

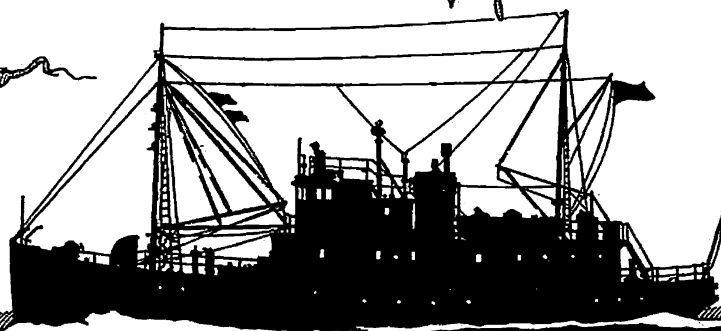


**DEPARTMENT OF  
OCEANOGRAPHY  
UNIVERSITY OF  
WASHINGTON**

**Technical Report No. 29  
DEPOSITION OF SALTS FROM SEA WATER  
BY  
FRIGID CONCENTRATION**

**Office of Naval Research  
Contract N8onn-520/III  
Project NR 083 012**

**Reference 54-13  
April 1954**



**SEATTLE 5, WASHINGTON**

UNIVERSITY OF WASHINGTON DEPARTMENT OF OCEANOGRAPHY  
(Formerly Oceanographic Laboratories)  
Seattle, Washington

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BY FRIGID CONCENTRATION

by

Kurt H. Nelson and Thomas G. Thompson

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Richard H. Fleming  
Executive Officer

## ABSTRACT

The order of formation of solid phases when sea water freezes has been investigated down to a temperature of  $-40^{\circ}$  C. About 88 percent of the water present in the original quantity of sea water is transformed into ice before the first salt crystallizes. Sodium sulfate decahydrate, the first salt formed, begins to separate at  $-8.2^{\circ}$  C. and the sulfate concentration in the brine decreases markedly. When the temperature of the system reaches  $-22.9^{\circ}$  C., sodium chloride dihydrate precipitates in large quantities. The concentration of sodium in the brine decreases rapidly as the temperature decreases below  $-22.9^{\circ}$  C. There is a decrease in the concentrations of magnesium and potassium in the brine below  $-36.0^{\circ}$  C. when potassium chloride and magnesium chloride dodecahydrate precipitate. Thermal analysis studies indicate that calcium chloride hexahydrate begins to form at  $-54^{\circ}$  C. The last of the brine probably solidifies at a temperature slightly below  $-54^{\circ}$  C.

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## INTRODUCTION

One of the earlier studies of the sequence of deposition of salts by the evaporation of sea water was made in 1849 by Usiglio (1849). Since then the chemical processes and changes occurring during the evaporation of sea water have been rather thoroughly investigated. van't Hoff, together with a number of co-workers (1905, 1909), studied the equilibria between various salts at 25° and 83° C. in order to explain the origin of the strata of the famous Stassfurt salt deposits. D'Ans (1933) and others established the equilibrium conditions in detail for the chlorides and sulfates of sodium, potassium, calcium and magnesium at temperatures from 0° to 120° C. A summary of present knowledge concerning the deposition of oceanic salts during the evaporation of sea water is given by Phillips (1947).

On the other hand, only meager information appears to be available dealing with the deposition of salts as sea water is concentrated by freezing. Since prehistoric times, inhabitants of the polar regions have obtained sodium chloride by this method. The removal of the ice as it formed on ponds of sea water resulted in a concentrated brine from which sodium chloride would precipitate on further freezing. More generally, however, the concentrated brine was evaporated over fires in order to secure the salt.

In experiments on the freezing of sea water, Ringer (1906) found that ice was the only solid formed during the interval from the

initial freezing point to a temperature of about  $-8.2^{\circ}$  C. The precipitation of the first salt, sodium sulfate, occurred from about  $-8.2^{\circ}$  C. to approximately  $-23^{\circ}$  C., and was followed by the deposition of the dihydrate of sodium chloride at temperatures below  $-23^{\circ}$  C. Ringer supposed that magnesium chloride precipitation began at  $-36^{\circ}$  C. The disappearance of a portion of the potassium from the brine between  $-36^{\circ}$  C. and  $-40^{\circ}$  C. was presumably due to formation of either potassium chloride or a double salt with magnesium chloride. The end point at which all the liquid had become solid was postulated as being slightly below the eutectic point of calcium chloride. However, few data are available in support of this order of precipitation.

Thus the object of the present study was to investigate the actual deposition of the various salts by the frigid concentration of sea water.

## METHODS AND APPARATUS

### Source of Sea Water

Surface sea water was collected in seasoned 20 and 50 liter glass carboys about 100 miles off the Washington coast at  $47^{\circ} 52.5' N$  and  $126^{\circ} 17.0' W$ . The sea water was filtered through a sintered glass filter of F porosity. The chlorinity of the sea water was 18.01 ‰.

### Apparatus

Temperatures were measured by means of calibrated Western Electric 14B Thermistors and a Wheatstone bridge. To permit immersion of the thermistors in the brines, they were sealed in glass tubes containing a drop of mercury for thermal conduction.

The apparatus used in freezing the sea water samples consisted of (1) a freezer capable of maintaining any temperature down to  $-45^{\circ}$  C. with a variation of  $\pm 3^{\circ}$  C., (2) a 3 liter freezing container with a removable bottom, (3) a freezing tube with a capacity of about 500 ml., and (4) 2 concentration vessels of 8 and 50 liter capacities for concentrating the sea water by freezing.

Freezer. The freezer was 197 cm. long, 78 cm. wide and 89 cm. high with an interior opening 100 cm. long, 33 cm. wide and 27 cm. deep. Extending downward from the bottom of this interior opening were three wells 23 cm. in diameter and 25 cm. deep. The cooling coils were positioned behind the sheet metal interior walls but did not extend down around the wells. The insulation in the walls, bottom and lid was 15 cm. thick cork slabs and the exterior finish was Masonite. The refrigerator unit was a Frigidaire Meter Miser MM-3 compressor unit employing F12 as the coolant.

Freezing Container. The 3 liter freezing container, shown in Figure 1, consisted of a Lucite cylinder 13 cm. in diameter by 30.5 cm. high clamped to a removable Lucite bottom. The lower end of the cylinder was machined to give a close fit with the bottom. Lucite blocks 2.5 cm. by 3.8 cm. by 1.3 cm. were cemented on the exterior of the cylinder near the bottom to aid in clamping the cylinder and bottom together.

The bottom was constructed from a Lucite disk 14 cm. in diameter and 1.3 cm. thick. A shallow cone was machined in the upper

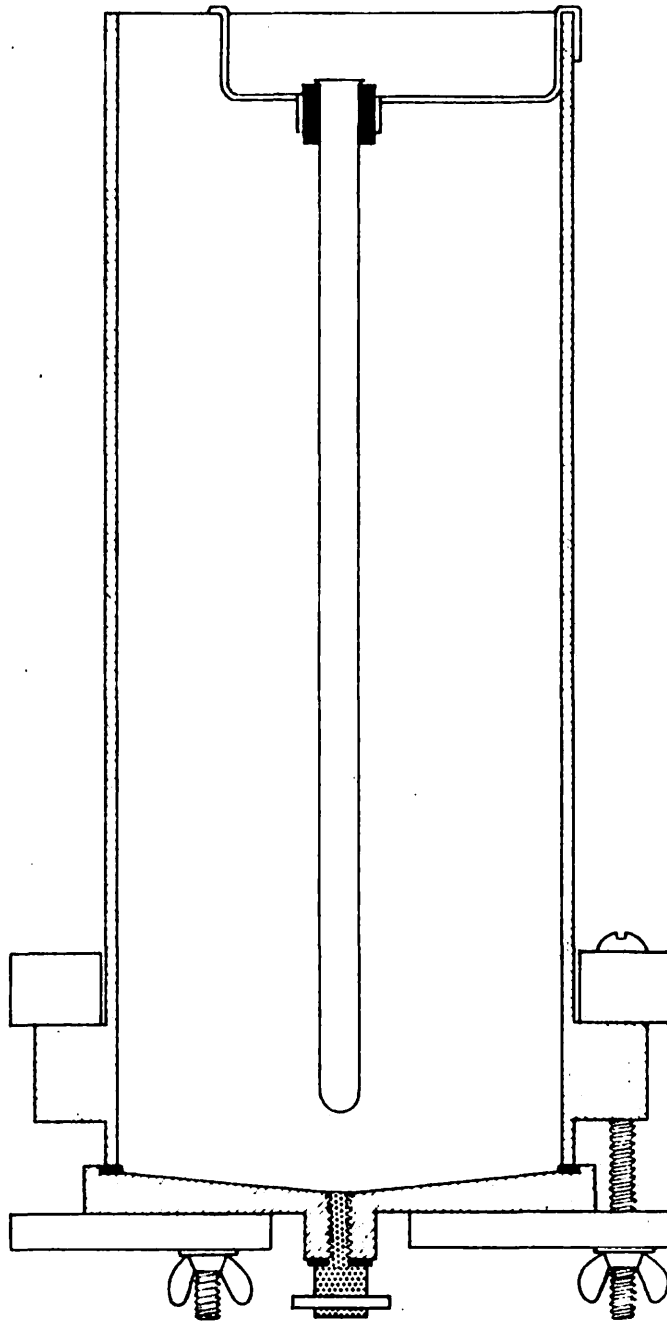


FIGURE 1. Lucite Container with Capacity of 3 liters used for Freezing Samples.

surface of the disk leaving a ridge to position a rubber gasket between the cylinder and the bottom. In the center of the bottom was a tapped drainage hole extending through a small Lucite block cemented to the underside of the disk. This hole was closed by a plastic screw plug fitted with a rubber gasket and a brass rod handle. The clamping device consisted of a plywood disk and ring held together by long bolts.

