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PROJECT COMPLETION REPORT

MEASUREMENT OF THERMODYNAMIC PROPERTIES OF SALINE SOLUTIONS

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ABSTRACT

MEASUREMENT OF THERMODYNAMIC PROPERTIES OF SALINE SOLUTIONS

Engineers must be able to predict the thermodynamic properties of saline solutions in order to properly design water purification plants. It was the primary goal of the investigation to develop equations to predict those properties of engineering consequence as functions of temperature, pressure, and salt concentration. The equations that were derived can be used to predict specific heat, vapor pressure, heat of vaporization, specific volume, enthalpy, and entropy for unsaturated sodium chloride solutions ranging in temperature from 32 to 350°F and for pressures ranging from 0 to 5000 psig. The results of this investigation are presented in equations, graphs, and tables. The equations can readily be programmed. A detailed account of the derivations, experiments conducted, and the results is presented in Dr. James C. Chou's dissertation entitled:

<u>Thermodynamic Properties of Aqueous Sodium Chloride</u>

<u>Solutions from 32 to 350°F</u>

Oklahoma State University

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MEASUREMENT OF THERMODYNAMIC PROPERTIES OF SALINE SOLUTIONS
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KEYWORDS--thermodynamic properties*/specific heat/ vapor pressure/ heat of vaporization/ specific volume/ enthalpy/ entropy/ temperature/ pressure/ NaCl concentration

Project Objectives:

As a result of the attention directed in recent years toward the use of evaporation processes for purifying saline water, knowledge of the thermodynamic properties of brines at temperatures in the range of evaporator operation has become a matter of great concern. In ordinary sea water, sodium and chloride ions constitute about 86% of the dissociated ions; these ions are also frequently the principal contaminants in brackish water. Based on this fact, engineers have frequently made the assumption that the properties of sodium chloride solutions may be used as a first approximation to those of sea water in designing desalination evaporators.

It was the primary object of this project to develop equations to predict these properties. The data used in developing the equations was obtained through experiments conducted in this study, as well as from data obtained from literature. The resulting equations that were developed can be used to predict:

1. specific heat
2. vapor pressure
3. heat of vaporization
4. specific volume
5. enthalpy
6. entropy

The independent variables for these functions were temperature, pressure, and sodium chloride concentration. The equations, when programmed, offer the engineer a quick way to evaluate properties for temperatures ranging from 32 to 350°F, for pressures ranging from 0 to 5000 psig, and for all NaCl concentrations ranging from zero to that for the saturated solution. A detailed description of the work done in this study may be obtained from Dr. James Chia-San Chou's dissertation entitled:

Thermodynamic Properties of Aqueous Sodium Chloride
Solutions from 32 to 350°F

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If time permitted, we also planned to conduct additional tests with equipment built with funds for this project to measure the effect of composition, surface tension, capillary pressure, and nucleation sites on the properties listed above.

Plan of Attack

First an extensive literature survey was made to determine what data was available on the thermodynamic properties of sodium chloride solutions. This survey indicated a lack of experimental data on:

1. specific heat at high temperatures
2. specific volume of NaCl solutions
3. heat of vaporization

However the survey did reveal sufficient related experimental data to calculate specific heat using thermodynamic theory.

Next a heat of vaporization calorimeter, believed to be of unique design, was built to measure heat of vaporization over a wide range of temperature, pressures, and fixed salt concentration. The salient features of this calorimeter are presented in Appendix A.

Also a P-v-T cell was built to measure the specific volume of NaCl solutions for various temperature, pressures, and NaCl concentrations. The schematic diagram of the apparatus, the experimental procedure followed, and the results obtained are presented in Appendix B. This appendix, written in the form of a technical paper, is presently under consideration for publication.

Initial Effort

Our initial effort was directed toward the design and construction of the heat of vaporization calorimeter. Considerable progress was made in this endeavor during the first year of the program. However, a turn over of graduate student help resulting from graduation greatly impaired progress.

Revised Program

During the second year, it was decided that the best chance of attaining our main objective of predicting thermodynamic properties could be realized if we reduced effort on the calorimeter, and focused our attention on the analytical work and the experimental program to obtain P-v-T-x data for NaCl solutions. Following this course of action, a significant portion of our original project objectives were realized.

Degree of Achievement of Project Objectives

In the original proposal, a program was outlined to determine the properties of solutions containing a variety of salts alone and in combination. If time permitted, additional tests were planned to determine the effects of surface tension, capillary pressure, and nucleation sites on such thermodynamic properties as the heat of vaporization. As the project progressed, it was decided to concentrate on developing equations to predict the thermodynamic properties of NaCl solutions. This goal was realized; the equations for calculating these properties are listed in the next section of this report.

Results

The following equations were derived to predict the thermodynamic properties of NaCl solutions of interest to the engineer. The independent variables in each case are temperature, pressure and sodium chloride concentration.

1. Specific Heat:

$$c_p = 1.3165380 - 8.9594831x + 23.807251x^2$$
$$-(0.20328368\text{x}10^{-2} - 0.036271808x + .062168183x^2)T$$
$$+ (0.32218320\text{x}10^{-5} - 0.61529617\text{x}10^{-4}x + 0.10557408\text{x}10^{-3}x^2)T^2 \qquad (1)$$

$P = 10$ atmospheres

c_p, calories per gram per degree

x, mole fraction

T, degrees Kelvin

The data used in deriving this equation were osmotic coefficient data, solubility data, specific heat, data of pure water, and specific heat data for solid salt. The details on how this equation was derived are presented in Chou's thesis which was referenced in the first section of this report.

2. Vapor Pressure:

$$\ln \frac{p_1}{p_1^\circ} = -1.2275791x + 15.026523x^{1.5}$$
$$-574.51650x^2 - (331.63222x - 3322.7702x^{1.5} - 16390.844x^2)/T$$
$$+ (0.040568938x - 3.8316690x^{1.5} + 87.479492x^2)\ln T \qquad (2)$$

x, mole fraction

T, degrees Kelvin

p_1, vapor pressure of the solution

p_1°, vapor pressure of the pure water

The vapor pressure of pure water can be calculated from the following formula:

$$\ln p_1^\circ = 71.0571369 - 7381.6477/T - 9.0993037\ln T + 0.0070831558T \tag{3}$$

p_1°, absolute pressure in kilograms per square centimeter

T, degrees Kelvin

3. Heat of Vaporization:

The heat required for the phase transition of water from the solution phase to the vapor phase at constant temperature and composition is determined by using Table III of Appendix C in the following manner. The value in Table III, at the desired temperature and salt concentration, is added to the value for the heat of vaporization determined from the steam tables. For example the heat of vaporization of a solution containing 10 grams of salt per 100 grams of solution at 230°F is 945.5 + 1.2 Btu/lb mass.

4. Specific Volume:

$$v = A(T) - P\cdot B(T) - P^2\cdot C(T) + x\cdot D(T) + x^2\cdot E(T) - xP\cdot F(T) - x^2P\cdot G(T) - 1/2\ xP^2\cdot H(T) \tag{4}$$

$$A(T) = 5.916365 - 0.010357941T + 0.92700482\text{x}10^{-5}T^2 - 1127.5221/T + 100674.1/T^2 \tag{5}$$

$$B(T) = 0.52049144\text{x}10^{-2} - 0.10482101\text{x}10^{-4}T + 0.83285321\text{x}10^{-8}T^2 - 1.1702939/T + 102.27831/T^2 \tag{6}$$

$$C(T) = 0.11854697\text{x}10^{-7} - 0.65991434\text{x}10^{-10}T. \tag{7}$$

$$D(T) = -2.5166005 + 0.011176552T - 0.17055209\text{x}10^{-4}T^2 \tag{8}$$

$$E(T) = 2.8485101 - 0.015430471T + 0.22398153\text{x}10^{-4}T^2 \tag{9}$$

$$F(T) = -0.0013949422 + 0.77922822\text{x}10^{-5}T - 0.17736045\text{x}10^{-7}T^2 \tag{10}$$

$$G(T) = 0.0024223209 - 0.13698670\text{x}10^{-4}T + 0.20303356\text{x}10^{-7}T^2 \tag{11}$$

$$H(T) = 0.55541298\text{x}10^{-6} - 0.36241535\text{x}10^{-8}T + 0.60444040\text{x}10^{-11}T^2 \tag{12}$$

where

P, kilograms per square **centimeter**

v, cubic centimeters per gram

T, degrees Kelvin

x, grams NaCl per 100 grams solution

5. Enthalpy

A somewhat complicated method was used to calculate the enthalpy of NaCl solutions. A full description of the calculations, together with a table of enthalpy values, are presented in Appendix C. This Appendix is presented in the form of a technical paper which is now under consideration for publication.

