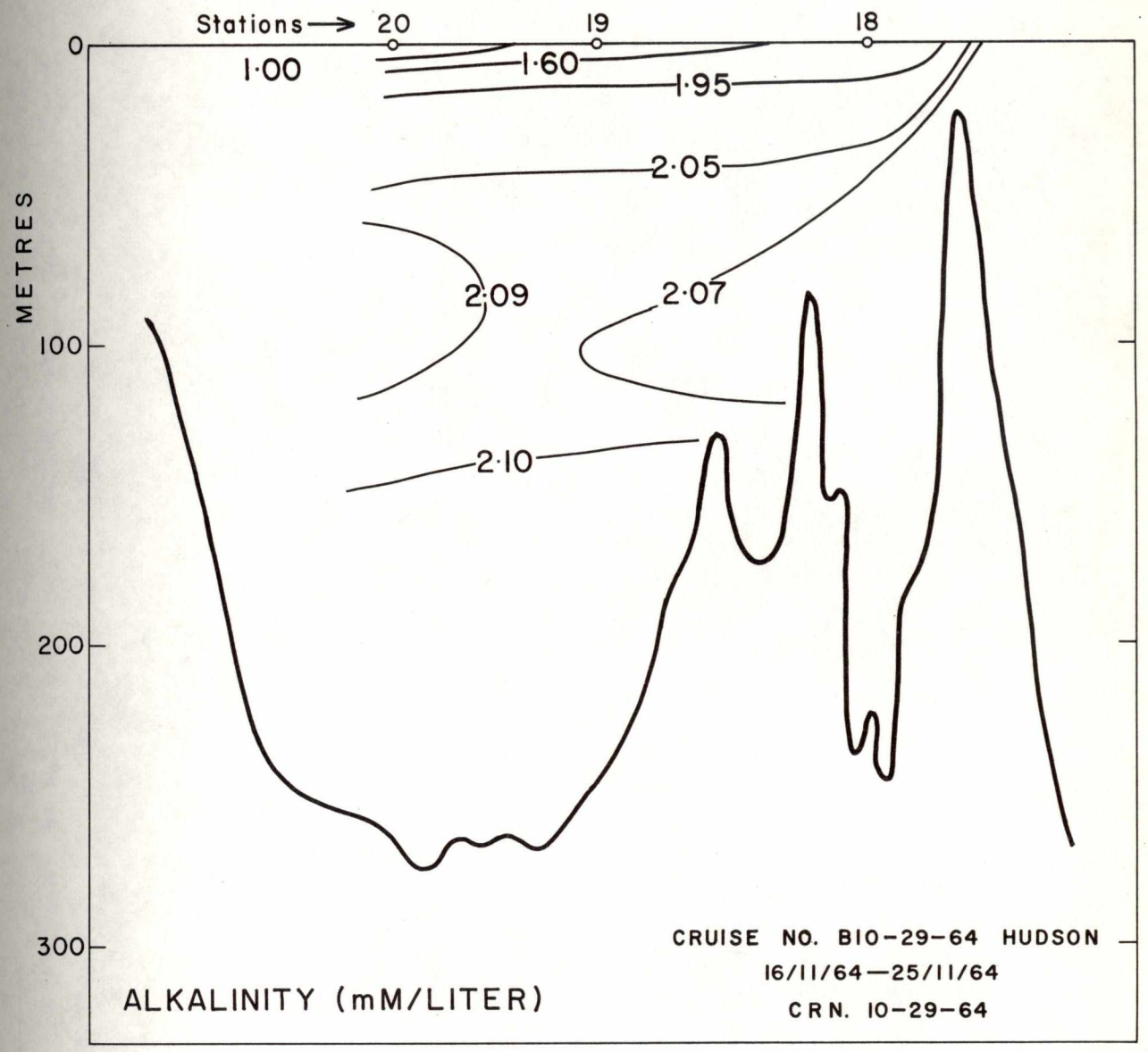
Distribution of Chlorinity for Saguenay River Section

Fig. 22



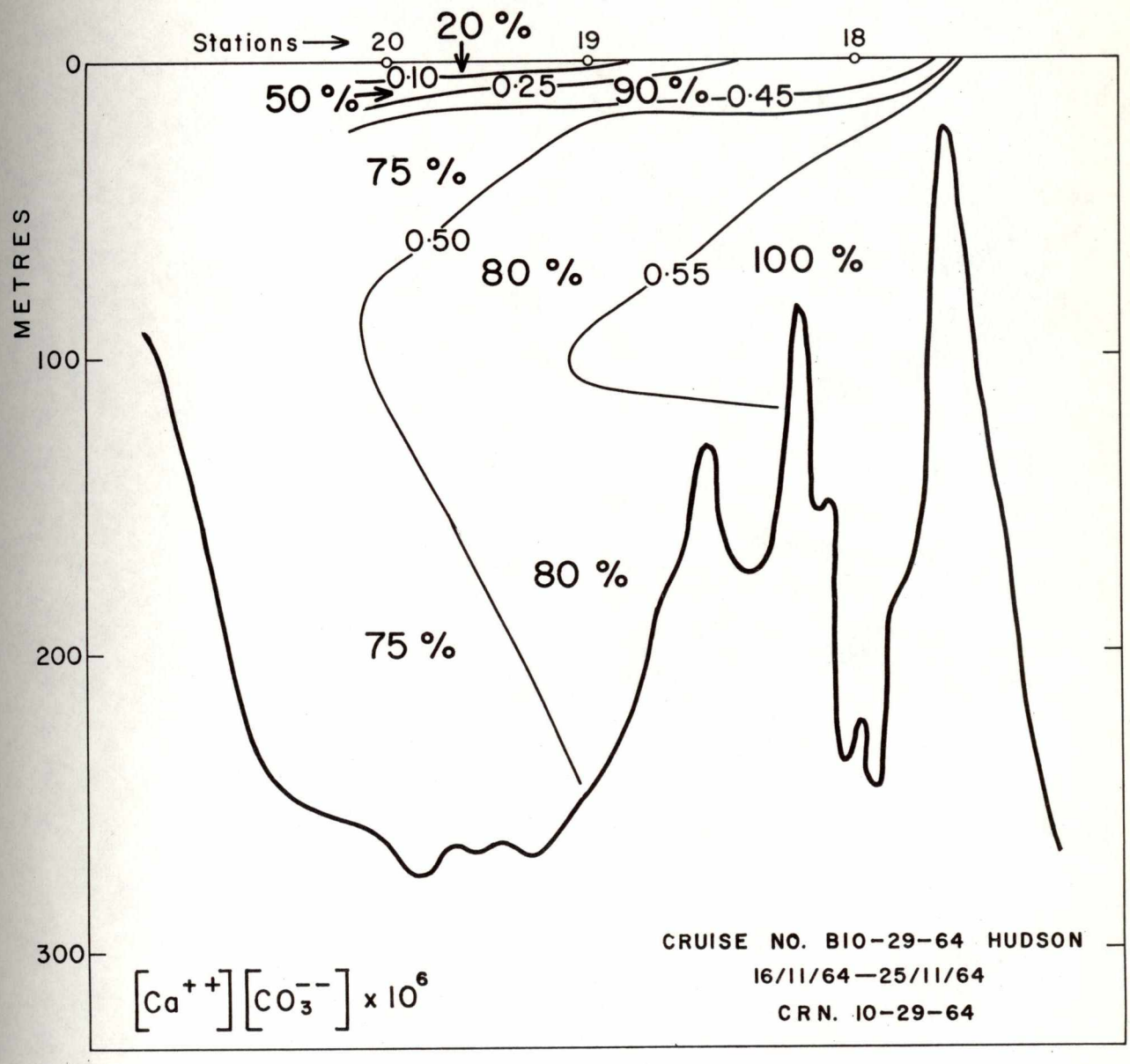
Distribution of pH for Saguenay River Section

Fig. 23



Distribution of Alkalinity for Saguenay River Section

Fig. 24



Distribution of Dissolved $CaCO_3$ for Saguenay River Section

Table 4

Temperature Data (°C) - St. Lawrence River

Stn. 17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1
1.8	1.5	1.4	0.7	0.9	1.6	1.8	1.5	2.8	2.2	1.5	2.2	2.4	3.2	3.6	4.7	4.7
1.1	0.9	1.4	0.6	1.4	1.0	1.1	1.3	2.5	2.1	1.3	2.2	2.2	3.2	3.4	4.3	4.7
1.3	1.0	2.1	1.4	1.6	1.4	1.4	2.1	2.5	2.1	1.3	2.2	2.2	3.2	3.4	4.3	4.7
1.3	1.8	1.4	1.3	2.1	1.7	2.4	2.4	2.5	2.1	1.3	2.2	2.0	3.2	3.5	4.3	4.6
1.2	2.0	0.9	1.7	2.0	2.5	2.3	1.0	2.0	2.1	1.3	1.4	1.7	2.8	3.3	0.8	4.0
1.2	1.6	0.6	0.8	1.1	0.6	0.5	0.7	0.6	0.9	1.3	0.2	0.7	0.2	0.5	0.8	2.2
1.0	0.8	1.0	0.7	0.6	0.8	0.4	0.5	2.3	0.0	0.2	1.0	0.0	0.3	0.6	0.4	0.5
	1.9	2.1	1.4	1.7	2.0	1.9	0.7	3.7	0.5	1.2	2.2	0.4	1.8	0.1	1.7	0.6
	2.1	3.2	3.0	3.2	3.2	3.1	4.4	2.2	2.7	3.8	2.3	3.7	2.4	3.5	3.5	3.5
		3.9	4.0	4.0	3.9	4.0	4.1	4.7	3.6	3.8	4.4	3.4	4.5	4.0	4.3	4.8
		4.2		4.4	4.4		4.5		4.2	4.4	4.6	4.1	4.7	4.6	4.3	4.4
				4.4	4.4				4.6	4.7	4.7	4.5	4.6	4.4	4.3	4.2
									4.7	4.7		4.7		4.4	4.3	4.4