An air inlet tube was placed in the container by means of a rubber stopper and wire framework. This tube consisted of a sufficient length of 8 mm. Pyrex tubing sealed at the lower end and flanged at the top. After the container had been filled with sea water, the top of the container was covered with heavy gauge aluminum foil fastened in place with tape to prevent the loss of water by evaporation.

Freezing Tube. The freezing tube was constructed from a vertical Lucite tube, 45 cm. long and 3.8 cm. in diameter, closed at the bottom with a removable stopper. This stopper was a close fitting one hole rubber stopper inserted in the tube and expanded to give a tight fit. The expansion was accomplished by tightening a wing nut on a machine screw passing through the hole in the rubber stopper. Washers on each side of the rubber stopper held the machine screw in place and aided in the expansion of the rubber stopper. The washer and the head of the machine screw were coated with neoprene paint to prevent corrosion and subsequent contamination of the brines. During the freezing of the brine, an air inlet tube was positioned in the freezing tube and the top was closed with heavy gauge aluminum foil.

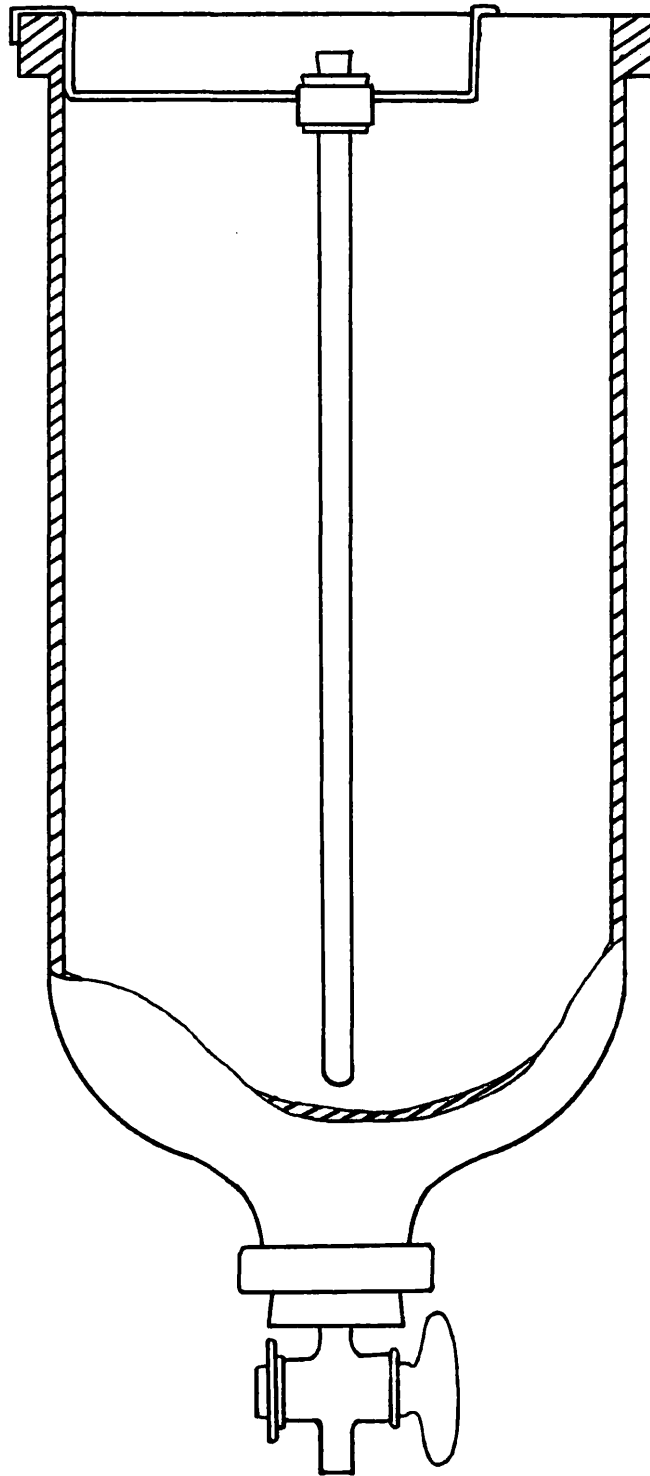
Concentration Vessels. Since only a small amount of brine remained at the lower temperatures, large quantities of sea water were subjected to a preliminary concentration by freezing and the resulting brines were then used for the low temperature investigations. Two concentration vessels were constructed for this purpose.

The small concentration vessel, pictured in Figure 2, was converted from a bell jar of nine liters capacity. A one hole rubber stopper and a stopcock were used to close the small opening in the neck of the bell jar. After inverting the bell jar, the wire framework holding the air inlet tube was placed in position. The top of the vessel was covered with heavy gauge aluminum foil after the vessel had been filled with sea water.

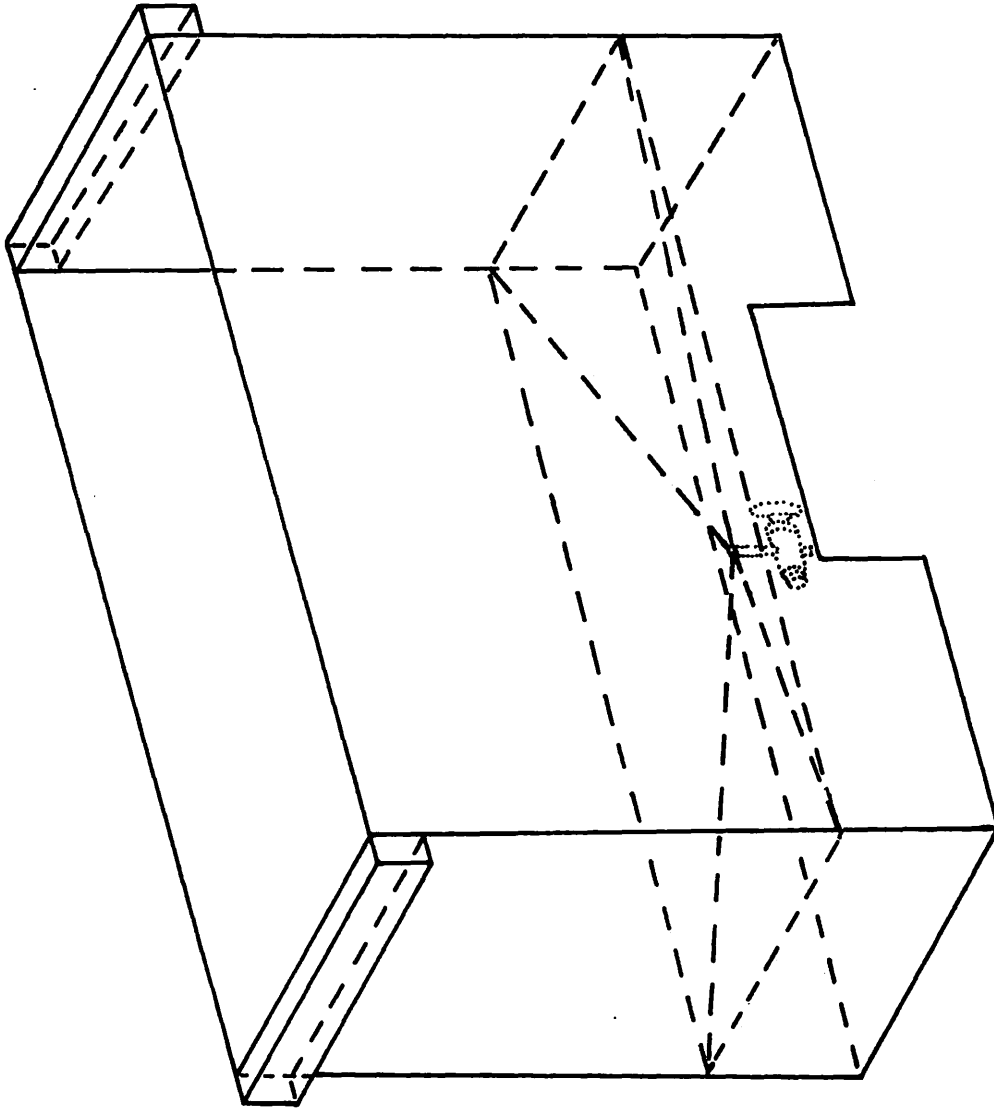
The large concentration vessel shown in Figure 3 was 72.5 cm. long, 24.0 cm. wide and 55.5 cm. high. The sloping bottom was 41.5 cm. below the top edge along the sides of the vessel and 47.5 cm. below the top at the center of the bottom. The tank was fabricated from 6 mm. thick Lucite sheets, and a 2.5 cm. by 3.8 cm. by 22.5 cm. Lucite block was cemented along the top edge of each end for a handle. Drainage of the brine was through a stopcock fastened to a short plastic tube cemented to the center of the bottom. An air inlet tube was positioned in the vessel by a wire framework. Heavy gauge aluminum foil fastened with tape closed the top of the vessel during the freezing of the sea water.