6. Entropy

$$s = s_o + \int_{T_o}^{T} \frac{c_p}{T}\, dT - \int_{P_o}^{P} \left(\frac{\partial v}{\partial T}\right)_P dP \qquad (13)$$

where

$$s_o = 0.0876 + 0.067594387x - 1.2767431x^2 + 1.7277596x^2 \qquad (14)$$

The reference temperature, T_o, is 298°K (25°C) and the reference pressure, P_o, is 1 atmosphere.

The integrals in the above equation were evaluated in a manner similar to that presented in Appendix C. Table I presents the results of the evaluation of Equation (13).

Only the final results have been presented in this report. The reader is referred to Chou's dissertation, referenced in the first section of this report, for details concerned with the derivation of these equations. Included in this dissertation is the print out of a computer program, written in Fortran IV, that predicts properties for the cases where the pressure effect on property behavior is negligible.

This program predicts vapor pressure, heat of vaporization, specific volume, enthalpy, and entropy as functions of temperature and salt concentration.

APPENDIX A

HEAT OF VAPORIZATION CALORIMETER

Figure 1 shows the salient features of the heat of vaporization calorimeter that was constructed during the first year of this project. For sake of clarity, many details have been omitted from this schematic diagram. The cell will be used to measure heat of vaporization, as well as vapor pressure. It is hoped that with slight modification the apparatus can also be used to measure osmotic pressure.

The calorimeter works in the following manner. The liquid to be tested is placed in the high pressure, stainless steel container A. The liquid level in the cell is maintained constant by means of detector B and a controlled rate displacement pump C. The liquid contained in the cell is vaporized with heater D. The electrical energy input into the heater is measured with an appropriate external circuit E. The vapor is withdrawn through line F. A Heiss gage G is used to measure vapor pressure. The vapor is condensed and collected in a calibrated burret H. Circulating pump I circulates liquid from the cell where it is cooled. Liquid of a much lower salt concentration is injected into the system with pump C. This liquid has the same composition as that condensed and collected in burret H. This recirculation - injection system maintains the fluid level and salt concentration constant in the cell. Hence, all the energy liberated by heater D causes vaporization of the liquid of fixed composition in the cell. Temperatures and heat losses are detected by approximate thermocouple arrangements such as J. Bath K minimizes the heat loss across the walls of the cell.

A - CALORIMETER CELL
B - LIQUID LEVEL DETECTOR
C - POSITIVE DISPLACEMENT PUMP
D - HEATER
E - ENERGY MEASUREMENT CIRCUIT
F - VAPOR EXIT LINE
G - HEISS GAGE
H - GRADUATED CYLINDER
I - CIRCULATING PUMP
J - THERMOCOUPLES
K - BATH
L - PREHEATER