Table 5

Chlorinity (‰) Data - St. Lawrence River

Stn. 17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1
16.9	16.4	16.3	15.9	16.1	15.2	16.4	16.6	17.6	17.6	17.8	17.7	17.6	17.5	17.5	17.5	17.7
16.8	16.3	16.3	15.9	16.4	15.4	16.4	16.7	17.5	17.6	17.7	17.6	17.6	17.5	17.5	17.4	17.8
16.9	16.4	17.4	16.5	17.1	15.9	16.5	17.2	17.5	17.6	17.7	17.6	17.6	17.5	17.5	17.4	17.8
16.9	16.9	17.7	17.2	17.7	16.7	17.0	17.6	17.4	17.6	17.8	17.6	17.7	17.5	17.5	17.4	17.8
16.9	17.6	17.9	17.5	17.8	17.6	17.6	17.8	17.8	17.6	17.8	17.7	17.7	17.6	17.5	17.8	17.9
17.5	17.8	18.1	18.0	17.9	18.0	18.0	17.9	18.0	17.8	18.2	17.8	17.9	18.1	17.9	18.0	18.1
18.2	18.2	18.3	18.0	18.1	18.2	18.2	18.1	18.3	18.1	18.4	18.1	18.1	18.2	18.1	18.2	18.2
	18.5	18.6	18.4	18.4	18.5	18.5	18.5	18.6	18.3	18.7	18.2	18.2	18.5	18.2	18.5	18.4
	18.6	18.8	18.8	18.7	18.8	18.8	18.7	18.9	18.6	18.9	18.6	18.6	18.9	18.6	18.8	18.7
		19.0	19.0	19.0	19.0	19.0	19.0	19.1	18.9	19.0	18.9	18.8	19.1	18.9	19.0	19.0
		19.0		19.1	19.1		19.1	19.1	19.0	19.2	19.1	19.0	19.1	19.1	19.2	19.0
				19.1	19.1				19.1	19.2	19.2	19.2	19.2	19.2	19.3	19.1
									19.2			19.1		19.2	19.3	19.0
																19.0

Table 6

pH Data - St. Lawrence River

Stn. 17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1
7.98	7.96	7.73	7.71	7.72	7.95	7.95	8.01	8.10	8.09	8.05	8.08	8.10	8.17	8.08	8.08	8.10
7.98	8.00	7.73	7.74	7.78	7.97	7.96	8.03	8.10	8.09	8.07	8.08	8.12	8.17	8.09	8.07	8.12
8.00	8.00	7.78	7.71	7.72	7.96	7.97	8.02	8.11	8.10	8.07	8.09	8.12	8.16	8.09	8.07	8.12
7.99	7.98	7.75	7.69	7.76	7.96	8.01	8.02	8.10	8.10	8.07	8.08	8.12	8.16	8.10	8.09	8.12
7.99	8.00	7.74	7.72	7.78	8.03	8.02	8.01	8.05	8.10	8.07	8.04	8.10	8.15	8.09	8.13	8.12
7.97	7.99	7.67	7.69	7.73	7.94	7.94	7.95	7.97	8.03	8.07	8.00	8.05	8.03	8.02	7.98	8.11
7.89	7.81	7.61	7.68	7.68	7.90	7.91	7.93	7.93	7.96	7.94	7.98	8.00	7.96	8.05	7.98	8.07
	7.80	7.75	7.60	7.59	7.78	7.85	7.81	7.82	7.95	7.83	7.87	7.97	7.90	8.02	7.93	8.03
	7.79	7.56	7.60	7.53	7.71	7.80	7.72	7.76	7.81	7.77	7.84	7.81	7.84	7.92	7.87	7.97
		7.54	7.50	7.50	7.69	7.71	7.69	7.75	7.80	7.70	7.84	7.75	7.87	7.89	7.85	7.98
		7.54		7.52	7.68	7.68	7.69	7.74	7.72	7.70	7.84	7.74	7.88	7.81	7.91	7.96
				7.52	7.68				7.74	7.75	7.85	7.82	7.93	7.91	7.96	7.96
									7.80	7.75		7.87		7.93	7.95	7.95
																7.95

Table 7

Titration Alkalinity ($x10^3$ moles/liter) - St. Lawrence River

Stn. 17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1
2.11	2.08	2.11	2.10	2.06	2.07	2.10	2.10	2.15	2.17	2.18	2.16	2.16	2.15	2.15	2.12	2.15
2.12	2.09	2.11	2.09	2.09	2.06	2.12	2.12	2.13	2.16	2.18	2.18	2.18	2.16	2.13	2.15	2.15
2.12	2.10	2.16	2.13	2.08	2.12	2.14	2.15	2.17	2.18	2.18	2.18	2.16	2.16	2.14	2.13	2.17
2.12	2.12	2.18	2.12	2.15	2.12	2.14	2.16	2.15	2.17	2.18	2.18	2.18	2.16	2.14	2.13	2.17
2.12	2.17	2.19	2.18	2.16	2.16	2.19	2.18	2.18	2.17	2.18	2.18	2.18	2.16	2.15	2.17	2.20
2.15	2.18	2.20	2.21	2.18	2.20	2.24	2.20	2.22	2.20	2.18	2.21	2.19	2.20	2.15	2.20	2.22
2.21	2.22	2.22	2.20	2.21	2.23	2.21	2.21	2.22	2.21	2.22	2.23	2.21	2.22	2.18	2.21	2.21
	2.25	2.25	2.24	2.24	2.25	2.25	2.23	2.25	2.23	2.23	2.24	2.22	2.23	2.20	2.26	2.22
	2.25	2.26	2.25	2.27	2.27	2.28	2.26	2.27	2.25	2.24	2.26	2.24	2.25	2.23	2.25	2.28
		2.28	2.27	2.28	2.33	2.30	2.30	2.25	2.27	2.30	2.28	2.27	2.28	2.29	2.36	2.36
		2.29		2.28		2.33	2.35	2.29	2.28	2.33	2.28	2.29	2.28	2.28	2.36	2.36
				2.33				2.35	2.33	2.35	2.30	2.32	2.29	2.32	2.33	2.32
									2.35	2.32		2.32		2.29	2.28	2.34
																2.40

Table 8

Calcium Carbonate Ion Product ($x10^8$) - St. Lawrence River

Stn. 17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1
63	59	54	50	51	48	57	65	91	88	85	86	90	104	88	88	95
62	61	62	51	55	52	57	68	88	87	84	86	94	104	88	86	99
66	62	68	53	62	55	60	71	91	90	84	88	94	102	89	85	101
65	64	66	55	66	59	70	76	89	90	84	86	94	102	91	89	101
64	73	67	62	74	78	77	76	84	90	84	79	89	101	89	96	103
66	74	63	61	65	65	66	67	73	80	84	73	82	78	75	70	98
60	63	62	59	59	62	63	65	68	68	66	71	79	68	82	72	87
	55	54	53	51	52	54	53	58	71	56	60	71	66	77	71	84
	53	51	55	48	47	48	47	54	56	52	63	56	65	69	67	82
		49	45	45	47	45	48	56	58	48	67	52	71	72	69	90
		49		47	47		49	56	50	49	69	53	73	63	80	89
				47	48				56	57	71	65	84	78	88	86
									64	62		72		82	85	87
																89

Table 9

Temperature, Chlorinity, and pH Data - Saguenay River

Temperature °C

Stn.	20	19	18
	1.5	0.1	1.3
	1.4	1.4	1.4
	1.8	1.6	1.5
	1.7	1.8	1.5
	1.7	1.8	1.5
	1.9	1.8	1.5
	1.9	1.8	1.5
	1.3	1.7	1.5
	1.3	1.6	
	1.4	1.6	

Chlorinity ‰

Stn.	20	19	18
	6.2	8.8	14.9
	12.4	13.7	15.4
	16.1	15.9	16.1
	16.3	16.3	16.4
	16.6	16.6	16.6
	16.7	16.7	16.7
	16.8	16.8	16.7
	16.9	16.9	16.8
	16.9	16.9	16.8
	17.0	17.0	

Table 9 (contd.)

pH

Stn.	20	19	18
	7.68	7.76	7.92
	7.85	7.92	7.96
	7.88	7.94	7.96
	7.87	7.93	7.97
	7.87	7.92	7.98
	7.89	7.92	7.98
	7.89	7.92	7.99
	7.82	7.89	7.97
	7.83	7.90	
	7.83	7.90	

Table 10

Alkalinity and $CaCO_3$ Ion Product Data - Saguenay River

Stn.	Alkalinity ($\times 10^3$ moles/liter) 20	19	18
	0.84	1.16	1.81
	1.61	1.66	1.92
	1.98	1.98	2.00
	2.02	2.01	2.03
	2.05	2.04	2.07
	2.08	2.05	2.07
	2.09	2.07	2.08
	2.10	2.10	2.08
	2.12	2.11	
	2.12	2.10	

Stn.	$[Ca^{++}] \cdot [CO_3^{=}]$ ($\times 10^6$) 20	19	18
	0.03	0.07	0.39
	0.22	0.30	0.47
	0.45	0.52	0.53
	0.45	0.52	0.57
	0.47	0.53	0.60
	0.50	0.53	0.60
	0.52	0.55	0.62
	0.44	0.52	0.60
	0.46	0.53	
	0.46	0.53	