#### Freezing of Samples

The method for obtaining brines and salts consisted of lowering the temperature of a sample of sea water to a desired value and



**FIGURE 2. Container of 9 liters Capacity for Concentrating Brine by Freezing.**



**FIGURE 3. 100 liter Lucite Container for Concentrating Large Volumes of Sea Water by Freezing.**

then separating the brine, salts and ice. The freezing procedure varied somewhat depending upon the desired final temperature of the brine.

The entire freezing process for each of Samples 1 to 18 in Table I was conducted in the freezing container. After filling with 3 liters of filtered sea water, the container was placed in a well in the freezer. The container sides were insulated with tightly packed cloth in order to enhance freezing downward from the top surface of the water. When the temperature had reached the desired value, the sealed end of the air inlet tube was broken off with a long rod in order to insert the thermistor into the brine for the temperature measurements. After the brine was drained off through the drainage hole in the bottom, the bottom of the container was removed and the salts were transferred to a small specimen jar. Although most of the salt crystals were found on the bottom of the container, there were a few crystals adhering to the under surface of the ice. This was found to occur more frequently as the temperature decreased. The ice was allowed to melt after fastening another bottom to the cylinder. After the quantities of brine and water from the melted ice were determined, samples of the brine were taken for analysis.

The sea water used for each of Samples 19 through 22 was subjected to a preliminary concentration by freezing. Eight liters of sea water were allowed to freeze to a temperature of about  $-8^{\circ}$  C. in the small concentration vessel. After the brine was transferred to the freezing container, the freezing was continued in the manner described for the first samples.

TABLE I

QUANTITY OF BRINE REMAINING FROM ONE KILOGRAM  
OF SEA WATER AND CONCENTRATIONS OF THE MAJOR  
IONS IN BRINES AT VARIOUS TEMPERATURES

Sample No.	Temp. °C.	Grams Brine	Na °/°o	Mg °/°o	Ca °/°o	K °/°o	Cl °/°o	SO <sub>4</sub> °/°o
1	- 2.20	696.2	12.05	1.65	0.48	0.44	22.80	
2	- 4.40	309.4	23.23	3.19	0.86	0.85	42.71	5.97
3	- 5.50	212.3	28.39	3.92	1.02	1.03	51.18	
4	- 6.10	205.9	30.44	4.34	1.11	1.12	56.49	
5	- 6.90	147.1	33.42	4.83	1.21	1.24	62.41	8.61
6	- 8.30	89.9	37.87	5.66	1.38	1.42	71.89	
7	- 8.60	68.7	38.76	5.81	1.42	1.46	74.47	8.85
8.	- 9.60	79.3	41.19	6.31	1.54	1.58	81.01	
9	-10.60	66.1	43.69	6.79	1.65	1.68	87.31	5.48
10	-10.75	49.3	44.18	6.83	1.66	1.70	87.98	
11	-13.10	39.3	49.44	7.74	1.89	1.94	99.73	3.81
12	-14.70	27.8	53.13	8.29	2.03	2.10	107.08	
13	-15.20	34.3	54.12	8.50	2.08	2.15	109.82	
14	-16.25	25.5	56.36	8.86	2.17	2.25	114.30	2.69
15	-18.50	27.2	61.23	9.67	2.36	2.46	123.27	
16	-19.20	21.3	62.67	9.86	2.42	2.54	126.61	
17	-20.60	25.2	65.81	10.31	2.48	2.67	131.72	1.77
18	-22.20	15.0	68.83	10.86	2.59	2.79	138.91	
19	-23.25	35.9	69.35	11.65	2.84	3.11	142.37	
20	-23.75	34.5	65.86	13.62	3.18	3.53	144.02	
21	-24.70	14.4	60.02	16.63	3.98	4.48	146.11	
22	-25.60	9.9	54.17	19.77	4.76	5.10	147.78	
23	-26.40	7.9	48.57	22.41	5.57	6.01	149.12	1.06
24	-27.90	2.8	40.03	27.19	6.66	7.41	152.33	
25	-29.95	3.6	30.15	34.35	8.09	9.24	155.96	0.69
26	-32.90	2.6	20.53	43.20	9.68	12.21	161.01	
27	-34.90	1.8	16.08	48.58	10.77	15.05	165.83	
28	-36.25	1.0	14.22	50.77	12.02	19.29	166.78	
29	-36.55	0.9	13.76	50.36	14.52	20.31	167.49	
30	-40.20	0.5	10.90	46.89	44.74	16.75	173.49	
31	-43.15	0.3	8.49	58.96	10.53	13.84	174.60	

For Samples 23 through 25, 50 liters of sea water were frozen in the large concentration vessel until the temperature of the brine was around  $-8^{\circ}$  C. The resulting brine was divided into 3 equal portions. Each portion was then frozen individually in the freezing container in a manner analogous to that of the first samples.

For each of the remaining samples, 50 liters of sea water were first concentrated by freezing to a temperature of  $-17^{\circ}$  C. in the large concentration vessel and then further concentrated by freezing to  $-25^{\circ}$  C. in the small concentration vessel. The brine was then transferred to the freezing tube and the freezing was continued in a manner similar to the procedure used for the first samples.

#### Identification of Salts

The ions present in a salt were identified by qualitative analysis carried out on a microscope slide under a petrographic microscope (2).

#### Analysis of Brines.

For some analyses, a 25 ml. sample of the brine was diluted to one liter in a Normax volumetric flask. Aliquots were taken from this solution for analysis.

Sodium and Potassium Ions. The concentrations of sodium and potassium ions in the brines were determined using a Beckman Model DU Spectrophotometer with the Flame Photometry Attachment Model 9200. The 2000 megohm resistor was replaced with a 10000 megohm resistor to increase the sensitivity of the instrument five times. A series of standard solutions with compositions covering the range of concentra-

tions in the diluted brines were prepared from distilled water and Baker's Analyzed Grades of sodium chloride, potassium chloride, magnesium carbonate, and calcium carbonate. The carbonates were dissolved in a minimum amount of C.P. hydrochloric acid. For determining sodium, the percent transmission was obtained first for the low standard, then the diluted brine, then the high standard, and finally the flame background with distilled water. This procedure was repeated twice and the readings for each solution were averaged. The flame background was subtracted from the transmission readings of the standards and the diluted brine before graphically interpolating to find the concentration of sodium in the diluted brine. The sodium concentration in the undiluted brine was then calculated. A similar procedure was followed in determining the concentrations of potassium in the brines.

Calcium Ion. A 25 ml. aliquot of the diluted brine was treated with a solution of 1 N sodium hydroxide to raise the pH to about 10 and precipitate the magnesium. Three drops of a saturated aqueous solution of ammonium purpureate were added as the indicator. The ammonium purpureate solution should be freshly prepared each day due to decomposition of the indicator when in solution. The aliquot was then titrated with a 0.01 N standard disodium (ethylenedinitrilo)-tetraacetate solution until its color matched that of a comparison solution consisting of 2 drops of cresol red indicator solution in 50 ml. of a saturated borax solution.

Magnesium Ion. To a 25 ml. aliquot of the diluted brine, 1 ml. of buffer solution was added to raise the pH to about 10 without precipitating the magnesium. The buffer solution was composed of

67.5 gm. of ammonium chloride dissolved in 570 ml. of concentrated ammonium hydroxide and enough water added to make one liter. Five drops of indicator solution, consisting of 0.50 gm. Eriochromeschwarz-T dissolved in 100 ml. of ethanol, were added to the aliquot. The sum of calcium and magnesium ions in the aliquot was titrated with a 0.01 N standard disodium (ethylenedinitrilo)-tetraacetate solution until the color of the aliquot matched that of a comparison solution consisting of 1 drop of bromophenol blue indicator solution in 50 ml. of saturated borax solution. The concentration of magnesium ion was obtained by subtracting the concentration of calcium ion as obtained by the calcium titration above.

Chloride Ion. The concentration of chloride ion in a brine was determined by a Mohr chloride titration. 25 ml. aliquots of the diluted brines were titrated with 0.1 N standard silver nitrate solution using 1 ml. of a saturated potassium chromate solution as the indicator.

Sulfate Ion. Gravimetric sulfate determinations were made on the brines by the procedure described by Thompson, Johnston and Wirth (6). For the brines with freezing points above  $-17^{\circ}$  C., a weighed 25 ml. sample was used. The size of the sample was increased for the brines with lower freezing points.