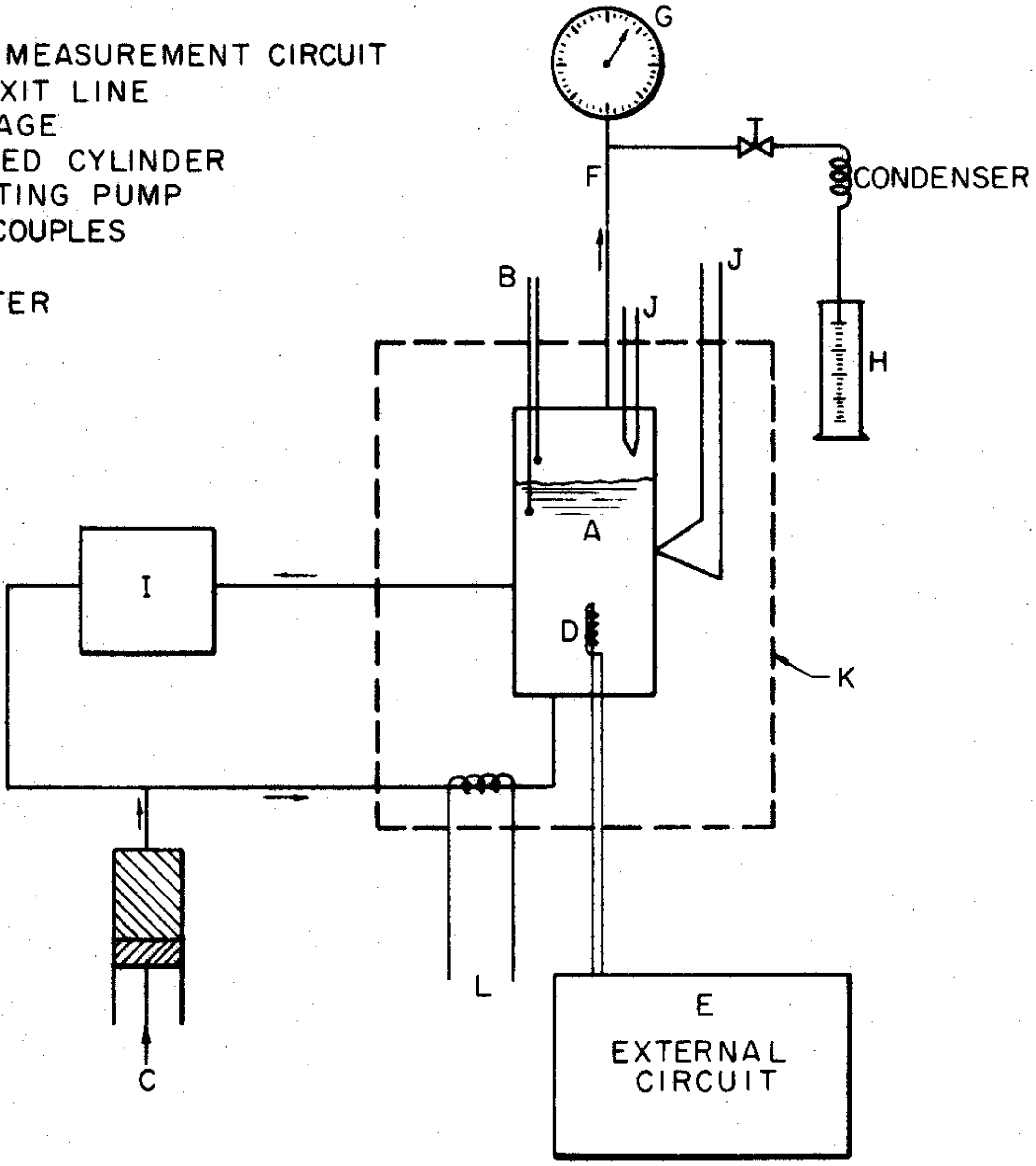

Fig. 1 - SCHEMATIC OF HIGH TEMPERATURE HIGH PRESSURE ENVIRONMENTAL CHAMBER

APPENDIX B

COMPRESSIBILITY OF AQUEOUS SODIUM CHLORIDE SOLUTIONS

Compressibility of Aqueous Sodium Chloride Solutions

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SUMMARY

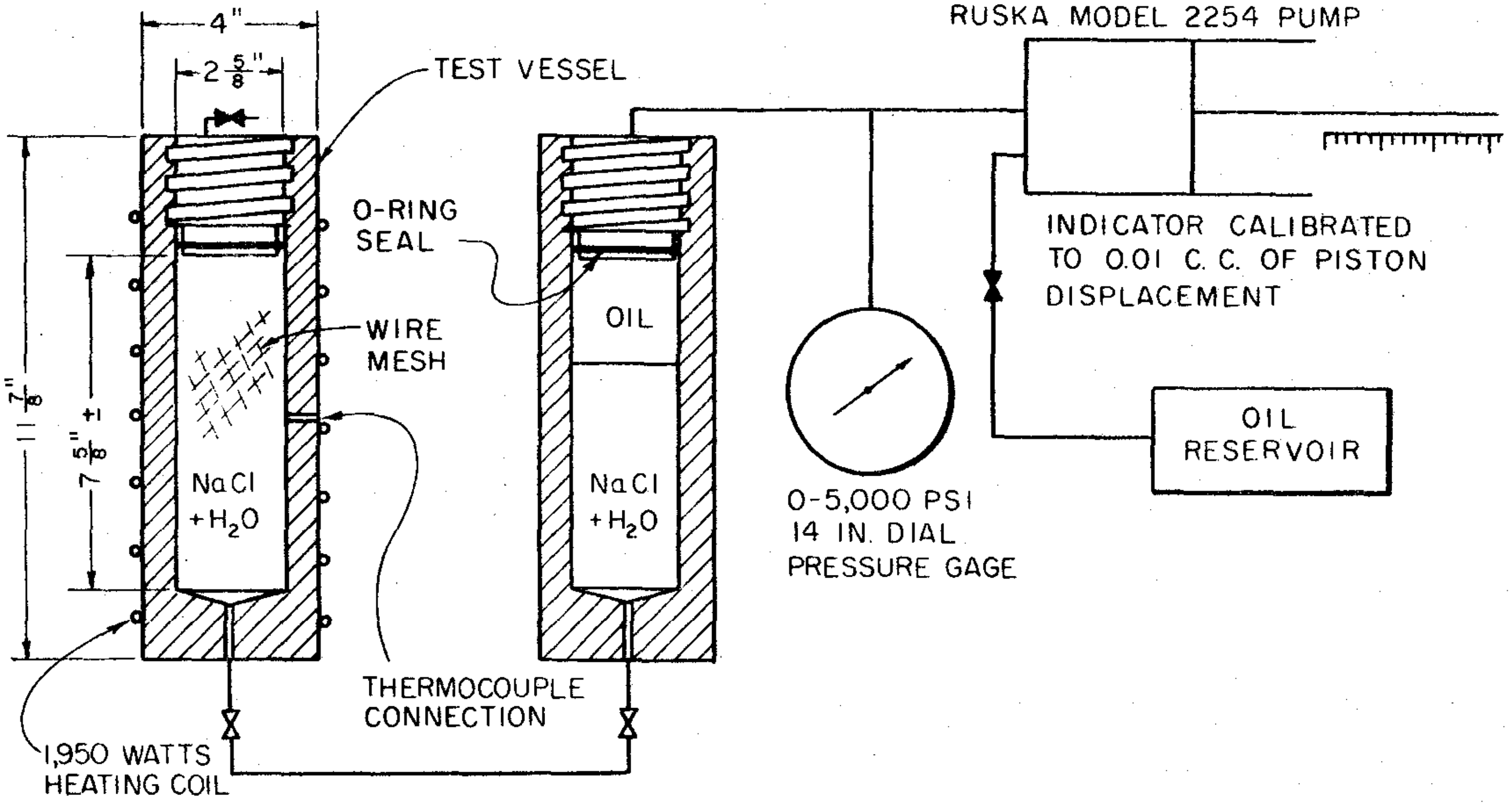
The derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ of NaCl solution has been experimentally determined in the temperature range from 0 to 175°C for concentrations of 5 to 25 grams salt per 100 grams solution and for pressures up to 5,000 psig. An interpolation formula which describes the P-v-T-x relation has been developed to fit these experimental results as well as the density data found in the literature.

Because of the increasing importance in converting salt water to potable water, there is a considerable amount of interest in the thermodynamic properties of aqueous NaCl solutions. A survey of the literature indicated the lack of experimental data on compressibility for NaCl solutions at temperature above 40°C; measurements were therefore made to obtain the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$. The results were then used to derive an appropriate pressure-volume-temperature-concentration (P-v-T-x) relation. The principle of the experimental method is to measure, by means of a calibrated positive-displacement pump, the change of specific volume with pressure at a fixed temperature.

EXPERIMENTAL

The apparatus is shown schematically in Figure 1. The vessel which contains only the solution was made of stainless steel, surrounded by three electrical heating coils of 650 watts each, and insulated with a layer of 1½" thick mineral wool. The electric current through the coil was controlled by a variable resistor in order to maintain the desired temperature of solution in the vessel. To minimize the variation of temperature of the solution, 415 feet of 0.01" o.d. nickel chromium wire was placed inside the vessel to distribute the heat uniformly throughout the solution. The piston of the pump, which was calibrated to 0.01 cubic centimeter of piston displacement, could be advanced or retreated at a uniform speed from 0 to 100 cubic centimeters of displacement per minute by means of a motor and gear box. Saltrol 160, a light oil, was used to separate the solution in the second vessel from the pump and the pressure gage. This 14" dial bourdon tube Heiss pressure gage was calibrated with a dead weight tester before and after the experiment. Each division on the dial of the gage represented 5 psi, and the gage could record a maximum pressure of 5,000 psig. The temperature of the solution was measured by a Conax 20 gage iron constantan thermocouple in conjunction with a Leeds and Northrup millivolt potentiometer. The thermocouple was placed in the middle of the vessel. The readings from the potentiometer were checked with a standard glass thermometer suspended in the vessel before the experiment, and the agreement was within 1°F at the boiling point of water. The solutions were prepared from distilled water and reagent grade sodium chloride with a purity of 99.7%. To avoid possible contamination, the interior surface of the vessel was cleaned with dilute acid solution and thoroughly rinsed with distilled water. After the vessel was filled with solution, any entrained air was carefully

Figure 1. Arrangement of Apparatus for Determining Derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$


4"
2 5/8"
TEST VESSEL
RUSKA MODEL 2254 PUMP
O-RING SEAL
INDICATOR CALIBRATED TO 0.01 C.C. OF PISTON DISPLACEMENT
WIRE MESH
OIL
11 7/8"
7 5/8" ±
NaCl + H2O
NaCl + H2O
OIL RESERVOIR
0-5,000 PSI 14 IN. DIAL PRESSURE GAGE
THERMOCOUPLE CONNECTION
1,950 WATTS HEATING COIL

driven out through the top of the vessel.

The experimental procedure followed was first to raise the pressure of the system to 5,000 psig after the apparatus was assembled. The system was kept at the high pressure for more than 30 minutes to assure no leakage through the joints. The next step was to adjust the electrical resistor and to wait for the attainment of thermal equilibrium. Then, the pressure of the system was gradually lowered by reversing the motion of the piston at a very slow speed, and the piston displacements were recorded at intervals of 250 psi pressure. During this operation, the temperature of the solution dropped slightly; hence it was necessary to raise slightly the current through the heating coils to maintain a constant temperature. After the pressure was lowered to 185 psig, the valve underneath the test vessel was closed to isolate the solution in this vessel from the system. Next, the pressure was again raised to 5,000 psig. The pressure was once more lowered, and the readings of piston displacement were repeated for every 250 psi. Two sets of data, one taken with the valve open and one with the valve closed, were needed to account for the volume changes attributed to the test vessel.