Table 11

Average of results for 23 Stations in the Labrador Sea

Depth (m)	$[Ca^{++}]$ ($\times 10^2$ M)	$[Ca^{++}]/Cl\%$	$[CO_3^{=}]$ ($\times 10^4$ M)	pCO_2 ($\times 10^4$ atm)	$[Ca^{++}] \cdot [CO_3^{=}]$ ($\times 10^6$)	Percent saturation of $CaCO_3$
0	1.04	0.0217	1.40	3.2	1.45	190
	± 0.02	± 0.0005	± 0.05	± 0.2	± 0.07	± 10
10	1.04	0.0217	1.40	3.2	1.45	190
20	1.04	0.0217	1.45	3.2	1.50	190
30	1.04	0.0217	1.50	3.0	1.55	200
50	1.05	0.0218	1.35	3.3	1.40	180
75	1.05	0.0218	1.35	3.4	1.40	180
100	1.05	0.0218	1.30	3.4	1.35	180

Thus one needs only consider the salinity effect on the solubility product. An estimate of this can be made from an equation of Hindman (1942):

$$pK'_{CaCO_3} = 8.290 - \frac{4.762\sqrt{\mu}}{1.1143\sqrt{\mu}} \quad \text{at } 25^{\circ}C \qquad (2)$$

Hindman states that the second term on the right of this equation is not temperature dependent over the range 15-30°C and it is assumed here that this holds down to 5°C. The first term on the right of equation (2) may be identified with the thermodynamic solubility product of $CaCO_3$ and the second term with log $\gamma_{\pm}(CaCO_3)$ but this is not justified at the high ionic strength of sea water. It should be understood that Hindman's equation is purely empirical and was devised to fit experimental results for $\mu > 0.1$. It can not be expected to hold in more dilute solutions where forces treated in the Debye-Huckel theory are dominant, because the constants 4.762 and 1.143 have no relation to the Debye-Huckel constants that must apply at low concentrations.

The variation of K'sp calcite with μ at constant temperature follows from subtraction of equation (2) from itself at two ionic strengths x and y.

$$K'sp_{(\mu=x)} \cdot \text{antilog}\left(-\frac{4.762\sqrt{x}}{1+1.143\sqrt{x}}\right) =$$

$$K'sp_{(\mu=y)} \cdot \text{antilog}\left(-\frac{4.762\sqrt{y}}{1+1.143\sqrt{y}}\right) \qquad (3)$$

and if K'sp at y = 0.708 (Cl‰ 19) is taken as 0.72×10^{-6} at 0-4°C, then

$$K'sp_{(\mu=x)} = \frac{0.67 \times 10^{-8}}{\text{antilog}\left(- \frac{4.762 \sqrt{x}}{1 + 1.143\sqrt{x}} \right)} \qquad (4)$$

where x is obtained from the Lyman and Fleming (1940) equation

$$x = \mu = .00147 + .03592\ Cl + .000068\ Cl^2 \qquad (5)$$

Equations (4) and (5) have been solved to show the dependence of K'sp $CaCO_3$ on chlorinity. As is apparent from Fig. 25, the variation of K'sp with Cl‰ is almost linear.

The solubility product appropriate to the in situ chlorinity has been used in calculation of percent saturation from the field data. The expression is:

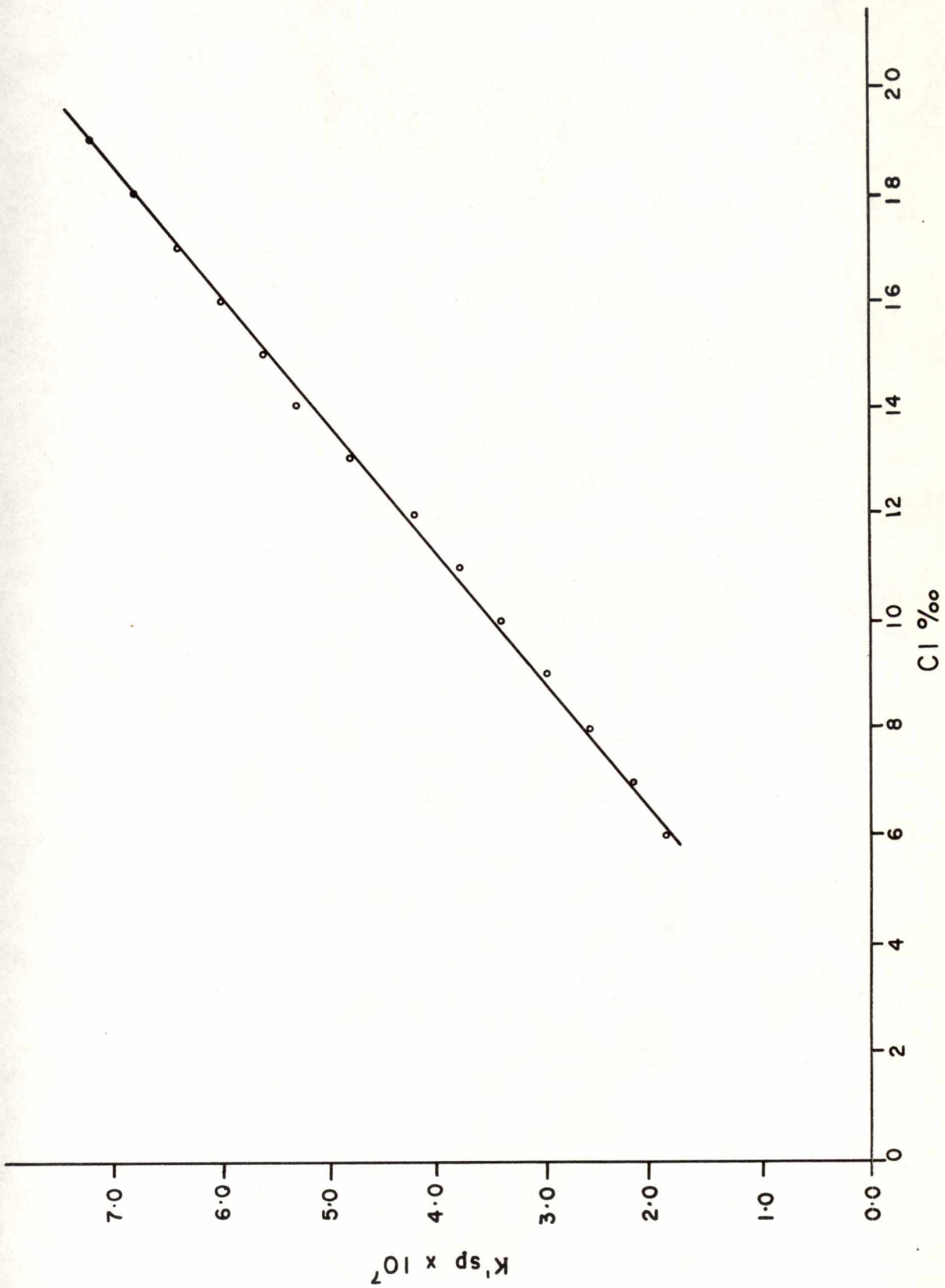
$$\frac{[Ca^{++}] \cdot [CO_3^{=}]}{K'sp\ (\text{at in situ Cl‰})} \times 100 = \text{percent saturation} \qquad (6)$$

(d) Distribution of Dissolved Calcium Carbonate in the St. Lawrence and Saguenay Rivers

The saturation state of the St. Lawrence and Saguenay Rivers with respect to calcite is indicated in the space between the $[Ca^{++}] \cdot [CO_3^{=}]$ ion product contours on Figures 10 and 24.

A general trend to lower saturation state is apparent from Cabot Strait (Station 1) to the head of the Saguenay River (Station 20), with values decreasing from 140% saturation to 50% saturation. The fresh water of the surface layer in the Saguenay is still further

Fig. 25



Variation of K'sp Calcite with Chlorinity at 0 - 5°C

undersaturated, but the error in obtaining K'sp at such low salinities reduces the accuracy of the saturation estimate. The saturation values in the St. Lawrence may be compared with the open ocean value of 180% to 200% saturation in the Labrador Sea.

In the St. Lawrence the saturation is lower in the bottom water than at the surface, while in the Saguenay the saturation approximately correlates with chlorinity. Alkalinity and chlorinity have similar distributions, as expected. The pH distribution (Fig. 22) of the Saguenay stations can be explained as a result of the transition from more basic saline water to more acidic fresh water.

A study of Fig. 17 shows that pH decreases with depth in the St. Lawrence in a manner that does not correlate well with chlorinity. Quite low pH values occur near the mouth of the Saguenay, where bottom values are about 7.60 pH units.

No justification for this low pH has been found, but a sufficient number of stations were done in the region to indicate that the values are not in error. All measurements have been made at depths less than 500 meters, so that, according to Buch and Gripenberg (1932) and the calculations of Owen and Brinkley (1941), pressure changes cannot account for the pH and K'sp calcite distributions.

The calcium carbonate distribution reflects mainly the pH variation, with a secondary effect from salinity variation. This

distribution could be quite different in the warmer months when the St. Lawrence has a temperature stratification, as temperature would then be a significant variable.

Deviations from saturation with respect to calcite in the St. Lawrence River were so small that rapid solution or inorganic precipitation could not occur. A tendency toward greater biological $CaCO_3$ deposition should exist near Cabot Strait and perhaps produce more calcium carbonate in the sediments. Many plants and animals continue to form calcareous parts in undersaturated water so that none of the recent St. Lawrence sediments should be free of calcium carbonate. Introduction of detrital calcium carbonate from the country rock would alter the above deposition pattern considerably. Nota and Loring (1964) have recently observed the $CaCO_3$ content of St. Lawrence sediments and found an increase in $CaCO_3$ from the Saguenay to Cabot Strait, in agreement with the above conclusions. This agreement may result from the compensation of many interfering factors.