#### Thermal Analysis

Thermal analyses were made on sea water samples and several brines. For all samples except 29 and 31, 10 ml. of the sea water or brine under examination were placed in a small test tube containing a thermistor. A smaller volume of brine was used for Samples 29 and 31.

The sample was frozen in an acetone-dry ice bath so that the frozen mass surrounded the thermistor. The frozen sample was removed from the bath and placed in a cotton-filled can 22 cm. high by 9 cm. in diameter. The interior of the cotton packing had been cooled for several hours with dry ice in a test tube. The thermistor was connected to the Wheatstone bridge and the temperature was determined at intervals as the frozen sample slowly melted. Depending upon the rate of change of the temperature, the intervals varied from as short as 20 seconds to as long as 2 minutes or more. A time-temperature curve was then plotted for the sample.

## RESULTS

### Quantity of Brine

The amount of brine in equilibrium with the ice when 1 kilogram of sea water was frozen to various temperatures is shown in Figure 4 from data given in Table I. It will be noted that a large portion of the water was transformed into ice during the initial stages of freezing. Approximately 80 percent of the water had solidified when the temperature had decreased to only  $-6^{\circ}$  C. Below this temperature, the amount of ice formed was small.

### Analysis of Brines

The results of the analyses for the major ions in each brine are given in Table I and shown in Figure 5 through 10.

Concentration of Sodium. From the initial freezing point of sea water to a temperature of  $-8.2^{\circ}$  C., the concentration of sodium in

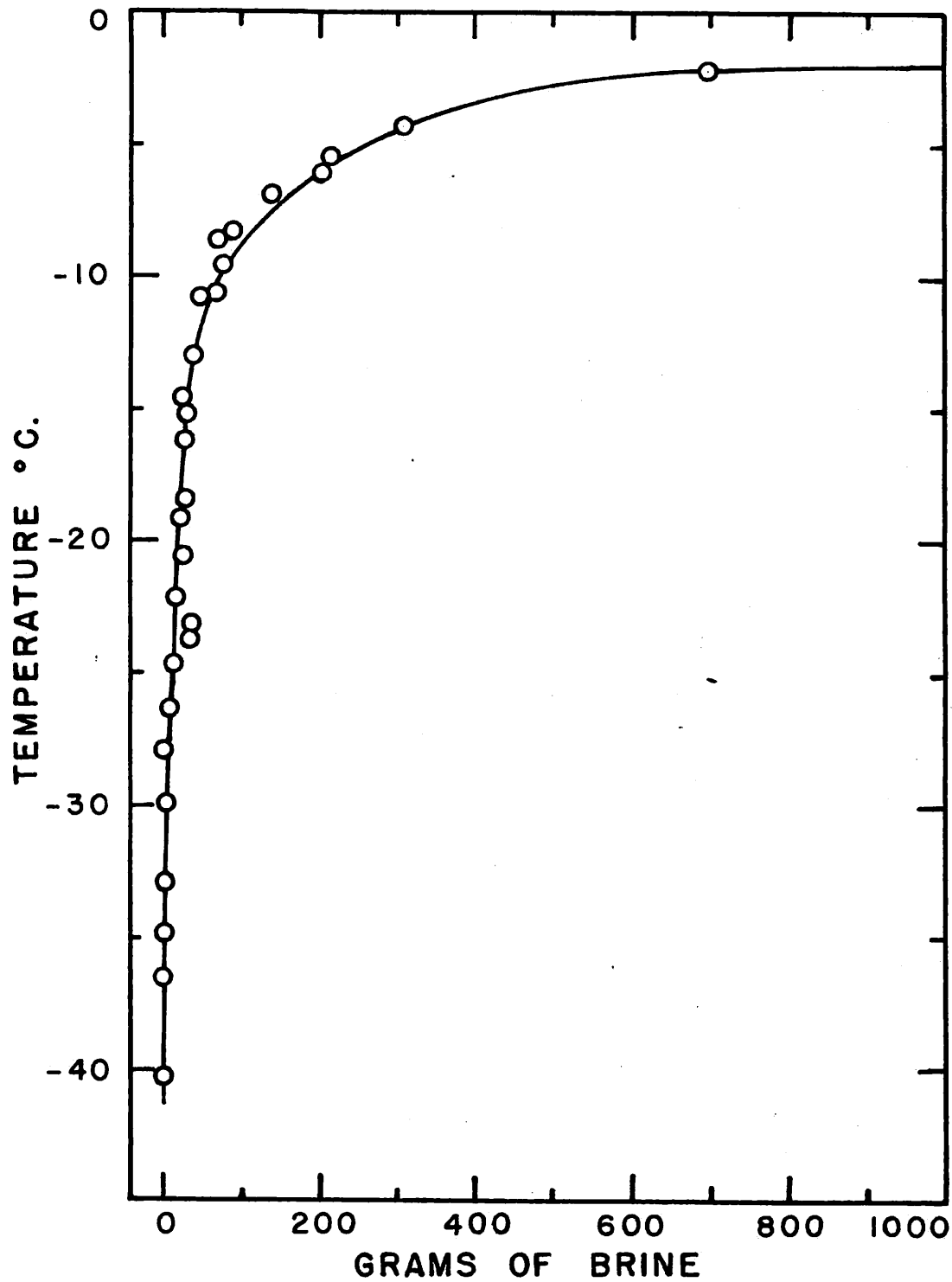


FIGURE 4. Grams of Unfrozen Brine remaining after Freezing 1 kilogram of Sea Water at Various Temperatures.

the brine continually increased. In the temperature range  $-8.2$  to  $-22.9^{\circ}$  C., the increase was slightly less due to the formation of sodium sulfate decahydrate. A marked decrease in the sodium concentration occurred in the brines with temperatures below  $-22.9^{\circ}$  C. This was due to the precipitation of large quantities of sodium chloride dihydrate. The changes in the sodium concentration as the temperature decreased are illustrated in Figure 5.

Concentration of Magnesium. Until the freezing point reached  $-22.9^{\circ}$  C., the concentration of magnesium in the brine increased gradually as ice and sodium sulfate decahydrate crystallized from the brine. During the formation of sodium chloride dihydrate between  $-22.9$  and  $-36.0^{\circ}$  C., the increase in magnesium content of the brine decreased as the temperature of system was lowered below  $-36.0^{\circ}$  C. This was due to the crystallization of salts containing magnesium. These changes in the magnesium content of the brine in equilibrium with the ice and precipitated salts at various temperatures are shown in Figure 6.

Concentration of Calcium. In Figure 7 the concentration of calcium in the brine is shown as a function of the temperature of the system. From the initial freezing point of sea water to  $-22.9^{\circ}$  C., there was a slow increase in the concentration of calcium in the brine as ice and sodium sulfate decahydrate formed. Between  $-22.9$  and  $-36.0^{\circ}$  C. the formation of a large amount of sodium chloride dihydrate removed a considerable amount of water from the brine. This resulted in a four-fold increase in the calcium concentration in the brine. Below  $-36.0^{\circ}$  C. the concentration of calcium in the brine increased considerably.