The fundamental measurements made in this experiment were the piston displacements taken at every 250 psi pressure change for both the open and closed valve positions. A series of measurements taken at 350°F and 25% NaCl is shown in Figure 2. The difference between the two piston displacements taken at the same pressure, ΔV, gives the change in volume of test vessel and its contents. The results of these measurements are tabulated in Table I. There are six such sets of data taken at six different temperatures for each of the six different concentrations. Many trial tests were made to determine the degree of consistency of the data. The variation of the average value of ΔV of any set of data was found to be within ½%. A slight nonlinearity of the data is evident. However, the differences of the volume changes for the two valve positions were assumed to be linear with the mean values of pressure in all calculations made in this study. Since the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ does not vary with pressure rapidly, its mean value over a small pressure change ΔP is approximated by the equation

$$-\left(\frac{\partial v}{\partial P}\right)_{T,x} = \frac{\Delta V - \Delta V_e}{M\Delta P} \tag{1}$$

where ΔV represents the volume change of the isolated solution plus the volume change of the vessel containing only solution due to the pressure change ΔP at a constant temperature, M is the mass of solution isolated from the system after closing of the valve, and ΔV_e is the dilation of the vessel subjected to the internal pressure change of ΔP. Let v_i be the specific volume of the isolated solution, V_o the volume of the vessel at room temperature, and V_t the increase in volume of the vessel due to the thermal expansion of metal at temperture t. Then, Equation (1) can be written as

$$-\left(\frac{\partial v}{\partial P}\right)_{T,x} = \frac{v_i(\Delta V - \Delta V_e)}{(V_o + V_t)\Delta P} . \tag{2}$$

The increase of volume ΔV_e with internal pressure was determined experimentally by weighing the overflow of pure water from the top of the vessel in the following manner. The valve under the vessel was

Figure 2. Typical Measurements of Piston Displacement for Compression Test

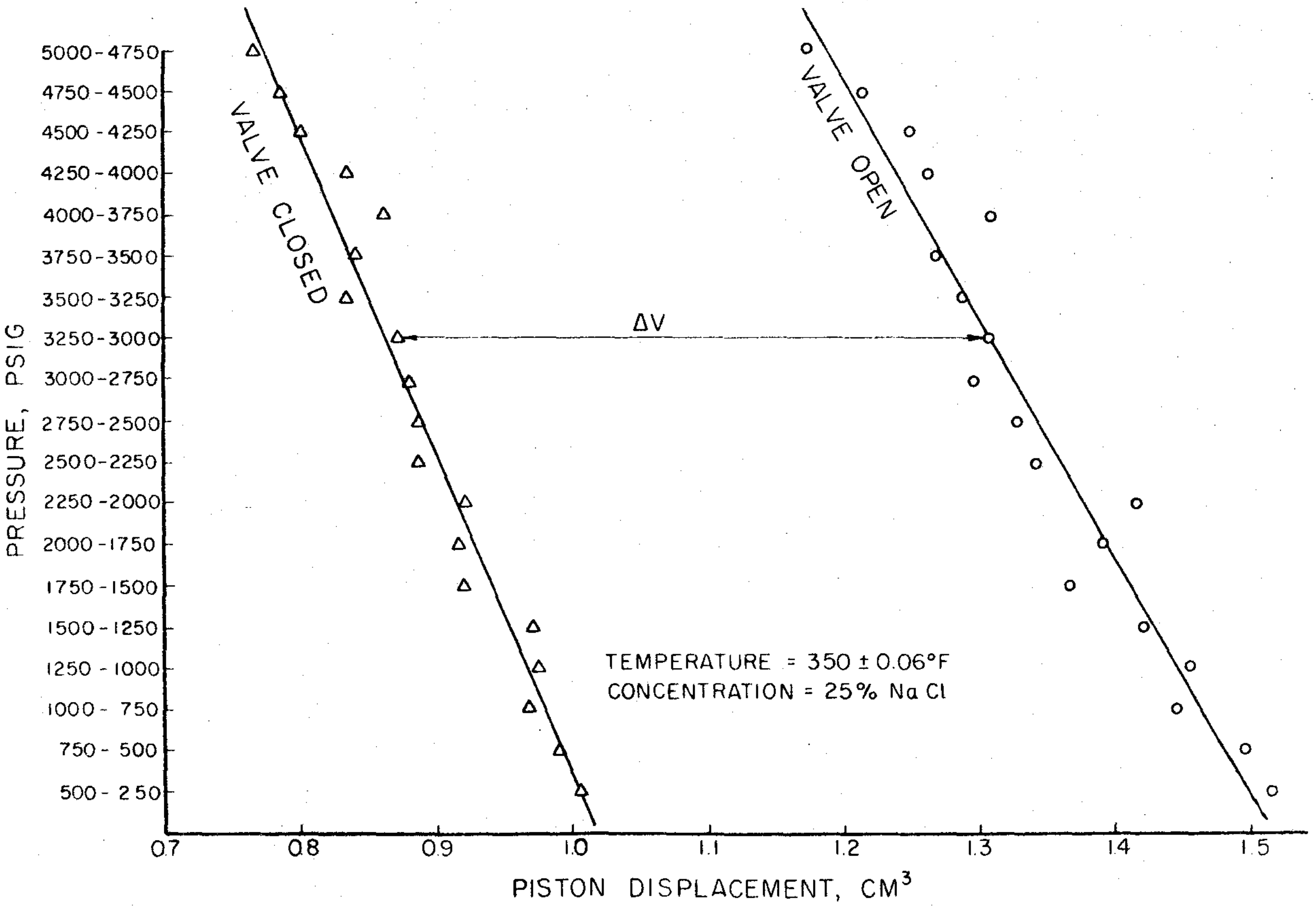

PRESSURE, PSIG
5000-4750
4750-4500
4500-4250
4250-4000
4000-3750
3750-3500
3500-3250
3250-3000
3000-2750
2750-2500
2500-2250
2250-2000
2000-1750
1750-1500
1500-1250
1250-1000
1000-750
750-500
500-250
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
PISTON DISPLACEMENT, CM^3
VALVE CLOSED
VALVE OPEN
ΔV
TEMPERATURE = 350 ± 0.06°F
CONCENTRATION = 25% Na Cl

TABLE I

DIFFERENCE OF VOLUME CHANGE BETWEEN THE TWO EXPERIMENTAL CONDITIONS, ΔV IN CUBIC CENTIMETER

Pressure psig	Salt Weight, gm/100 gm Solution					
	0	5	10	15	20	25
(Temperature = 72°F)						
5000-4750	0.500	0.460	0.405	0.385	0.355	0.325
4750-4500	0.505	0.470	0.420	0.385	0.350	0.340
4500-4250	0.510	0.470	0.425	0.390	0.365	0.345
4250-4000	0.515	0.465	0.415	0.380	0.360	0.340
4000-3750	0.505	0.475	0.435	0.410	0.365	0.340
3750-3500	0.535	0.475	0.455	0.420	0.365	0.310
3500-3250	0.515	0.465	0.425	0.400	0.355	0.350
3250-3000	0.515	0.490	0.415	0.400	0.380	0.330
3000-2750	0.540	0.495	0.435	0.410	0.365	0.350
2750-2500	0.485	0.465	0.450	0.405	0.365	0.340
2500-2250	0.490	0.480	0.410	0.400	0.385	0.345
2250-2000	0.570	0.495	0.450	0.415	0.395	0.350
2000-1750	0.495	0.485	0.445	0.415	0.365	0.335
1750-1500	0.565	0.495	0.370	0.405	0.385	0.360
1500-1250	0.530	0.490	0.440	0.425	0.395	0.370
1250-1000	0.545	0.505	0.455	0.430	0.390	0.380
1000-750	0.540	0.525	0.535	0.440	0.415	0.370
750-500	0.540	0.505	0.515	0.455	0.430	0.380
500-250	0.560	0.495	0.455	0.445	0.395	0.400
(Temperature = 125°F)						
5000-4750	0.485	0.450	0.410	0.385	0.360	0.315
4750-4500	0.505	0.460	0.410	0.390	0.360	0.340
4500-4250	0.480	0.440	0.395	0.395	0.360	0.345
4250-4000	0.495	0.465	0.390	0.390	0.345	0.335
4000-3750	0.490	0.465	0.425	0.390	0.370	0.350
3750-3500	0.535	0.485	0.425	0.390	0.380	0.350
3500-3250	0.490	0.475	0.420	0.395	0.360	0.365
3250-3000	0.500	0.445	0.425	0.405	0.375	0.375
3000-2750	0.520	0.470	0.440	0.400	0.365	0.355
2750-2500	0.515	0.447	0.440	0.415	0.370	0.345
2500-2250	0.520	0.485	0.455	0.425	0.380	0.370
2250-2000	0.495	0.480	0.430	0.400	0.390	0.360
2000-1750	0.490	0.470	0.420	0.410	0.385	0.365
1750-1500	0.510	0.475	0.440	0.425	0.380	0.355
1500-1250	0.530	0.500	0.440	0.415	0.405	0.365
1250-1000	0.545	0.490	0.470	0.420	0.410	0.365
1000-750	0.535	0.480	0.480	0.430	0.410	0.360
750-500	0.560	0.500	0.445	0.410	0.375	0.375
500-250	0.550	0.515	0.480	0.420	0.415	0.375