Any but the most tenuous geological conclusions would require surveys in the Gulf of St. Lawrence at other seasons to determine whether the same saturation states are maintained throughout the year.

(e) Carbon Dioxide Exchange

Studies on carbon dioxide exchange were not made on the St. Lawrence cruise. Some generalizations on CO_2 exchange were made for the Labrador Sea area. (MacIntyre and Platford (1964)).

Recent work by Hood et al. (1959) has cast some doubt on the use of pCO_2 calculated from pH and alkalinity, since surface waters often yield quite different values when direct infra-red determinations of pCO_2 in equilibrium with the water are made. This means that in sea water the hydration of CO_2 may be quite slow. Recent studies of CO_2 exchange by Takahasi (1961), Keeling et al. (1965), and Waterman (1965) have been carried out using direct measurement of pCO_2 in the water.

Direct measurements of CO_2 exchange was not undertaken because an infra-red gas analyzer was not available. Also the matter was incidental to the study of dissolved calcium carbonate, in which the only concern is for the portion of carbon dioxide in equilibrium with carbonic acid. The considerations of Hood et al. (1959) preclude the use of pCO_2 as a measurement for fixing the dissolved carbonic acid species, because the pCO_2 measured may not be an equilibrium value. This implies that stoichiometric dissociation constants independent of pH measurements as suggested by Dr. P. Williams (private communication) would not be useful for field studies.

(f) Test of the Wattenberg Relation

Triplicate analysis of samples from the surface, ten meters and twenty meters for a station in the Saguenay are given in Table 12. The calcium concentrations from the Wattenberg relation (equation(1)) are in good agreement with those from titration at $Cl‰ > 16$, but there is a greater divergence at lower chlorinities. At $Cl‰ \simeq 6$ the $[Ca^{++}]$ from titration is about 7% lower than the Wattenberg value. This large deviation is barely acceptable because it introduces a corresponding error in the ion product. Fortunately most stations in this survey have $Cl‰ > 15$ so the above discrepancy has not been a practical problem.

The trend of the results is difficult to explain. River water which has leached the country rock should have gained a quantity of calcium and very little chloride ion. That is, $[Ca^{++}]/Cl‰$ should be greater for river water in the surface layer of the Saguenay than for the more oceanic St. Lawrence water below. The results indicate that $[Ca^{++}]/Cl‰$ is lower at the surface than at twenty meters, if the titration $[Ca^{++}]$ is correct. The Wattenberg calcium cannot show a trend as it is based on the assumption that the calcium to chlorinity ratio is constant. The author believes that there were no systematic errors in the titrations of sufficient magnitude to produce the above trend.

Table 12

Comparison of $[Ca^{++}]$ from Wattenberg's Relation with $[Ca^{++}]$ from EDTA* Titration after Ion Exchange Separation

	mls EDTA	Cl‰	Titration $[Ca^{++}]$	Wattenberg $[Ca^{++}]$
		Surface		
a	2.09	6.17	0.312	0.336
b	2.11	6.17	0.315	0.336
c	2.10	6.17	0.314	0.336
		Ten Meters		
a	4.32	12.36	0.647	0.668
b	4.34	12.36	0.650	0.668
c	4.34	12.36	0.650	0.668
		Twenty Meters		
a	5.86	16.14	0.877	0.866
b	5.80	16.14	0.868	0.866
c	5.78	16.14	0.865	0.866

* Normality of EDTA = 0.01497

(Samples from Station 20 (Saguenay River))

(a, b, and c are separate portions of water sample).

(g) Comparison of Direct and Indirect Alkalinity Titrations

Since Station 20 in the Saguenay was sheltered, providing a stable laboratory, and a large range of alkalinities were found by the method of Anderson and Robinson (1946), the situation was ideal for a check of the alkalinity results against alkalinities from direct titration. Calculations made before the cruise were applied to determine the proper pH of the end point in the direct alkalinity determinations.

The alkalinity end point is clearly shown by Sillen's (1959) presentation of titration conditions. When the solution reaches the alkalinity end point the principal species must be H_2CO_3. Sillen gives a logarithmic diagram for carbonic acid from which the relation $[H^+] = [HCO_3^-]$ at the alkalinity end point may be read directly.

This can be proven in another way from a statement of electroneutrality for sea water

$$[\Sigma \text{cations}] + [H^+] = [\Sigma \text{anions}] + [OH^-] + [HCO_3^-] + 2[CO_3^{=}] \qquad (7)$$

By definition, alkalinity is the excess of $[\Sigma \text{cations}]$ over $[\Sigma \text{anions}]$ and therefore at the alkalinity end point:

$$[\Sigma \text{cations}] = [\Sigma \text{anions}] \qquad (8)$$

and since $[CO_3^{=}]$ and $[OH^-]$ must be small in relation to the

other species present at the alkalinity end point, thus:

$$[H^+] = [HCO_3^-] \qquad (10)$$

From this and the definitions of K'_1, K'_2 and ΣCO_2 it may be easily shown that:

$$[H^+]^2 + K'_1 [H^+] + K'_1 K'_2 = \Sigma CO_2 \cdot K'_1 \qquad (11)$$

It is then assumed that the alkalinity from the Anderson and Robinson method is approximately correct. The total carbon dioxide is calculated from the relation:

$$\Sigma CO_2 = \frac{\text{Alk} \times \left(a'_H + K'_2 + \frac{a_H^2 \alpha_s}{K'_1 a_{H_2O} \alpha_o} \right)}{(a'_H + 2K'_2)} \qquad (12)$$

using the tables of Strickland and Parsons (1960) which give the result as a function of the in situ pH, temperature and chlorinity. ΣCO_2 and the K' values of Lyman (1956) are then substituted in equation (11) which is solved for $[H^+]$ and the result converted to pH. The end point pH is dependent on the environment and composition of the water mass sampled. The final calculation of the proper end point therefore has to be made after the initial alkalinity determination.

Anderson and Robinson alkalinities, the end point pH for direct titration and alkalinities by direct titration for the samples from Station 20 follow in Table 13.

Table 13

Comparison of Direct and Anderson and Robinson (1946) Alkalinities

Depth (m)	Anderson and Robinson Alk x 10^3 moles/liter	pH end pt.	Direct Titration Alk x 10^3 moles/liter
0	0.84	4.68	0.85
10	1.61	4.50	1.59
20	1.98	4.44	2.01
30	2.02	4.43	2.05
40	2.05	4.43	2.08
50	2.08	4.42	2.10
75	2.09	4.42	2.11
100	2.10	4.42	2.12
150	2.12	4.42	2.13
200	2.12	4.42	2.13

Strickland's tables for equation (12) were not calculated for Cl‰ < 15, so the equation had to be calculated for the first two samples of Table 13. The required K' values were interpolated from Lyman's (1956) tables and the values of $\frac{\alpha_s}{\alpha_o}$ were obtained at low chlorinities by combining the values of Buch (1951) with those of Harned and Davis (1943).

Comparison of the direct and calculated alkalinities shows fair agreement. The alkalinity resulting from the Anderson and Robinson method thus is of sufficient accuracy for survey purposes. In the laboratory it appears bes t to use the direct titration method. However, it must be realized that the K's of carbonic acid are needed to calculate the end point in the direct titration, but the error introduced by application of incorrect dissociation constants in the direct titration method should be less than in the Anderson and Robinson method. Also one must do a preliminary titration to obtain an approximate alkalinity and ΣCO_2. The ΣCO_2 is then used in the end point calculation as above. For open ocean water the end point is $\simeq$ pH 4.40 and the preliminary titration can be omitted.

CHAPTER VIII

CONSIDERATIONS ON pH MEASUREMENT OF SEA WATER

(a) The temperature correction of pH

The usual method of pH determination of sea water samples is given by Strickland and Parsons (1960). Samples are taken with Knudsen or Nansen bottles. Reversing thermometers give the in situ temperature. Samples are taken from the bottles as quickly as possible and stored in stoppered polyethylene containers until room temperature is reached. The pH meter is standardized at room temperature and the pH of the water then measured. The relation of Buch and Nynas (1939) is used to correct from room temperature to insitu pH. This procedure has two important weak points; loss of carbon dioxide during warming of the sample must be prevented in order to obtain an accurate pH, and the relation of Buch and Nynas must be quite exact if the difference in temperature between the sea and laboratory is large.

During the St. Lawrence cruise the pH procedure was varied accidentally when the author failed to allow samples to warm before measuring the pH. Standardization had been carried out carefully at room temperature. The in situ temperature was about 2°C and the samples were measured without warming more than 4°C. The temperature at each pH measurement was recorded.

Duplicate samples were taken at the next station, the meter standardized at room temperature and one set of samples was measured without warming. The other set was allowed to reach room temperature before taking pH, (the usual procedure). Only small differences were found, and these always gave the pH as 0.01 - 0.02 units more basic in solutions that had been allowed to warm.

Table 14

pH Before and After Warming Water Samples

Stn. 16			Stn. 17		
Depth	Before	After	Depth	Before	After
0	7.76	7.77	0	7.76	7.78
10	7.79	7.80	10	7.76	7.78
20	7.79	7.80	20	7.77	7.79
30	7.78	7.80	30	7.77	7.77
50	7.80	7.82	50	7.75	7.76
75	7.78	7.80	75	7.69	7.70
100	7.70	7.72			
150	7.62	7.64			
200	7.60	7.62			

The results of the above table were corrected from room temperature to in situ temperature whether or not the sample was brought to room temperature because the meter was standardized at room temperature.