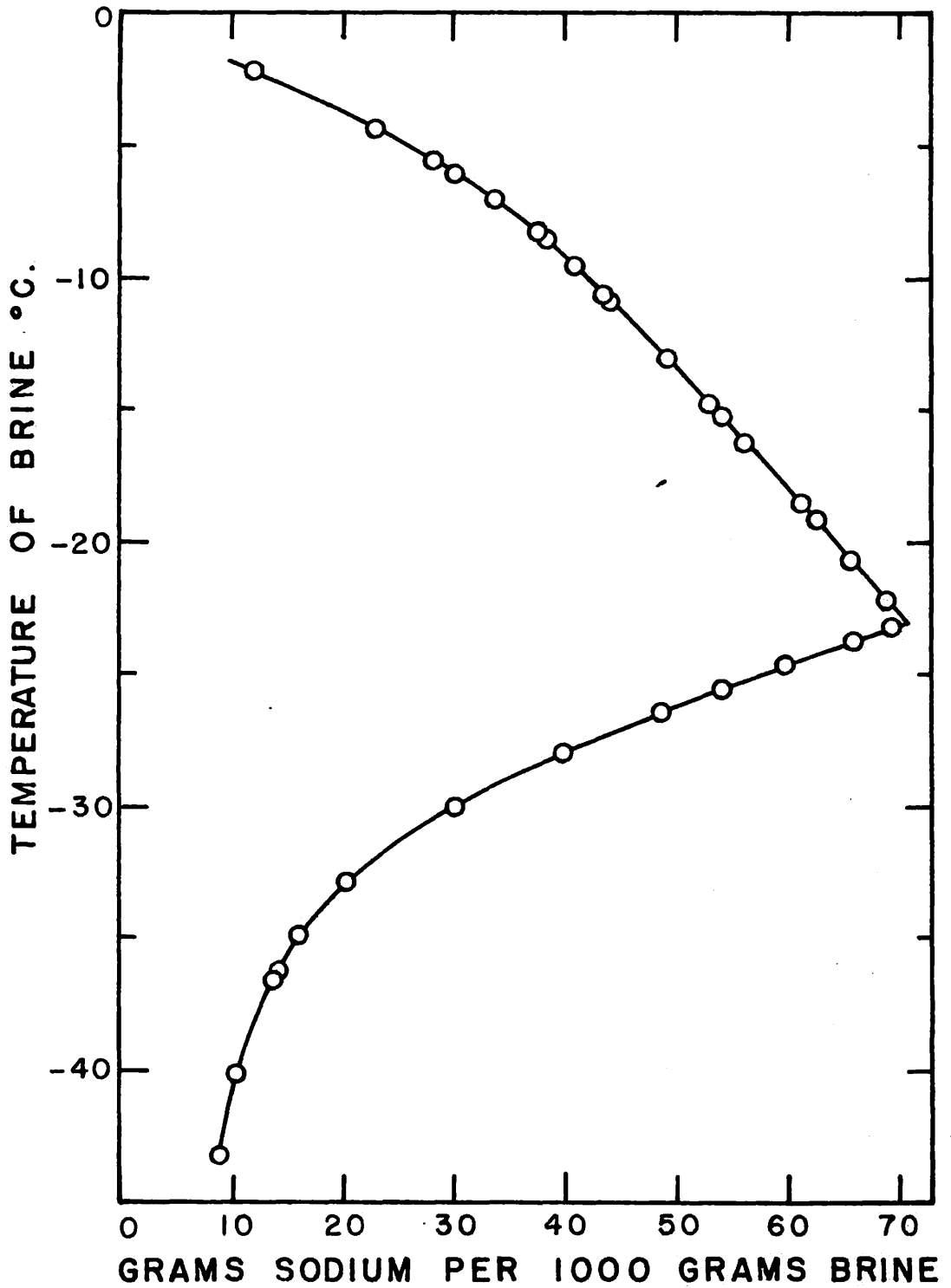


FIGURE 5. Concentration of Sodium in Sea Water Brines at Various Temperatures.

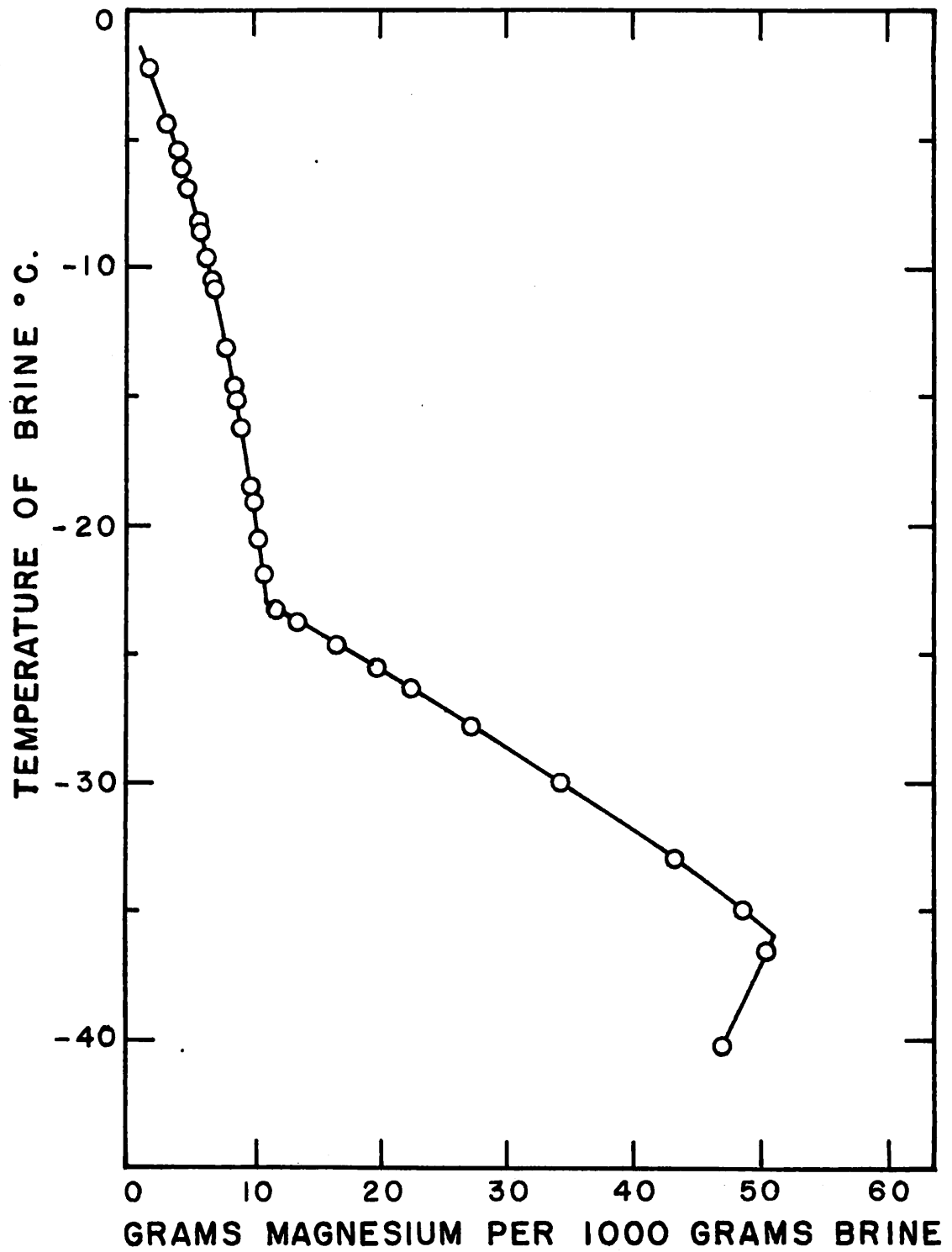


FIGURE 6. Concentration of Magnesium in Sea Water Brines at Various Temperatures.

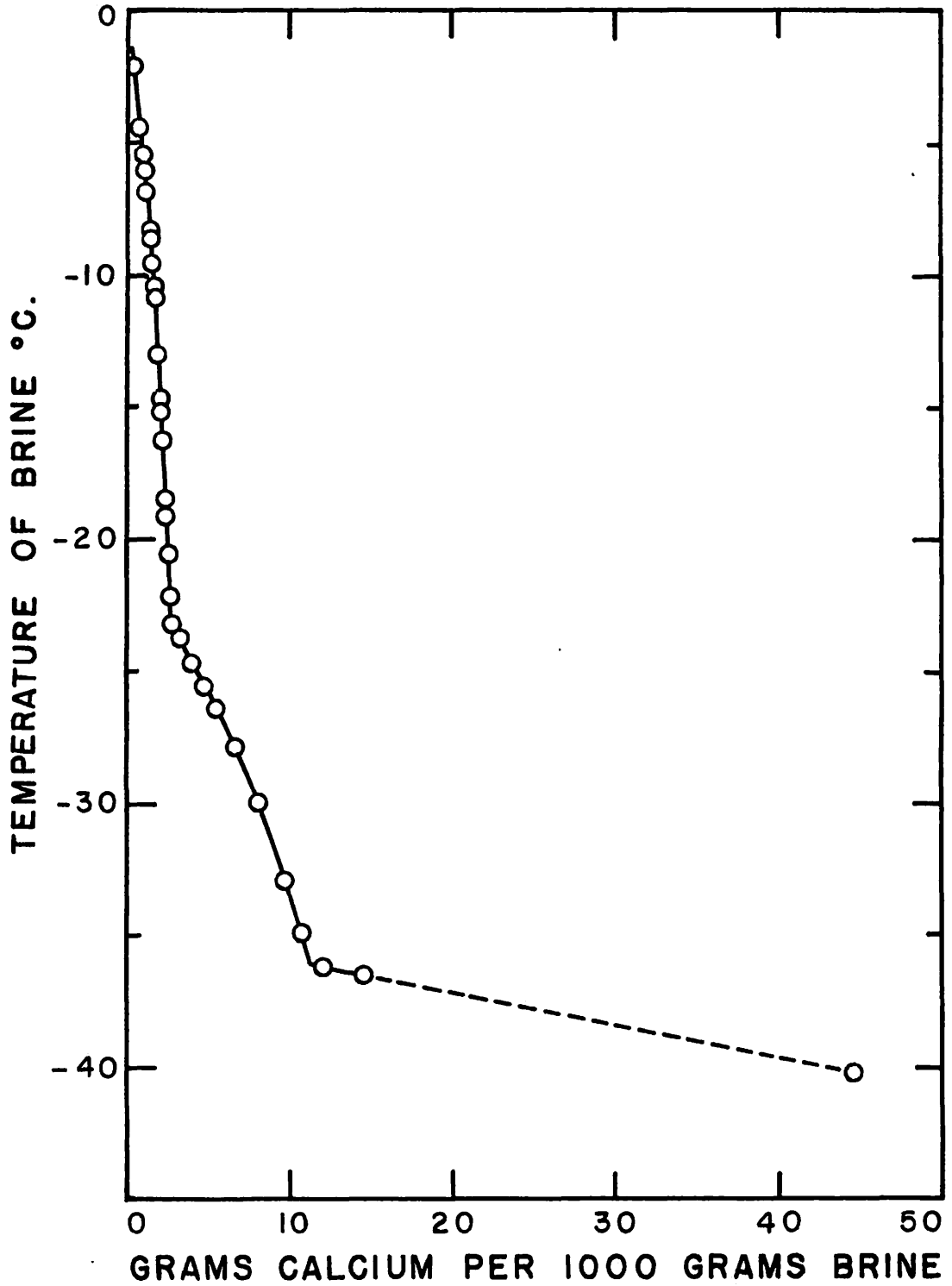


FIGURE 7. Concentration of Calcium in Sea Water Brines at Various Temperatures.