TABLE I - Continued

Pressure psig	Salt Weight, gm/100 gm Solution					
	0	5	10	15	20	25
(Temperature = 180°F)						
5000-4750	0.390	0.450	0.420	0.390	0.370	0.335
4750-4500	0.505	0.455	0.435	0.405	0.385	0.345
4500-4250	0.500	0.465	0.455	0.405	0.415	0.360
4250-4000	0.525	0.475	0.430	0.410	0.385	0.350
4000-3750	0.510	0.460	0.465	0.420	0.405	0.355
3750-3500	0.505	0.490	0.455	0.410	0.395	0.365
3500-3250	0.535	0.475	0.445	0.430	0.375	0.360
3250-3000	0.500	0.490	0.445	0.400	0.375	0.350
3000-2750	0.535	0.495	0.465	0.430	0.410	0.365
2750-2500	0.525	0.485	0.560	0.405	0.385	0.380
2500-2250	0.505	0.465	0.490	0.425	0.390	0.345
2250-2000	0.515	0.490	0.470	0.405	0.385	0.385
2000-1750	0.520	0.535	0.475	0.460	0.425	0.395
1750-1500	0.545	0.485	0.455	0.430	0.395	0.360
1500-1250	0.540	0.500	0.455	0.415	0.410	0.365
1250-1000	0.565	0.530	0.495	0.445	0.380	0.375
1000-750	0.575	0.465	0.470	0.450	0.430	0.390
750-500	0.545	0.500	0.470	0.450	0.410	0.405
500-250	0.545	0.505	0.480	0.470	0.415	0.410
(Temperature = 250°F)						
5000-4750	0.560	0.490	0.450	0.405	0.390	0.350
4750-4500	0.550	0.495	0.455	0.415	0.420	0.375
4500-4250	0.525	0.515	0.455	0.415	0.400	0.380
4250-4000	0.540	0.500	0.465	0.420	0.410	0.375
4000-3750	0.555	0.515	0.455	0.440	0.410	0.395
3750-3500	0.540	0.520	0.480	0.455	0.425	0.375
3500-3250	0.585	0.535	0.470	0.460	0.415	0.385
3250-3000	0.555	0.505	0.435	0.465	0.435	0.385
3000-2750	0.585	0.495	0.490	0.440	0.445	0.395
2750-2500	0.585	0.530	0.475	0.460	0.420	0.390
2500-2250	0.565	0.540	0.485	0.470	0.430	0.410
2250-2000	0.555	0.525	0.500	0.445	0.445	0.400
2000-1750	0.600	0.540	0.505	0.465	0.435	0.380
1750-1500	0.570	0.555	0.500	0.465	0.420	0.410
1500-1250	0.580	0.535	0.535	0.455	0.460	0.445
1250-1000	0.585	0.540	0.525	0.475	0.485	0.400
1000-750	0.630	0.575	0.470	0.495	0.470	0.415
750-500	0.615	0.560	0.555	0.460	0.415	0.395
500-250	0.615	0.555	0.510	0.505	0.455	0.405

TABLE I - Continued

Pressure	Salt Weight, gm/100 gm Solution					
psig	0	5	10	15	20	25
(Temperature = 300°F)						
5000-4750	0.590	0.535	0.520	0.460	0.400	0.390
4750-4500	0.615	0.540	0.490	0.470	0.445	0.410
4500-4250	0.595	0.550	0.495	0.465	0.430	0.400
4250-4000	0.615	0.545	0.510	0.470	0.425	0.415
4000-3750	0.640	0.550	0.485	0.470	0.445	0.390
3750-3500	0.600	0.560	0.500	0.485	0.460	0.435
3500-3250	0.620	0.565	0.490	0.460	0.455	0.430
3250-3000	0.610	0.575	0.535	0.500	0.445	0.465
3000-2750	0.615	0.560	0.520	0.500	0.445	0.410
2750-2500	0.620	0.570	0.540	0.495	0.470	0.400
2500-2250	0.630	0.605	0.525	0.490	0.455	0.410
2250-2000	0.640	0.625	0.510	0.495	0.445	0.425
2000-1750	0.655	0.565	0.535	0.510	0.470	0.415
1750-1500	0.615	0.590	0.555	0.495	0.455	0.420
1500-1250	0.650	0.580	0.530	0.505	0.465	0.395
1250-1000	0.675	0.585	0.560	0.505	0.500	0.400
1000-750	0.705	0.595	0.580	0.495	0.465	0.400
750-500	0.710	0.645	0.570	0.530	0.460	0.445
500-250	0.690	0.625	0.575	0.520	0.490	0.420
(Temperature = 350°F)						
5000-4750	0.595	0.595	0.500	0.505	0.450	0.405
4750-4500	0.720	0.605	0.525	0.505	0.455	0.425
4500-4250	0.665	0.590	0.515	0.520	0.465	0.445
4250-4000	0.675	0.615	0.545	0.520	0.475	0.425
4000-3750	0.700	0.620	0.555	0.510	0.470	0.445
3750-3500	0.715	0.640	0.560	0.505	0.480	0.425
3500-3250	0.740	0.635	0.545	0.525	0.480	0.450
3250-3000	0.715	0.635	0.540	0.545	0.500	0.435
3000-2750	0.705	0.640	0.600	0.530	0.510	0.415
2750-2500	0.710	0.650	0.575	0.565	0.490	0.440
2500-2250	0.770	0.675	0.620	0.545	0.460	0.455
2250-2000	0.745	0.620	0.585	0.575	0.495	0.495
2000-1750	0.745	0.660	0.590	0.545	0.515	0.475
1750-1500	0.740	0.665	0.630	0.550	0.485	0.445
1500-1250	0.750	0.700	0.560	0.550	0.515	0.450
1250-1000	0.780	0.695	0.605	0.545	0.510	0.480
1000-750	0.770	0.735	0.610	0.575	0.505	0.480
750-500	0.795	0.675	0.610	0.565	0.510	0.505
500-250	0.835	0.710	0.640	0.545	0.530	0.510

closed at the desired pressure, and the valve on the top was then opened until the pressure dropped to atmospheric pressure. The temperatures of water were observed before and after the expansion of water. From the P-v-T relation of water, the volume increase ΔV_e was computed and taken to be

$$\Delta V_e = 0.0322 \div (1.012 - 0.000167\ t) \tag{3}$$

where ΔV_e is in cubic centimeter per 250 psi of pressure change and t is in degrees Fahrenheit.

The measurement of the total volume V_o of solution in the vessel at room temperature was carried out by drying the interior surface and then measuring the amount of water required to fill the vessel.

The volume change V_t due to the thermal expansion of metal was determined by recording the piston displacements at different temperatures when the vessel contained pure water at 185 psig pressure. Then, the values of $(V_o + V_t)$ in cubic centimeters were fitted with the following interpolation formula:

$$V_o + V_t = 661.741245 - 0.0209182\ t + 0.172507 \times 10^{-3}\ t^2 \tag{4}$$

where t is in degrees Fahrenheit.