Further test of this phenomenon were made after the cruise using the same electrodes. The measurements were carried out

by another worker to avoid personal bias. The procedure was as follows: A Dewar flask and five polyethylene bottles were filled with water from the Bedford Basin. The samples were returned to the laboratory within 15 minutes, the pH meter was standardized in the usual way at room temperature and the pH of each bottle taken after a definite warming time.

	pH	t(mins)	T(°C)
Dewar flask	7.806	0	2.7
Bottle 1	7.806	5	11.5
Bottle 2	7.817	20	14.5
Bottle 3	7.828	35	15.3
Bottle 4	7.825	50	16.5
Bottle 5	7.83	90	22.0

(Recheck on buffer at $t = 95$ min.)

The meter remained stable during the experiment. It thus appeared that the sea water used showed a pH value nearly independent of the temperature, although the small pH increase could be a result of CO_2 loss while warming. To test the phenomenon further, the N.B.S. buffers were measured at various temperatures with the meter standardized at room temperature.

Standardization at 25°C with 4.01 and 9.18 buffers was followed by measurement of buffers that had been cooled in a refrigerator to 0°C. The buffer was measured at regular intervals during the warming period. When it had warmed to the standardization temperature the true pH should have been obtained.

Two runs were done, the first with cooled pH 9.18 buffer, the second with cooled 4.01 buffer.

First		Second	
pH	Temp°C	pH	Temp°C
9.09	5.7	4.00	4.0
9.09	8.0		
9.10	9.6		
9.11	11.0	4.005	10.0
9.13	14.0		
9.16	17.0		
9.17	18.5	4.01	25.0 (stand. temp.)
9.18	20.0		
9.19	25.0 (stand. temp.)		

The results indicated that the pH 4.01 buffer behaved similarly to sea water on warming, but that the pH 9.18 buffer did not. The phenomenon might be tentatively related to the temperature dependence of the buffers, those buffers with the greatest temperature dependence showing the greatest change on warming. However, the change on warming has been observed with standardization at room temperature, while the temperature dependence of the N. B. S. buffers is determined with standardization at the temperature of measurement (Bates (1964)). Any correlation between the two variations with temperature must be empirical, and could be checked if the temperature dependence of sea water were known under conditions of N. B. S. standardization.

Further study of the pH change of sea water on warming would require tests with many buffers and electrode systems. The

investigation was terminated without establishing whether other electrodes with different responses than the one used would yield the same result.

It appears that one can select an electrode that will perform as above. If so, the pH of a water sample can be measured without warming and the loss of CO_2 thus avoided.

After the pH has been determined in the laboratory it is corrected to the insitu pH from the tables of Buch and Nynas (1939). The accuracy of pH measurements in sea water is dependent upon these corrections which appear to have been accepted by later workers without further study.

Buch and Nynas obtained the temperature coefficient of pH in sea water from the relation:

$$\frac{1 + \frac{a_H}{K_{c1}} + \frac{K'_2}{a_H}}{1 + \frac{2K'_2}{a_H}} = \frac{\Sigma CO_2}{CO_3 \text{ Alk}} = A' \qquad (1)$$

The variation of K_{c1} and K'_2 with temperature and salinity was taken from the work of Buch et al. (1932). Dissociation constants for 20°C were inserted in the expression and A'was calculated for various values of a_H and Cl‰ . Buch and Nynas assumed that the resultant A' values were almost constant over the range 0-30°C, because they wanted the variation of pH at constant ΣCO_2.

The constancy of A' values is apparent if equation (1) is written as:

$$\frac{\sum CO_2}{[HCO_3^-] + 2[CO_3^=]} = A' \qquad (2)$$

and since Buch and Nynas' tables show that the maximum Δ pH over the 30°C interval is 0.3 pH units, this Δ pH is not sufficient to alter the denominator significantly in the presence of the twenty fold excess of bicarbonate over carbonate in sea water.

Dissociation constants for various salinities at temperatures 0, 10, and 30°C were substituted in equation (1) and the A' values were known from above. The pH at each chlorinity and temperature was obtained by solving equation (1). From this information a table was constructed for α (the temperature coefficient of pH). This temperature coefficient is used in the correction equation:

$$pH_{\text{in situ}} = pH_{lab} - \alpha(T_{\text{in situ}} - T_{lab}) \qquad (3)$$

Buch and Nynas' temperature coefficients depend on the accuracy of the dissociation constants. If Lyman's constants were used, α would be slightly different. Definition of constant $\sum CO_2$ is necessary in the study of a buffer equilibrium that involves a gas. However, there must be some variation in carbonate alkalinity with temperature. Buch and Nynas accept this error inherent in their method by stating that A' is almost constant with temperature.

A better temperature coefficient of pH or at least a confirmation of the results of Buch and Nynas should be given by the following method.

Sea water of known $\lesssim CO_2$, temperature, and chlorinity can be considered as a buffer and standardized against the N. B. S. buffers at temperatures from 0-35° C. The partial pressure of CO_2 over the water must be regulated to keep the $\lesssim CO_2$ constant. Higher pressures would be required at higher temperatures, where CO_2 is less soluble.

Repetition of the procedure with waters of different chlorinity and $\lesssim CO_2$ would yield data for a table similar to that of Buch and Nynas, because the standardizations would give pH as a function of temperature for each $\lesssim CO_2$ and chlorinity. The standardization technique has the advantage that dissociation constants are not used. Checks on the constancy of $\lesssim CO_2$ can be made by direct analysis.

An ideal test of the temperature coefficient for near surface waters would be to measure the in situ pH directly and compare this with the laboratory pH. This could be done most efficiently by measuring the in situ temperature, collecting the sample isothermally (Dewar flask) and returning it to the lab within a few minutes, where the pH would be measured with a meter

standardized at the in situ temperature. The sample would then be allowed to warm to laboratory temperature with precaution against change in ΣCO_2, and the pH determined with standardization at that temperature. The temperature coefficient of pH from this direct method should be close to that given by the tables.

The use of the Buch and Nynas tables to correct pH to a different temperature may appear unjustified since pH measured at one temperature has no quantitative significance relative to the pH at a different temperature (Bates (1964)). However the dissociation constants used in the calculation of temperature coefficients were themselves established by standardization at the temperature of pH measurement. In the pH correction one is simply correcting from measurement with standardization at one temperature to that with standardization at another temperature. This is more obvious for the proposed temperature coefficient calculation from buffer comparison. The correction from one standardization temperature to another is intended to alter the pH to a pH in situ that may be used with the in situ dissociation constants to calculate concentrations of dissolved species. It must not be presumed that one is correcting the acidity of the sea water.

(b) pH With High Ionic Strength Buffers

The present practice among oceanographers is to use the normal standardization technique with N. B. S. buffers to make a pH measurement in sea water yielding an a'_H that is neither equal to $[H^+]$ nor to the true a_H. Lyman (1956) has been the first to note this point on the basis of the work of Bates (1954).

pH is normally defined from the equation

$$pH = pH_{(s)} + \frac{(E_x - E_s)F}{RT \ln 10} \qquad (4)$$

Standard potentials including the liquid junction potentials at the calomel electrode must be equal for the E_s measurement in the dilute buffer and for E_x measurement in the sea water of $\mu =$ 0.7, if pH is to equal pa_H. Also in establishing the $pH_{(s)}$ $(=pa_H)$ for N. B. S. buffers with hydrogen-silver chloride cells without liquid junction, non-thermodynamic assumption of individual activity coefficients is required, but the solutions are sufficiently dilute to permit calculation.

There is no accurate means for evaluating the standard potential of the H_2-calomel electrode system, but as Lyman (1956) has observed there may be quite large deviations from the true pa_H when sea water is measured. The unknown and incalculable (at present) liquid junction potentials are responsible for most of the difference between the a'_H measured and the true a_H.

Fortunately, as Lyman and Keeling (personal communication) have noted, the quasi thermodynamic constants, e.g.

$$K'_1 H_2CO_3 = \frac{a'_H [HCO_3^-]}{[H_2CO_3]} \qquad (5)$$

can be used with a'_H measured in sea water to calculate the concentrations of the carbonic acid species. This is because a'_H has been used in the evaluation of the constant. The procedure is internally consistent, but a'_H is neither a concentration nor an activity.

At present Keeling (personal communication) is carrying out determinations of the dissociation constants of carbonic acid without using pH measurement. Other workers at present also favor this line of thought for concentrated ionic solutions. Keeling intends to obtain:

$$K'_1 H_2CO_3 = \frac{[H^+] [HCO_3^-]}{[H_2CO_3]} \qquad (6)$$

a true concentration constant.

If constants such as those of Keeling eventually come into use an estimate of $[H^+]$ rather than a'_H would be required of field pH measurements in order to maintain consistency and to yield correct calculated concentrations. Also the use of hydrogen ion concentration is apparently quite satisfying to biologists.

A possible measure of $[H^+]$ in sea water evolved from consideration of a statement by Bates (1964), "..., the use of buffers of low

concentration in an aqueous salt medium of high ionic strength may be advantageous when the main variable is to be hydrogen ion concentration".