When the temperatures of the separated brines rose, precipitation of calcium carbonate occurred. Generally, the time interval before precipitation was perceptibly decreased as the temperature decreased and the salinity of the brine increased. Thus for the brines with temperatures somewhat below the freezing point of the sea water, a period of several days at room temperature was required before any precipitate was visible. This time interval had decreased to several hours when the temperatures of the systems of the brines were slightly above  $-22.9^{\circ}$  C. The brines with temperatures between  $-22.9$  and  $-36.0^{\circ}$  C. showed a precipitate from a few hours to less than an hour after separation of the brine. Precipitation occurred almost immediately after separation of the brine from the salts and ice when the temperature of the brine was below  $-36.0^{\circ}$  C.

Concentration of Potassium. The concentrations of potassium in brines of various temperatures are shown in Figure 8. There was a gradual increase in concentration until a temperature of  $-22.9^{\circ}$  C. was reached. The removal of a large amount of water below  $-22.9^{\circ}$  C. as sodium chloride dihydrate resulted in a considerable increase in the potassium concentration in the brine. Below  $-36.0^{\circ}$  C., the decrease in the potassium content of the brine indicated the formation of salts containing potassium.

Concentration of Chloride. The concentrations of chloride in brines at various temperatures are illustrated in Figure 9. The removal of water from the brine as ice and as water of crystallization in sodium sulfate decahydrate resulted in a continuous increase in the concentra-

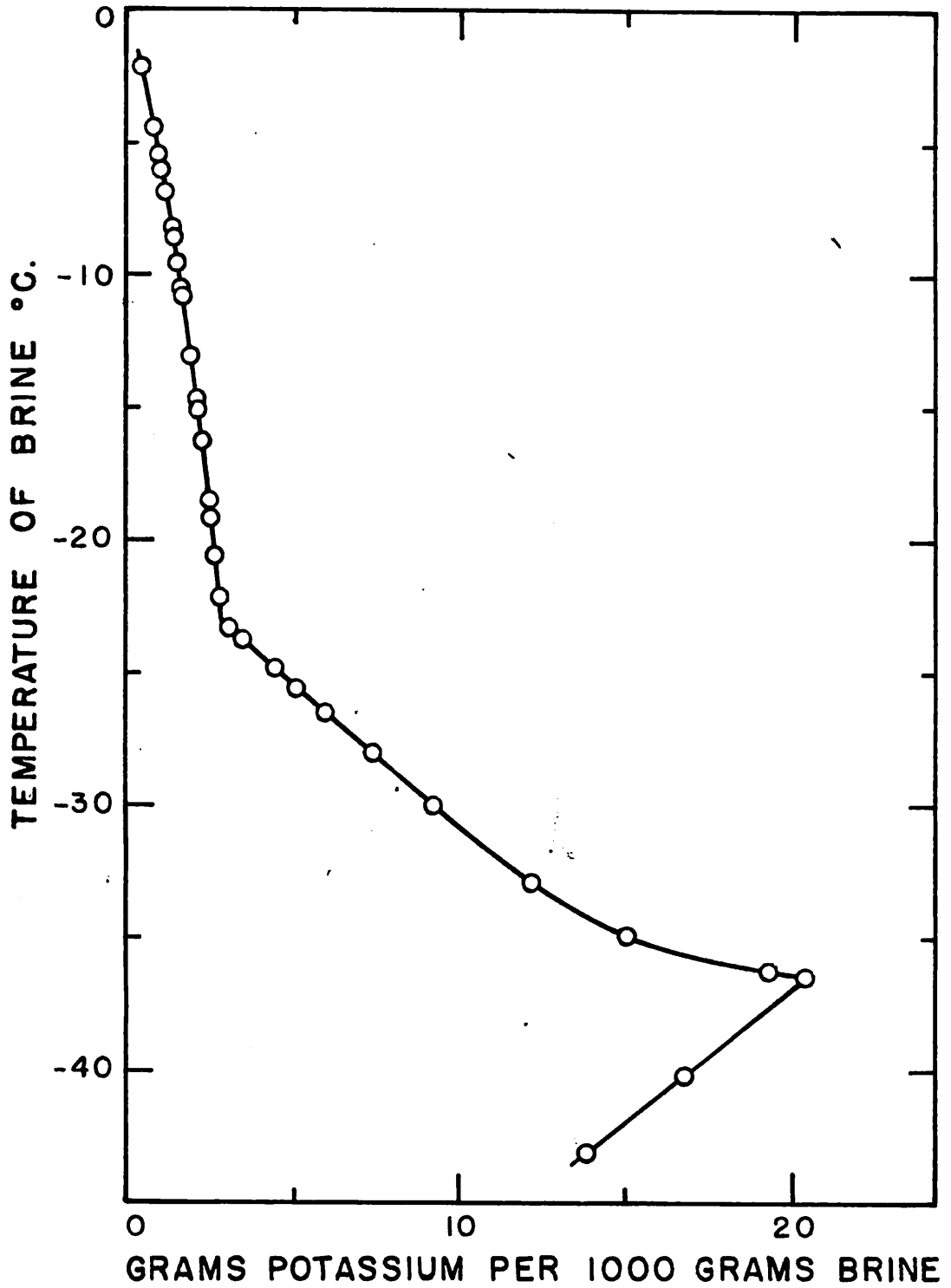


FIGURE 8. Concentration of Potassium in Sea Water Brines at Various Temperatures.

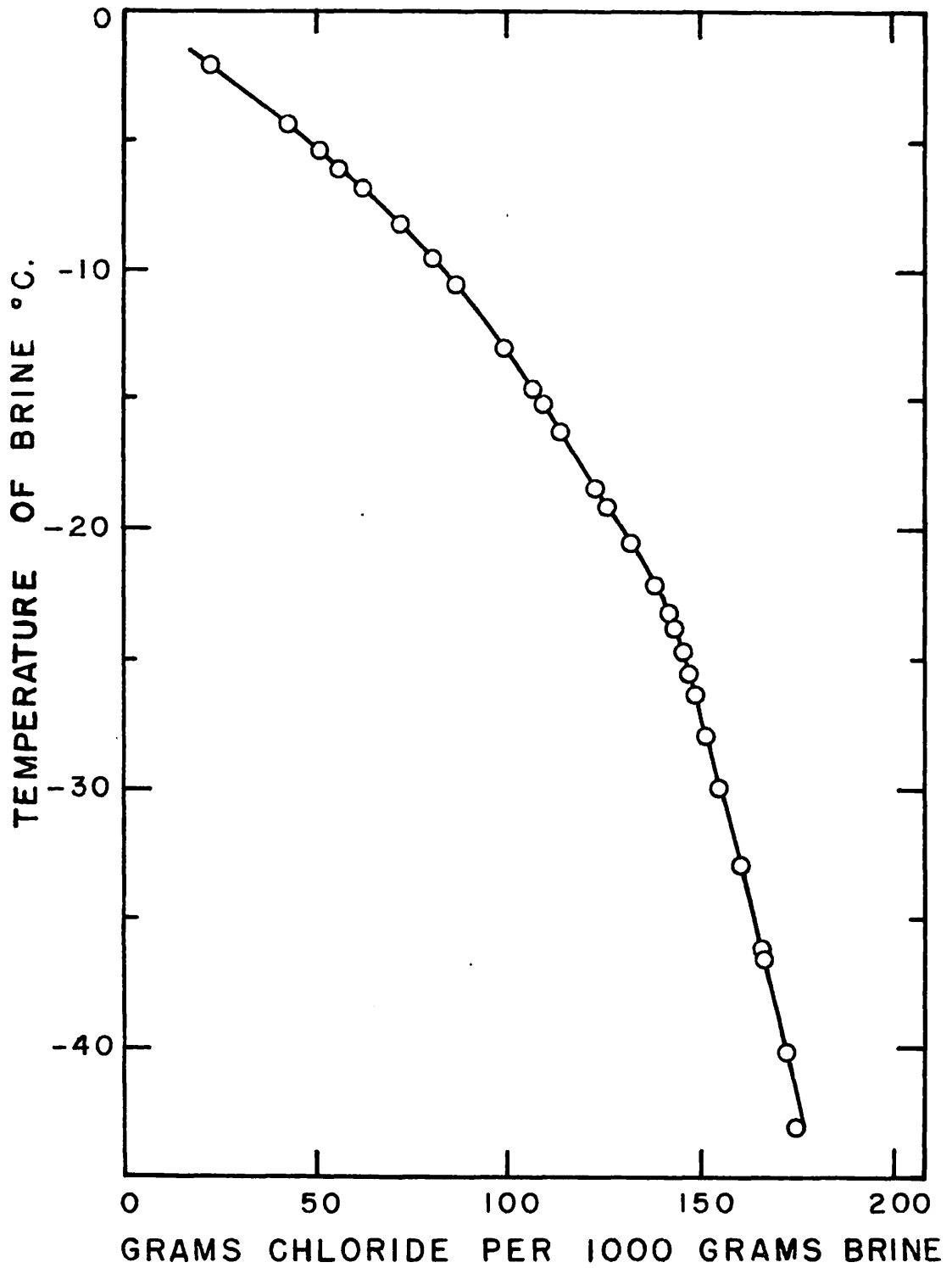


FIGURE 9. Concentration of Chlorides in Sea Water Brines at Various Temperatures.

tion of chloride until the temperatures reached  $-22.9^{\circ}$  C. Below this temperature, the chloride participated in the formation of salts and therefore the increase in chloride concentration was less than at higher temperatures.