The specific volume of solution, v_i, was determined in the following manner. The data on densities in grams per cubic centimeter in the region from 0 to 100°C and from 1 to 26 grams of salt per 100 grams of solution at 1 atmosphere are given in the International Critical Tables (7). From these data and the data obtained by Fabuss (1) at

100, 125, 150, and 175°C at 0.1, 1.0, 2.0, and 2.5 moles of salt per 1,000 grams of water at pressures near the vapor pressures, an interpolation formula was established to represent the specific volume of solution at low pressures with temperature and concentration as the only independent variables. Since the values of the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ lie between 0.00008 to 0.00002 cubic centimeter per gram per atmosphere, the change of v_i due to 185 psi of pressure change is about 0.00101 to 0.00025 cubic centimeter per gram. The error caused by using the interpolation formula for specific volume at low pressure to represent v_i at 185 psi in Equation (2) was not felt to be excessive in comparison with other experimental uncertainties.

RESULTS

By substituting the values of v_i, ΔV (smoothed), ΔV_e, V_o, and V_t into Equation (2), the values of the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ at 0, 5, 10, 15, 20, and 25 grams salt per 100 grams solution were obtained and are tabulated in Table II. Figure 3 shows the comparisons of the experimental values obtained for pure water with those calculated from Smith and Keyes' formula (4) and Equation (5) which fits the data and tolerances established by the Third International Conference of Steam Tables (6).

$$v = A(T) - P \cdot B(T) - P^2 \cdot C(T) \ . \qquad (5)$$

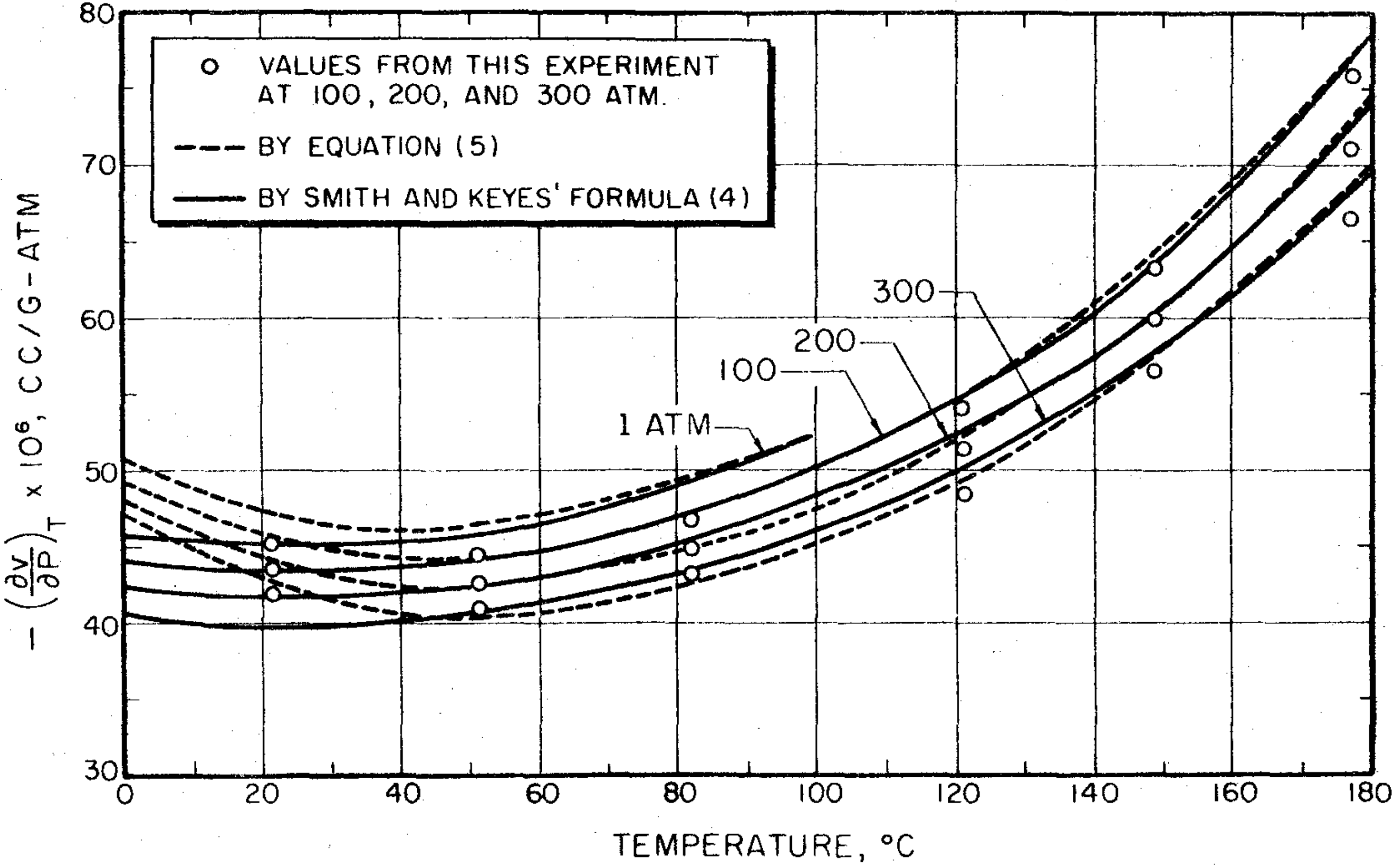
In Equation (5) v is in cubic centimeters per gram, P in kilograms per square centimeter, and T in degrees Kelvin. The three functions of temperature for specific volumes in the region between 0 to 180°C and up to 400 kilograms per square centimeter have been determined as follows:

TABLE II

VALUES OF $(\frac{\partial v}{\partial P})_{T,x}$ IN CUBIC CENTIMETER PER GRAM PER ATMOSPHERE, MULTIPLIED BY -10,000

Salt,%	t, °C	Pressure, atm			
		10	100	200	300
0	22.22	0.4655	0.4510	0.4349	0.4188
0	51.67	0.4630	0.4472	0.4296	0.4120
0	82.22	0.4890	0.4704	0.4497	0.4289
0	121.11	0.5676	0.5419	0.5134	0.4848
0	148.89	0.6666	0.6352	0.6004	0.5655
0	176.67	0.8070	0.7633	0.7147	0.6662
5	22.22	0.4098	0.3977	0.3843	0.3709
5	51.67	0.4117	0.3989	0.3847	0.3704
5	82.22	0.4322	0.4176	0.4014	0.3852
5	121.11	0.4944	0.4760	0.4554	0.4349
5	148.89	0.5698	0.5465	0.5207	0.4948
5	176.67	0.6662	0.6356	0.6016	0.5676
10	22.22	0.3627	0.3499	0.3356	0.3214
10	51.67	0.3663	0.3532	0.3386	0.3241
10	82.22	0.3863	0.3720	0.3560	0.3401
10	121.11	0.4357	0.4188	0.4001	0.3814
10	148.89	0.4917	0.4720	0.4501	0.4282
10	176.67	0.5654	0.5417	0.5154	0.4891
15	22.22	0.3234	0.3105	0.2962	0.2819
15	51.67	0.3297	0.3165	0.3019	0.2873
15	82.22	0.3479	0.3341	0.3188	0.3034
15	121.11	0.3877	0.3725	0.3557	0.3389
15	148.89	0.4321	0.4154	0.3969	0.3784
15	176.67	0.4885	0.4697	0.4488	0.4279
20	22.22	0.2899	0.2769	0.2624	0.2479
20	51.67	0.2985	0.2858	0.2718	0.2577
20	82.22	0.3146	0.3020	0.2878	0.2737
20	121.11	0.3466	0.3334	0.3186	0.3038
20	148.89	0.3816	0.3675	0.3517	0.3360
20	176.67	0.4254	0.4099	0.3927	0.3755
25	22.22	0.2623	0.2495	0.2353	0.2212
25	51.67	0.2725	0.2603	0.2467	0.2332
25	82.22	0.2846	0.2727	0.2594	0.2461
25	121.11	0.3115	0.2994	0.2860	0.2726
25	148.89	0.3405	0.3279	0.3139	0.2999
25	176.67	0.3747	0.3612	0.3463	0.3313