Correspondence with Bates aided in the formulation of a method for $[H^+]$ measurement based on the use of high ionic strength buffers. A 0.01 M strong acid (HCl or $HClO_4$) dissolved in synthetic sea water serves as the primary standard buffer. This standard is made by titration with a known base and has an $[H^+]$ = 1×10^{-2}M. The strong acid would normally cause a liquid junction potential at the calomel electrode widely different (0.03 pH units) from that if a dilute N.B.S. type buffer were used. However, if the comparison is made with both acid and N.B.S. buffer dissolved in sea water the difference in junction potential must be much less because t_H (the transference number of the hydrogen ion) has less control over the junction potential E_j. This may be seen from:

$$-E_j = \frac{RT}{F} \int_{\text{SOLN. X.}}^{\text{SAT. KCl}} \frac{t_i}{z_i} \, d \ln a_i \qquad (7)$$

Since E_j is similar for the N.B.S. type buffers in synthetic sea water and for the primary standard acid, the N.B.S. type buffers in synthetic sea water can be used as secondary standards. They do not have the N.B.S. pH value, due to salt effects, and must

be determined by comparison with the primary standard in a cell such as that used by Bates, Pinching, and Smith (1950):

Pt; H_2 , Primary Standard / Satd. KCl /

Secondary Standard, H_2; Pt. (A)

This comparison should be carried out for synthetic sea waters of various ionic strengths in the natural oceanic range and for temperatures 0-35°C. The resulting pH values of the secondary standards should also yield $[H^+]$ because the activity coefficient of the hydrogen ion should be nearly the same in both primary and secondary high ionic strength buffers.

Then a normal glass electrode system,

Glass; Soln. X / Sat. KCl; calomel (B)

where Soln. X is either a secondary standard buffer or the solution to be measured, can be used in the usual way.

$$\text{i.e. (pH unknown-pH stand.)} = \frac{(E \text{ unknown} - E \text{ stand.})F}{RT \ln 10} \qquad (8)$$

and

$$\text{(pH unknown-pH stand.)} - -\log [H^+]_{\text{unknown}} + \log [H^+]_{\text{stand.}} \qquad (9)$$

The above method is dependent on the invariance of junction potentials, as in the ordinary method, so the position might appear to be altered without improvement. However the E_j constancy is

more plausible for the high ionic strength buffer system with its resulting $[H^+]$.

The synthetic sea water used to dilute the buffers should contain no $NaHCO_3$. If any bicarbonate is present the buffers will receive a significant contribution from an undesired source. This is particularly harmful in the standardization of secondary buffers from the primary standard with cell (A) because the hydrogen electrodes gradually remove CO_2 and alter the buffer system. When the secondary buffers are used in cell (B) for $[H^+]$ measurement of sea water, there is thus a slight difference between the ionic media of the buffer and unknown, but this difference is certainly not great enough to have an effect on the junction potential.

The buffers that may be used as secondary standards in synthetic sea water must not form insoluble salts with ions of the sea water. For example, the phosphate buffers form insoluble calcium phosphate. It is best to bracket the pH of an unknown with buffers, but there are few available buffers for the pH range 7 - 9. The loss of the phosphate buffers is unfortunate because the pH of sea water lies in the pH 8 region.

For buffers producing precipitates, the sea water can be modified. This must be done in such a way that the liquid junction potentials of cells (A) and (B) are independent of the particular

synthetic sea water used, and are close to the potential values for normal sea water. In the case of the phosphate buffers, the alkaline earths would be omitted and the solution brought to the ionic strength of sea water by NaCl addition. The aim is thus to fix the ionic strength of the buffer and to maintain its composition as similar as possible to a bicarbonate free Lyman and Fleming (1940) synthetic sea water.

A more attractive alternative is the exclusive use of buffers compatable with sea water. Preliminary tests showed that, at buffer concentrations used by Bates, Pinching, and Smith (1950), precipitates were not formed in bicarbonate free synthetic sea water with these buffers:

KH Tartrate	pH - 3.6
NaH Succinate Na_2 Succinate	pH - 5.4
$Na_2B_4O_7$	pH - 9.2

Bates (personal communication) suggested 2-amino-2-(hydroxymethyl)-1,3 - propanediol, (THAM), and its hydrochloride salt as a buffer for the range 7.5 - 8.0 compatable with sea water. Potassium acid phthalate is also compatable with sea water, and has a low temperature coefficient of pH. Phthalate is reduced at platinized electrodes, but the difficulty can be avoided by using palladinized electrodes.

The scheme for pH measurement outlined above would require considerable time to investigate thoroughly. Various synthetic sea waters should be used to detect effects on liquid junction potentials. Other buffers should be sought, as those suggested above may have undesirable properties.

The author hopes to pursue the determination of hydrogen ion concentration with high ionic strength buffers and to apply the results to sea water.

CHAPTER IX

SPECTROPHOTOMETRIC DETERMINATION OF CARBONATE

(a) Description of Method

As noted in Chapter VI, difficulties arise in the determination of carbonate by the pH-alkalinity method. Other methods which would give at least partially independent measurements of carbonate were sought. The only hope appeared to lie in the use of some property which HCO_3^- and $CO_3^=$ possess to different degrees, thereby permitting them to be distinguished without a direct utilization of their relative acidities. One method considered was based on the work of Underwood and Howe (1962) who found that carbonate ion absorbs in the ultraviolet region much more strongly than bicarbonate ion or carbon dioxide. They developed spectrophotometric titrations for carbonate and bicarbonate based on the change in absorbance when acids (or bases) were added. Greater precision was claimed for the spectrophotometric technique than could be attained in a potentiometric titration. The data given indicate that the photometric method is markedly superior in its ability to locate the end point in carbonate determinations with a large excess of bicarbonate.

About tenfold excess of bicarbonate over carbonate exists in normal sea water. Potentiometric detection of the end point

at which carbonate is converted to bicarbonate cannot be carried out in sea water with the required accuracy.

Underwood and Howe's method was modified slightly and applied to the determination of carbonate ion in sea water. It was realized that the carbonate concentration range of $1\text{-}2 \times 10^{-4}$ M must lie at the extreme lower limit of the method from considerations of Underwood and Howe, who were unable to obtain accurate results in solutions where carbonate was less than 3×10^{-3}M. They explained this by noting that the product of the concentration and dissociation constant of a weak acid should be about 10^{-12} in order to show a clear end point. Also the product must be greater than 10^{-13} to show a break in the titration curve. Since the dissociation constants of carbonic acid are greater in sea water than in distilled water, the product CK'_2 of sea water is $\simeq 10^{-13}$ for a carbonate concentration of 1×10^{-4} M. It was thus clear that there was no guarantee of success, and that a fair experimental trial was necessary.

This trial was made according to the method of Underwood and Howe, in which hydrochloric acid is titrated into carbonate solutions contained in a quartz cell located in the sample compartment of a Beckman D. U. spectrophotometer. The absorbance is measured after each increment of HCl. The end point is the point

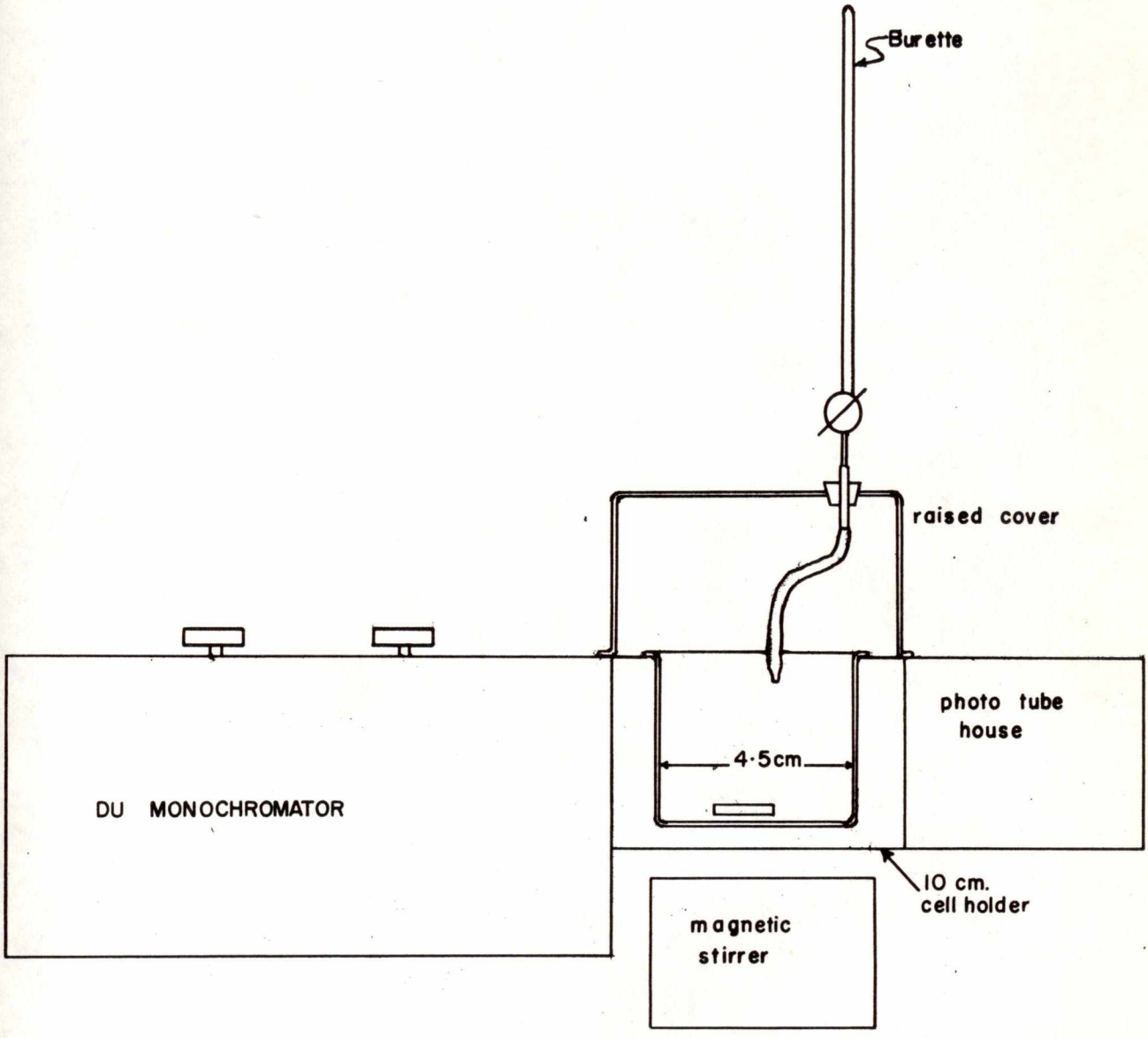
at which the absorbance remains constant with further addition of acid. The volume of HCl required to reach this end point is a direct measure of the carbonate concentration. Also, for a particular cell, wavelength, and temperature, the change of absorbance from start of the titration to the end point is proportional to the carbonate ion concentration, from Beer's law.