For calculating the initial freezing point of sea water from its chlorinity, Thompson (5) presented the equation

$$T = - 0.0966 Cl - 0.0000052 Cl^3$$

where T is the freezing point in degrees Centigrade and Cl is the chlorinity. This equation fits the data in Table I until the chlorinity has increased to about  $50^{\circ}/\text{oo}$  but deviates increasingly at higher chlorinities. From the data in Table I, recomputation of the coefficients in Thompson's equation yielded the equation

$$T = - 0.0966 Cl - 0.0000035 Cl^3$$

where T and Cl have the same meaning as before. This new equation is valid for chlorinities from about  $50$  to  $140^{\circ}/\text{oo}$ . At higher chlorinities the chloride begins to precipitate as sodium chloride dihydrate and the equation becomes invalid.

Concentration of Sulfate. The change in the concentration of sulfate in the brine as the freezing point decreased is portrayed in Figure 10. Until the temperature reached  $-8.2^{\circ}$  C., the change in sulfate concentration was that due to the removal of water as ice from the brine. Beginning at  $-8.2^{\circ}$  C., sodium sulfate decahydrate crystallized from the brine causing the concentration of sulfate in the brine to decrease rapidly.

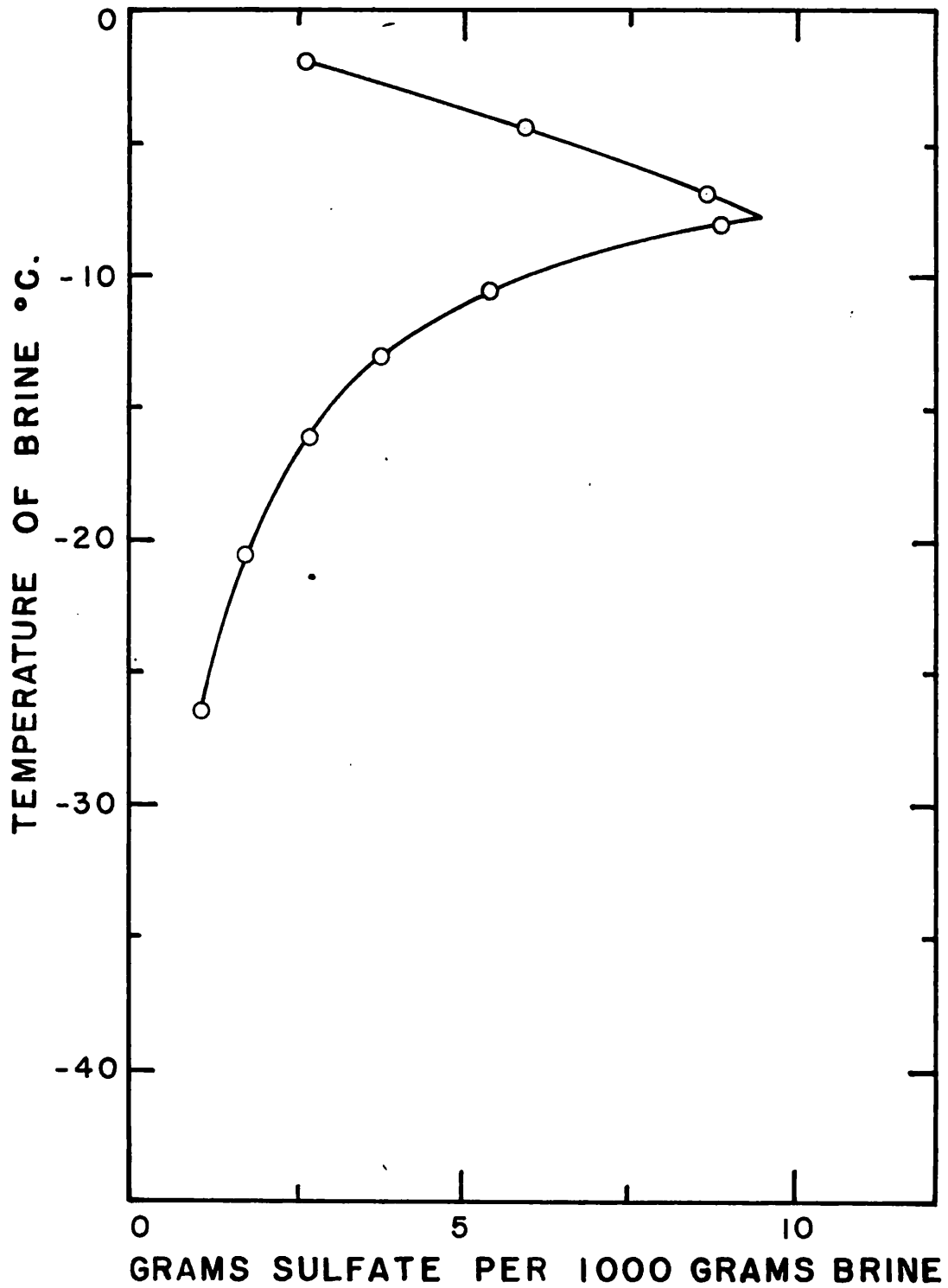


FIGURE 10. Concentration of Sulfates in Sea Water Brines at Various Temperatures.

## Thermal Analysis

The time-temperature curves obtained for samples of sea water and several brines are shown in Figure 11. For clarity, the curves have been displaced to the right from zero time. All the time-temperature curves had a small plateau at  $-38.87^{\circ}$  C. due to the melting of the mercury in the thermistor assembly.

The time-temperature curve for Puget Sound sea water showed a plateau above  $-5^{\circ}$  C. which resulted from the melting of the ice. The inflection point at  $-22.9^{\circ}$  C. in the curve arose from the dissolving of the sodium chloride dihydrate.

The sea water from  $47^{\circ} 52.5'$  N and  $126^{\circ} 17.0'$  W with a chlorinity of  $18.01$  ‰ gave a time-temperature curve similar to the curve obtained with Puget Sound sea water of chlorinity  $16.50$  ‰. A very small inflection point occurred in the curve at  $-36.0^{\circ}$  C.

The same inflection points occurred in the time-temperature curves for the brines of Samples 2, 9, and 17 as were present in the curves for sea water. However, due to the higher salt content of the brines, the curves had more distinct inflection points. As the chlorinity of the brine increased, the inflection points at  $-22.9$  and  $-36.0^{\circ}$  C. enlarged into plateaus while the plateau for the melting of the ice decreased in size and occurred at a lower temperature. In the curve for Sample 17, the plateau resulting from the melting of the ice disappeared. This indicates that only a small amount of ice forms at the lower freezing temperatures.

The time-temperature curves for the brines of Samples 23 and 26 showed a broadening of the  $-36.0^{\circ}$  C. inflection point into a plateau.