Figure 3. Comparison of $\left(\frac{\partial v}{\partial P}\right)_T$ of Water



○ VALUES FROM THIS EXPERIMENT AT 100, 200, AND 300 ATM.
BY EQUATION (5)
BY SMITH AND KEYES' FORMULA (4)
300
200
100
1 ATM
80
70
60
50
40
30
0
20
40
60
80
100
120
140
160
180
TEMPERATURE, °C
$-\left(\frac{\partial v}{\partial P}\right)_T \times 10^6$, CC/G-ATM

$$\begin{aligned} A(T) &= 5.916365 - 0.010357941T + 0.92700482 \times 10^{-5}T^2 \\ &\quad - 1127.5221/T + 100674.1/T^2, \\ B(T) &= 0.52049144 \times 10^{-2} - 0.10482101 \times 10^{-4}T + 0.83285321 \\ &\quad \times 10^{-8}T^2 - 1.1702939/T + 102.27831/T^2, \\ C(T) &= 0.11854697 \times 10^{-7} - 0.65991434 \times 10^{-10}T. \end{aligned}$$

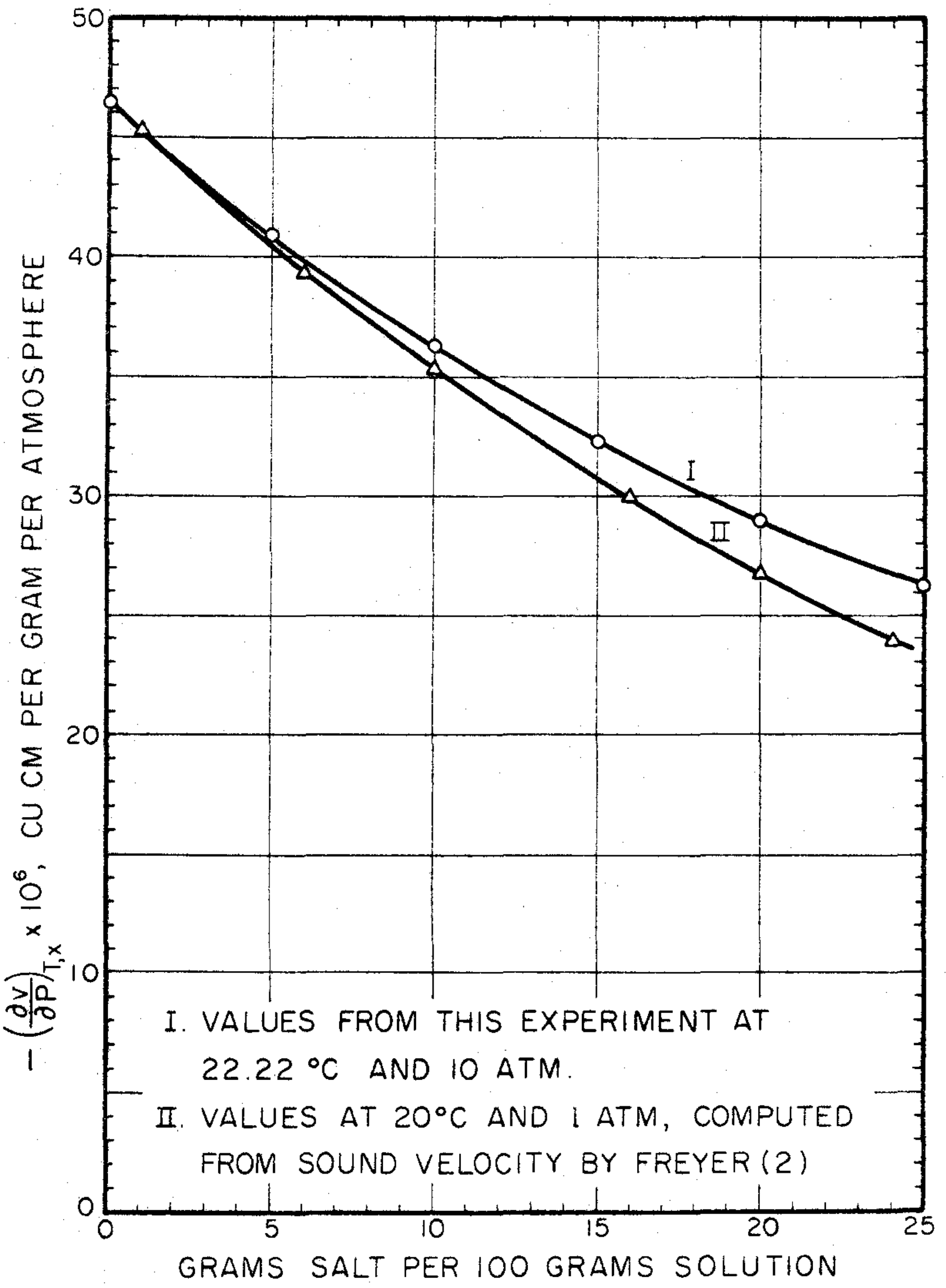
In comparing the values derived from the compressibilities of Kelly and Whalley's recent investigation at one atmosphere (3), Smith and Keyes' values appear too low at temperatures below 30°C. On the other hand, the values obtained in this study may be too low at temperatures above 100°C.

The velocities of sound through aqueous sodium chloride solutions at atmospheric pressure have been measured by Freyer (2). According to the measurements of sound velocity, the values of the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ at 20°C and 1 atmosphere were calculated and are tabulated as follows:

x	1	6	10	16	20	24
u	1497.0	1554.4	1600.6	1673.0	1722.5	1771.5
$-\left(\frac{\partial v}{\partial P}\right)_{T,x} \times 10^6$	45.24	39.41	35.38	30.00	26.83	23.97

where x denotes the concentration in grams salt per 100 grams of solution, u represents the sound velocity in meters per second, and the unit of the derivative is cubic centimeter per gram per atmosphere. These values are plotted in Figure 4 and compared with the values obtained at 72°F in this study. The difference between the two sets of data increases with the increase of salt concentration. A careful review of the testing procedures gave no reasonable explanation to account for such large discrepancies at high salt concentrations. The calculation of $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ from sound velocity was based on the assumption that

Figure 4. Comparison of $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ of Solution


50
40
30
20
10
0
0
5
10
15
20
25
I
II
$-\left(\frac{\partial v}{\partial P}\right)_{T,x} \times 10^6$, CU CM PER GRAM PER ATMOSPHERE
GRAMS SALT PER 100 GRAMS SOLUTION
I. VALUES FROM THIS EXPERIMENT AT 22.22 °C AND 10 ATM.
II. VALUES AT 20°C AND 1 ATM, COMPUTED FROM SOUND VELOCITY BY FREYER (2)

the velocity of wave transmission is solely dependent upon two physical properties of the medium, elasticity and density. A speculative opinion is that the electrostatic pressure due to the electric field around the ions may also have some effect on the velocity of sound through an electrolytic solution.