(b) Experimental - Series 1 and 2

The apparatus was arranged as described by Underwood and Howe (1962) except that a quartz beaker was used in preference to one of "Vycor". The assembly shown in Fig. 26 was found to have one defect not mentioned by previous authors. Oscillations of the D. U. meter needle were created when the stirrer magnet rotated slowly. It was found that these oscillations could be eliminated if the stirrer was operated at speeds sufficiently great that needle damping effectively reduced their amplitude. Thus titrations were carried out at appreciable stirring speeds, but it was always possible to avoid vortex formation.

Standard carbonate solutions were produced by adjusting the pH of bicarbonate solutions. Sodium bicarbonate solutions of normalities 0.05, 0.01, 0.005, 0.001, and 0.0005 were prepared and separate portions of each of these were brought to pH's 9, 10, and 11 by the addition of CO_2-free NaOH. This NaOH (about 0.1 N)

Fig. 26



Spectrophotometric Carbonate Titration Assembly

was prepared by dilution of the supernatant liquid of saturated NaOH with boiled distilled water. This was then run through an anion exchange column (Fisher Rexyn R. G. 1) prepared as suggested by Powell and Hiller (1957) to remove traces of carbonate, and stored in a large polyethylene bottle. Ascarite traps were fitted to the bottle so that the base could be pumped over to a burette without admission of air.

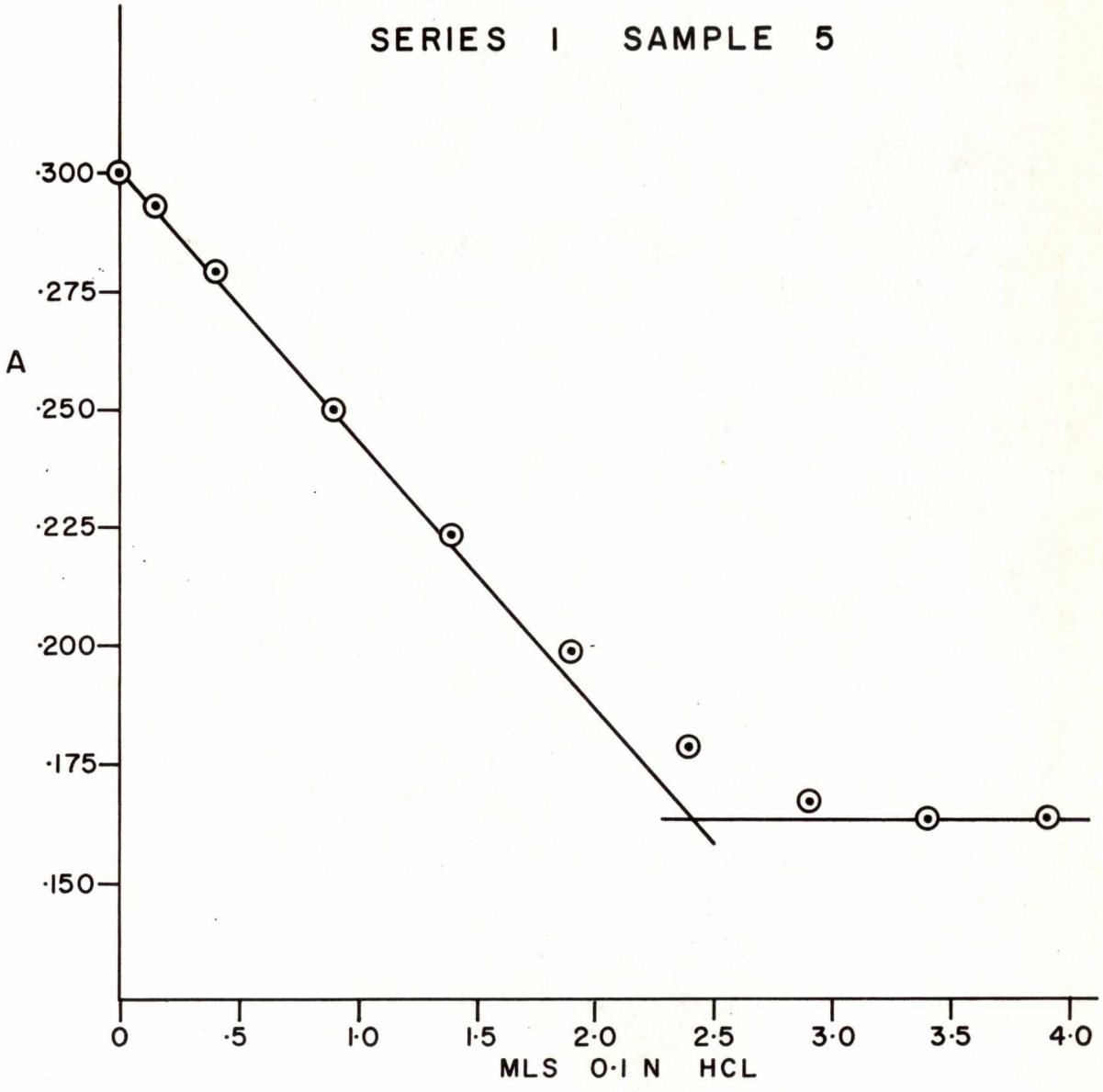
A fifty ml sample of carbonate solution was pipetted into the beaker, HCl of the required normality (0.1 or 0.01) was added in increments from the burette, and the absorbance recorded after the addition of each increment. The true absorbance against a distilled water blank was not required here. The absorbance was set at a convenient value and the change in absorbance during the titration recorded. All absorbances were read at 2300 Å wave length. A sample titration curve is shown in Fig. 27.

The $CO_3^{=}$ concentration was calculated as follows. It was assumed that $[HCO_3^-] \simeq \leqslant CO_2$ at sea water pH. It can then be shown from the dissociation constants of H_2CO_3 and the definition $\leqslant CO_2 = [H_2CO_3] + [HCO_3^-] + [CO_3^{=}]$, that:

$$[CO_3^{=}] = \frac{\leqslant CO_2 \quad K'_1 K'_2}{a_{H^+}^2 \quad + K'_1 a_{H^+} \quad + K'_1 K'_2} \qquad (1)$$

Series 1 was carried out with distilled water for which the carbonic acid dissociation constants given by Harned were employed.

Fig. 27



Titration of Carbonate

Series 2 was similar to Series 1 in all respects except that a 0.7 M NaCl solution was used. The dissociation constants used were:

Series 1

$K_1 = 4.45 \times 10^{-7}$ - Harned and Davis (1943)

$K_2 = 4.69 \times 10^{-11}$ - Harned and Scholes (1941)

Series 2

$K'_1 = 1.00 \times 10^{-7}$

$K'_2 = 7.5 \times 10^{-10}$ Lyman (1956)

All values given are for 25°C.

The carbonate concentration was also obtained from the number of equivalents of HCl needed to reach the titration end point. This was then compared with the concentration as calculated above.

(1) Results - Tables 15 and 16 show the results of Series 1 and 2. The values listed in the last column of the tables indicate the actual carbonate concentration from titrations. Change in absorbance during the titrations is given in the fourth column.

(2) Discussion - Carbonate concentrations were not as close to the calculated values as might be expected, particularly in Series 2. Also the results showed a greater degree of scatter than would be acceptable in an analytical method for carbonate. This scatter could be reduced by better handling techniques, but precision was sufficient for studying the feasibility of the method. Calculation and titration carbonate concentrations varied linearly with change in absorbance as expected, but the relation became less well defined as the carbonate concentration decreased.