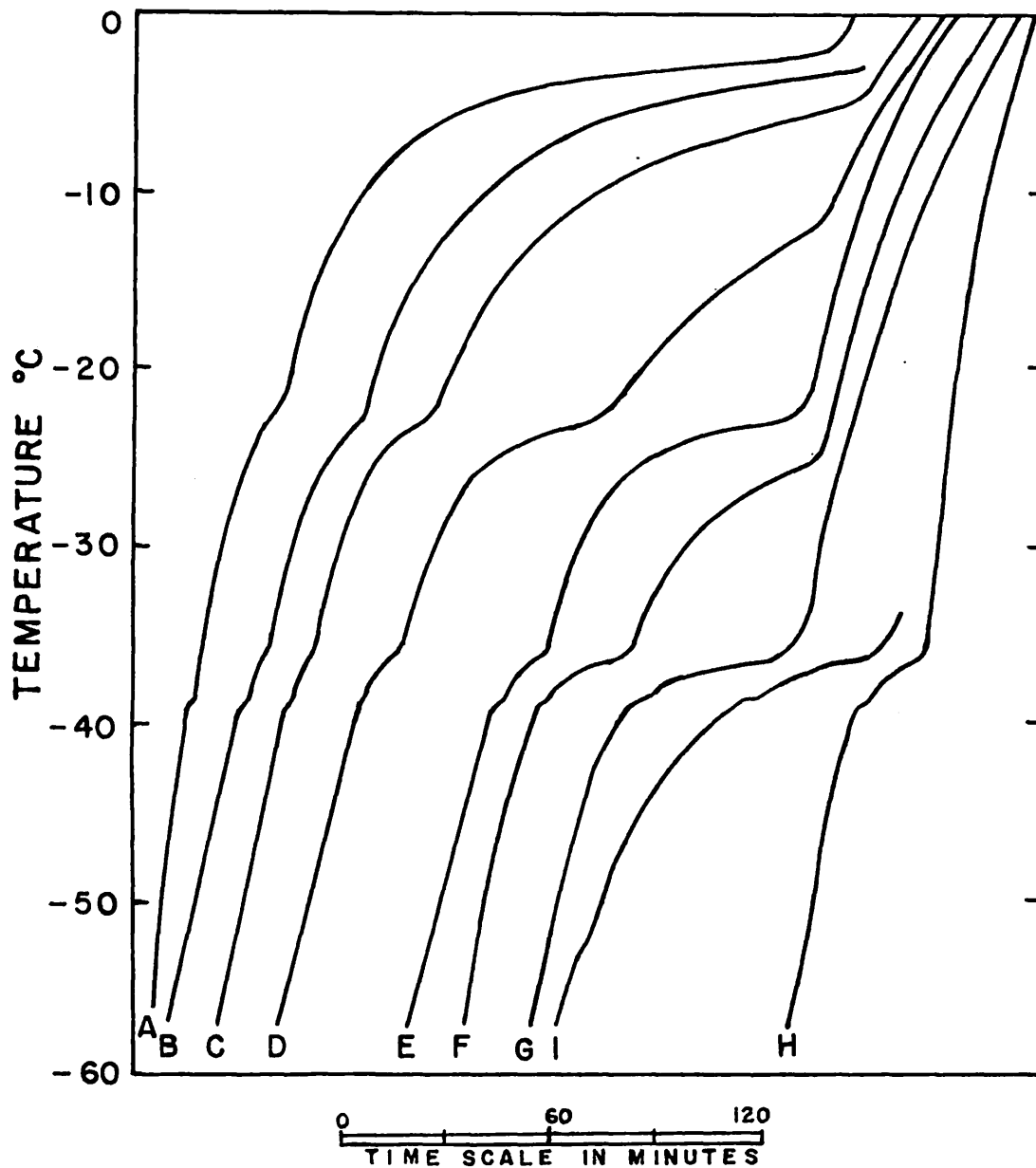
Simultaneously in the curve for Sample 23, the plateau due to the sodium chloride dihydrate decreased in size and occurred at a lower temperature. This plateau disappeared entirely in the curve for Sample 26.

The curves for the brines of Samples 29 and 31 were obtained with a smaller volume of brine. Therefore the shape of these curves should not be compared with the shapes of the other curves in Figure 11. In addition to the plateau at  $-36.0^{\circ}$  C., the time-temperature curve for Sample 29 had an inflection point at  $-54^{\circ}$  C. Although not readily apparent in Figure 11, this inflection point is discernible in a plot of the slope of the curve against the temperature.

The  $-54^{\circ}$  C. inflection point is easily seen in the time-temperature curve from the brine of Sample 31. This inflection point is probably due to the solidification of the last of the brine. The general shape of this curve differs from the other curves because the thermal analysis was conducted in the freezer at a temperature of  $-30^{\circ}$  C. in order to enhance the  $-54^{\circ}$  C. inflection point.

#### DISCUSSION

Since sea water is a dilute solution of very soluble salts, a large portion of the water must be removed from the solution before any salt will begin to crystallize. Therefore when sea water is exposed to freezing conditions, ice is the first solid phase formed. During the beginning of the freezing process, the temperature of the sea water decreases slowly due to the large quantity of ice formed.



A	SEA WATER PUGET SOUND	CHLORINITY	16.50 ‰
B	SEA WATER 47° 52.5' N 126° 17.0' W	CHLORINITY	18.01 ‰
C	BRINE FROM SAMPLE 2	CHLORINITY	42.71 ‰
D	BRINE FROM SAMPLE 9	CHLORINITY	87.31 ‰
E	BRINE FROM SAMPLE 17	CHLORINITY	131.72 ‰
F	BRINE FROM SAMPLE 23	CHLORINITY	149.12 ‰
G	BRINE FROM SAMPLE 26	CHLORINITY	161.01 ‰
H	BRINE FROM SAMPLE 29	CHLORINITY	167.49 ‰
I	BRINE FROM SAMPLE 31	CHLORINITY	174.60 ‰

FIGURE 11. Time Temperature Curves for Melting of Frozen Sea Water and Various Brines. (Curves are displaced to the right for zero time.)

Approximately 88 percent of the water in sea water has been transformed into ice before the first salt crystallizes from the resulting brine at  $-8.2^{\circ}\text{C}$ . The concentrations of the six major ions increase until the temperature of the system reaches  $-8.2^{\circ}\text{C}$ .

In addition to the continued formation of ice, crystals of sodium sulfate decahydrate begin to appear at  $-8.2^{\circ}\text{C}$ . The concentration of sulfate decreases markedly as the freezing point continues to decrease. For the other ions in the brine, there is an increase in concentration in the temperature interval from  $-8.2$  to  $-22.9^{\circ}\text{C}$ . The sodium sulfate decahydrate crystals form mainly on the bottom of the container with a few adhering to the under surface of the ice. The habit of the monoclinic crystals consists of well-formed columns, elongated tablets, and short prisms. Upon exposure to air, the crystals effloresce rapidly.

When the freezing point reaches  $-22.9^{\circ}\text{C}$ ., the amount of brine remaining is only about 2 percent of the initial quantity of sea water. From this concentrated brine, sodium chloride dihydrate precipitates as the temperature falls below  $-22.9^{\circ}\text{C}$ . The monoclinic crystals of sodium chloride dihydrate form initially as white spherulites on the bottom and lower walls of the vessel. As the freezing point decreases, these spherulites increase in size and number. In addition, the spherulites begin to form on the under surface of the ice. The spherulites eventually grow together into large masses of crystals in the bottom portion of the container and also begin forming throughout the ice. Most of the ice eventually has a white color due to the crystals of sodium chloride dihydrate. The sodium concentration in the brine shows a marked decrease during this precipitation phenomenon. The concentrations of potassium, magnesium, calcium and chloride in the brine continue to increase as the freezing point approaches

-36.0° C. Upon isolation from the brine, the crystals of sodium chloride dihydrate melt at 0.2° C. forming crystals of sodium chloride and a saturated solution of the salt.

Below -36.0° C., the concentrations of magnesium and potassium in the brine decrease. The thermal analysis studies show that a salt begins to precipitate at -36.0° C. Since the salt melted when the temperature increased, reliable optical identifications could not be made.

As the concentrations of sulfate in the brines are low, the brines are mainly aqueous solutions of the chlorides of sodium, potassium, calcium and magnesium. An inspection of the potassium chloride-magnesium chloride-water system shows that carnallite forms only from magnesium chloride rich solutions and at temperatures above -21° C. Below this temperature, potassium chloride and magnesium chloride dodecahydrate precipitate instead of carnallite. The system is scarcely changed by the addition of sodium chloride. Likewise, low concentrations of calcium chloride will not alter the system very much. From the available information and the examination of the simpler salt systems, the salt forming at -36.0° C. is a mixture of 2 single salts, potassium chloride and magnesium chloride dodecahydrate, rather than the double salt, carnallite.

The inflection point at -54° C. in the time-temperature curves for the brines of Samples 29 and 31 is probably due to the formation of calcium chloride hexahydrate. This is the only calcium containing salt formed at low temperatures in the various systems composed of water and the chlorides of calcium, sodium and magnesium. The last of the brine, which is rich in calcium chloride, solidifies at a temperature probably only slightly below -54° C.

## LITERATURE CITED

- CHAMOT, E. M., and MASON, C. W.  
1948. Handbook of Chemical Microscopy. Volume II. Wiley,  
New York.
- D'ANS, J.  
1933. Die Losungsgleichgewichte der Systeme der Salze ozean-  
ischer Salzablagerungen. Verlagsgesellschaft fur Ackerbau  
m. b. H., Berlin.
- PHILLIPS, F. C.  
1947. Oceanic Salt Deposits. Quart. Revs. (London), 1, 91-111.
- RINGER, W. E.  
1906. De veranderingen in samenstelling van zeewater bij het  
bevrozen. Chem. Weekblad, 3, 223-49.
- THOMPSON, T. G.  
1932. The Physical Properties of Sea Water.  
Bull. Nat. Research Council (U.S.), No. 85, p. 84.
- THOMPSON, T. G., JOHNSTON, W. R. and WIRTH, H. E.  
1931. The Sulfate-Chlorinity Ratio in Ocean Waters. J. conseil  
permanent intern. exploration mer, 6, 246-51.
- USIGLIO, J.  
1849. Analyse de L'eau de la Mediterranee sur le Cotes de  
France. Annal. de Chemie, 27, 92-107, 172-191.
- VAN'T HOFF, J. G.  
1905 and 1909. Zur Bildung der ozeanischen Salzablagerungen.  
Parts I and II. Vieweg.

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