Table 15

Titration of Series 1 with HCl

Sample No.	$NaHCO_3$ moles/liter	pH	$[CO_3^{=}]$ x10^4 calc.	ΔA	N HCl	mls HCl used	$[CO_3^{=}]$ x 10^4 from titration
1	0.05	10	157	.882	0.1	14.5	145
2	0.01	11	79.2	.293	0.1	5.5	55
3	0.005	11	39.6	.230	0.1	3.0	30
4	0.01	10	31.2	.148	0.1	2.4	24
5	0.05	9	22.3	.137	0.1	2.4	24
6	0.005	10	15.7	.070	0.1	1.2	12
7	0.001	11	7.9	.027	0.01	6.8	6.8
8	0.01	9	4.5	.026	0.01	4.5	4.5
9	0.0005	11	4.0	.022	0.01	4.0	4.0
10	0.001	10	3.1	.012	0.01	3.0	3.0
11	0.005	9	2.2	.007	0.01	2.1	2.1
12	0.0005	10	1.6	.006	0.01	1.5	1.5
13	0.001	9	0.4	.002	0.01	End pt. not sharp	
14	0.0005	9					

Table 16

Titration of Series 2 with HCl

Sample No.	$NaHCO_3$ moles/liter	pH	$[CO_3^{=}]$ x10^4 calc.	Δ A	N HCl	mls HCl used	$[CO_3^{=}]$ x10^4 from titration
1	0.05	10	04.41	.757	0.1	18.5	185.0
2	0.05	9	02.14	.253	0.1	7.0	70.0
3	0.01	11	98.7	.231	0.1	6.1	61.0
4	0.01	10	82.8	.176	0.1	3.7	37.0
5	0.005	11	49.3	.123	0.1	3.0	30.0
6	0.005	10	44.1	.119	0.1	2.1	21.0
7	0.01	9	43.0	.059	0.01	15.0	15.0
8	0.005	9	21.0	.025	0.01	6.5	6.5
9	0.001	11	9.8	.029	0.01	3.5	3.5
10	0.001	10	8.8	.016	0.01	3.4	3.4
11	0.0005	11	4.9	.013	0.01	2.3	2.3
12	0.0005	10	4.4	.010	0.01	2.5	2.5
13	0.001	9	4.2	.005	0.01	1.8	1.8
14	0.0005	9	2.1	.002			

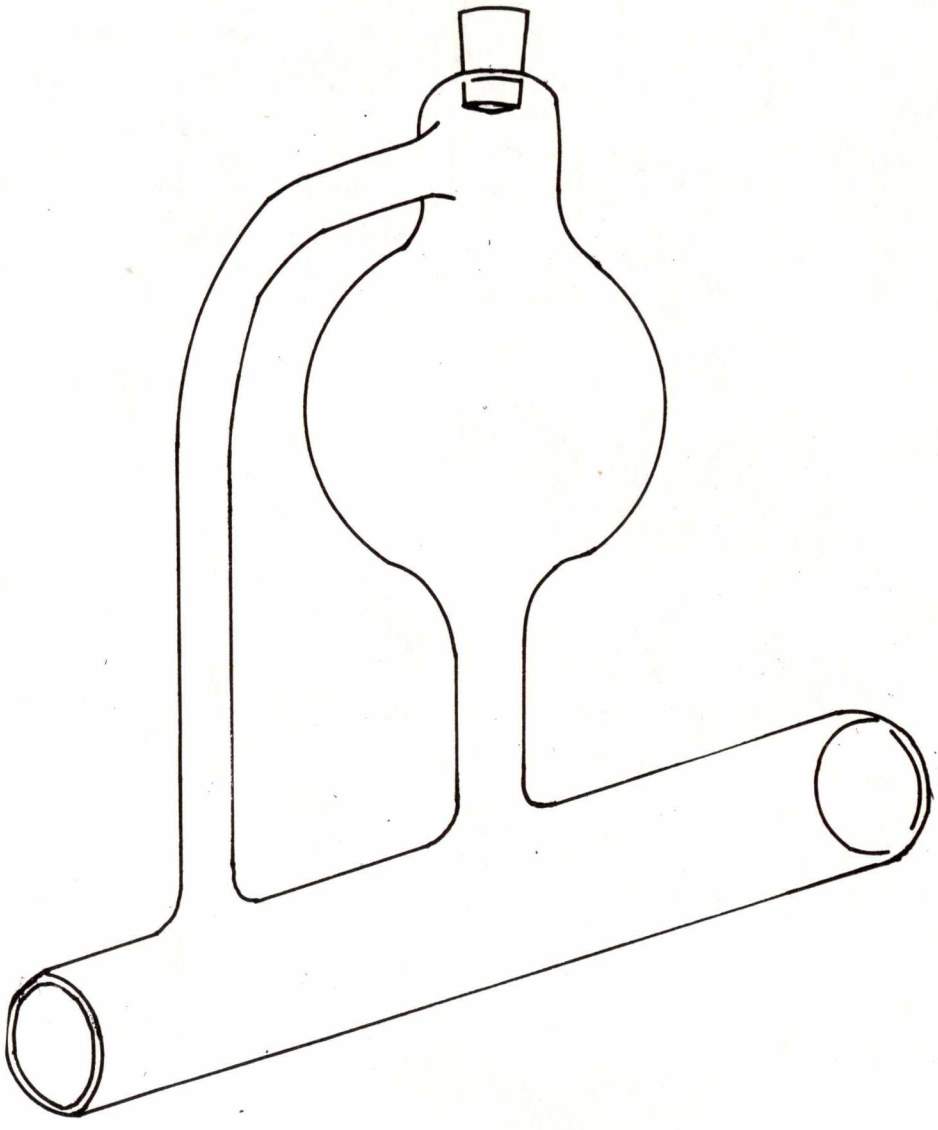
At about 2.5×10^{-4}M carbonate, the change in absorbance drops below 0.010 units. Carbonate cannot be determined in this region with accuracy better than $\pm$ 25% due to errors arising from limits of precision of the spectrophotometer and to absence of a sharp break in the titration curves. The method is therefore less useful than the pH-alkalinity method. There is no means of reducing the errors arising from the titration curve, but by increasing the length of the light path, absorbance might be increased so that instrument performance would be less critical.

(c) Experimental - Series 3 and 4

Series 3 and 4 were similar to the first two, but were adapted to measurement with a 10 centimeter light path. Titration in a beaker of 10 centimeter diameter is prohibited by the geometry of the D. U. assembly and by the inconveniently large volume of sample required.

In order to achieve the desired light path a standard Beckman 10 centimeter quartz cell was modified as shown in Fig. 28 so that HCl could be added and mixed in the cell. The main tube has a volume of about 30 mls while the bulb is a 40 ml mixing chamber. A special cell cover was made to permit the cell to be placed upright in the compartment.

Fig. 28



Ten Centimeter Cell with Mixing Chamber

Fifty ml samples were pipetted into the cell through the opening and the initial absorbance read. The cell was then removed, HCl added, the cell closed with a rubber cork and shaken to effect mixing. The absorbance was again read. This process could be repeated with successive additions of HCl to give a titration curve, but CO_2 from the atmosphere would be introduced at every shaking. To avoid this, HCl equivalent to the calculated carbonate concentration was added, the absorbance measured and the process repeated with successive 1 ml additions of HCl until there was no further change in absorbance.

The standard carbonate solution preparation used in Series 1 and 2 was found to lack the precision necessary for predicting volumes of HCl for the above scheme, so carbonate concentration was determined by alkalinity analysis in Series 3 and 4.

Solutions of $NaHCO_3$ were brought to a fixed pH as in the earlier series, using the same bicarbonate normalities. Two 50 ml aliquots of each sample were taken, one was analyzed by the standard pH-alkalinity method, the other placed in the absorption cell and treated as described above.

(1) Results - The method can only give a comparison of the change in absorbance (ΔA) with carbonate concentration, because the amount of HCl neutralized at the absorbance end point is not

accurately known. However, the carbonate concentration limit can be approximated as that concentration corresponding to $\Delta A = 0.010$.

Series 3 was carried out with 0.7 M NaCl. Lyman and Fleming synthetic sea water was used in Series 4, so samples had to be regulated to pH $<$ 9.0 to avoid precipitation of magnesium hydroxide. The results are shown in Table 17.

(2) Discussion - It is again apparent that with some care carbonate concentrations might be determined with fair accuracy in the 10^{-3} M range, but doubling the light path produces no improvement in the 10^{-4} M range. Experiments with a Beckman 50 centimeter cell have shown that no gains are made by going to a still longer light path. Cell positioning difficulties, inordinately large sample volumes, mixing problems, and light scattering from particles that could not be filtered from the samples, caused such wide variations in absorbances that no trend could be derived from the test series.

(d) Conclusions

The method of Underwood and Howe can be applied with no detected interference from the inorganic salts in synthetic sea water. The presence of dissolved organic material might alter this conclusion considerably. The lower limit for carbonate

Table 17

Titration of Series 3 with HCl

Sample No.	Initial pH	Alk x 10^3 moles/liter	$[CO_3^{=}]$ x10^4	ΔA
1	8.96	65.0	182	.559
2	10.92	20.4	101	.350
3	9.97	16.2	74	.280
4	10.93	11.4	56	.236
5	9.90	8.7	40	.156
6	8.92	10.82	29	.090
7	10.91	3.50	17	.060
8	8.92	5.54	15	.062
9	10.84	2.84	14	.022
10	9.83	1.98	8.9	.042
11	9.82	1.15	5.2	.021
12	8.83	1.28	3.1	.015
13	8.75	0.67	1.5	.007
14				

Titration of Series 4 with HCl

Initial pH	Alk x 10^3 moles/liter	$[CO_3^{=}]$ x10^4	ΔA
8.61	100.3	184.0	.517
8.97	57.4	163.0	.490
8.78	53.6	123.5	.358
8.57	51.7	89.3	.257
8.94	12.1	33.5	.095
8.77	11.2	25.5	.071
8.94	6.34	17.5	.074
8.75	6.04	13.4	.049
8.56	5.44	9.3	.035
8.89	1.37	3.6	.025
8.65	1.31	2.5	.016
8.46	1.20	1.7	.023
8.75	0.76	1.6	.013
8.36	0.66	1.2	.003

analysis in sea water is approximately equal to that determined by Underwood and Howe for distilled water. This means that the method cannot be applied to the carbonate of normal sea water, but could be used for measurements in idealized laboratory studies in solutions that could be made sufficiently basic without salt separation (e. g. $CaCO_3$ and $MgOH_2$).

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