Another comparison made to isothermal compressibilities is also available in the literature. Literature data are often reported in terms of mean isothermal compressibility k_m, defined as

$$k_m = \frac{(v_1 - v_p)}{v_1(P - 1)} \qquad (6)$$

where v_1 and v_P are the specific volumes in cubic centimeters per gram at the same temperature but under the pressures 1 and P atmospheres, respectively. Tait (5) has found that his experimental data at 0°C, for pressures up to 450 atmospheres and for salt concentrations of 3.88 to 17.63 grams of NaCl per 100 grams of solution, can be represented by the empirical expression

$$k_m = \frac{0.00186}{(36 + P + x)} \qquad (7)$$

where k_m is the mean compressibility per atmosphere, P is the pressure in long tons per square inch, and x is the number of grams of salt per 100 grams of solution. In order to compare the results of the present experiment with Tait's, the mean compressibilities were computed from values of specific volumes given by Equation (8) which fits the experimental results of this study. The disagreement between the values by Tait's formula and by Equations (6) and (8) is less than 2%, as shown

TABLE III

MEAN COMPRESSIBILITY PER ATMOSPHERE AT 0°C, MULTIPLIED BY 10,000

P, atm	Salt Weight, gm/100 gm Solution					
	5		10		15	
	(a)	(b)	(a)	(b)	(a)	(b)
10	45.88	45.29	41.23	40.38	37.24	36.42
100	45.30	44.65	40.68	39.87	36.71	36.01
150	44.98	44.30	40.37	39.59	36.42	35.78
200	44.67	43.96	40.07	39.31	36.12	35.56
250	44.35	43.62	39.76	39.04	35.83	35.33
300	44.03	43.29	39.45	38.77	35.53	35.11

Note: (a) By Equations (6) and (8).

(b) By Tait's Formula.

in Table III.

Many repeated tests were made, and the deviation in results was less than one percent of the average value of the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$. Based on the comparisons of results, it is believed that the probable errors of the derivatives obtained from this experiment are within the limits of ± 4.5% of the true values.

P-v-T-x RELATION

To fit the experimental data, a mathematical expression was arbitarily chosen as

$$v = A(T) - P \cdot B(T) - P^2 \cdot C(T) + x \cdot D(T) + x^2 \cdot E(T) - xP \cdot F(T) - x^2 P \cdot G(T) - \tfrac{1}{2} x P^2 \cdot H(T). \qquad (8)$$

If the concentration x of salt in solution is zero, Equation (8) is reduced to Equation (5) for which the functions A(T), B(T), and C(T) have already been determined.

Based on the values of $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ from this experiment and on the density data given by others (1,7), the functions D(T), E(T), F(T), G(T), and H(T) were determined as given below:

$D(T) = -2.5166005 + 0.011176552T - 0.17055209 \times 10^{-4}T^2$,

$E(T) = 2.8485101 - 0.015430471T + 0.22398153 \times 10^{-4}T^2$.

$F(T) = -0.0013949422 + 0.77922822 \times 10^{-5}T - 0.17736045 \times 10^{-7}T^2$,

$G(T) = 0.0024223209 - 0.13698670 \times 10^{-4}T + 0.20303356 \times 10^{-7}T^2$,

$H(T) = 0.55541298 \times 10^{-6} - 0.36241535 \times 10^{-8}T + 0.60444040 \times 10^{-11}T^2$,

for P in kilograms per square centimeter, v in cubic centimeters per gram, T in degrees Kelvin, and x in grams salt per 100 grams solution.

The estimated maximum deviation of the experimental data on specific volume from Equation (8) with the respective temperature functions is less than 1.5 parts per thousand for temperatures ranging from 0 to 150°C, for concentrations ranging from 0 to 25% of salt weight in solution, and for pressures up to 300 atmospheres. Equation (8) provides a concise representation of the large mass of data and may be used to determine the pressure effects on heat capacity, enthalpy, and entropy.

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APPENDIX C

ENTHALPIES OF AQUEOUS SODIUM CHLORIDE SOLUTIONS FROM 32 TO 350°F

ENTHALPIES OF AQUEOUS SODIUM CHLORIDE SOLUTIONS FROM 32 TO 350°F

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Summary

The enthalpies of sodium chloride solutions have been calculated and tabulated in the temperature range from 32 to 350°F using the specific heats derived from osmotic coefficients, specific heats of pure liquid water, specific heats of solid salt, and solubilities. The pressure dependency of enthalpy was evaluated from a P-v-T-x relation which holds for pressures up to 5,000 psig. Included in this paper are the enthalpy changes required for the phase transition of water in the solutions from liquid to vapor phase.

Symbols

A, B, C....	Empirical parameters
a	Activity
H, h	Enthalpy
n	Number of moles
P	Total normal pressure
p	Vapor pressure
q	Heat
R	Gas constant
T	Absolute temperature (Kelvin scale)
t	Temperature (Fahrenheit scale)

v	Specific volume
x	Mole fraction of salt
w	Weight fraction of salt
-	Placed above a letter to denote partial molal quantity
Subscripts and superscripts	Used to designate conditions, states, or components.

Introduction

In ordinary sea water, sodium and chloride ions constitute about 86 per cent of dissociated ions, and they are also frequently the principal contaminants in brackish water. Within the past several years there has been an increasing interest in the thermodynamic properties of aqueous sodium chloride solutions at temperatures in the range of evaporator operation. A great number of experimental data have been collected in the last century. Some of the early experiments were carried out meticulously, with a high degree of precision; however, the data remain scattered in the literature. This paper presents the values of enthalpy calculated from these prior data.

Enthalpy at 25°C and 1 Atmosphere

The enthalpy change accompanying the dilution of a solution at a given temperature and pressure is called the heat of dilution. If a solution which initially contains n_1 moles of solvent and n_2 moles of solute is diluted to an infinitely dilute solution by adding $(\infty - n_1)$ moles of pure solvent, the heat transfer during the process is

$$\begin{aligned}\Delta H &= (\infty \bar{h}_1^o + n_2 \bar{h}_2^o) - [n_1 \bar{h}_1 + n_2 \bar{h}_2 + (\infty - n_1) \bar{h}_1^o] \\ &= n_1 (\bar{h}_1^o - \bar{h}_1) + n_2 (\bar{h}_2^o - \bar{h}_2)\end{aligned}$$

where the superscript ^{o} denotes infinite dilution. This equation is based on the fact that the molal enthalpy of pure solvent is not different from the partial molal enthalpy of solvent in the infinitely dilute solution. Dividing ΔH by n_2 gives the integral heat of dilution to infinite dilution per mole of solute,

$$q_d = \frac{n_1}{n_2}(\bar{h}_1^o - \bar{h}_1) + (\bar{h}_2^o - \bar{h}_2). \tag{1}$$

If the infinite dilution is chosen as the reference state for the enthalpy of solute, $\bar{h}_2^o$ then becomes zero. It follows that the enthalpy h of solution can be related to the mole fraction of solute and the integral heat of dilution by the equation

$$h = (1 - x)\bar{h}_1^o - xq_d. \tag{2}$$

The integral heat of dilution is also equal to the heat of formation of the solution in the final state minus that in the initial state. The heats of formation at 25°C and 1 atmosphere for various concentrations have been compiled by Rossini (7). In order to be consistent with the values in the steam tables, the value of $\bar{h}_1^o$ of Equation (2) must be based on the convention of zero enthalpy for the saturated water at 0°C and is taken to be 25.015 calories per gram at 25°C and 1 atmosphere. The values of enthalpy have been calculated from Equation (2) for the concentrations at which the integral heat of dilution can be obtained from the data on heat of formation. The results are tabulated in Table I and may be adequately represented by the interpolation formula,

TABLE I

ENTHALPY AT 25°C AND 1 ATMOSPHERE

Salt, %	Heat of Dilution cal/gm Salt	Enthalpy, cal/gm Solution Eq. (2)	Eq. (3)
28.8524	8.1782	15.44	15.42
26.4960	8.0756	16.25	16.24
24.4954	7.9729	16.93	16.97
17.7822	6.1593	19.47	19.47
13.9571	4.6195	20.88	20.87
11.4863	3.4903	21.74	21.74
9.7588	2.6177	22.32	22.32
6.0931	0.6502	23.45	23.45
3.1423	-0.8897	24.26	24.26
1.5962	-1.4714	24.64	24.64
0.8045	-1.5398	24.83	24.83
0.3234	-1.2661	24.94	24.94
0.1619	-1.0266	24.98	24.98
0.0648	-0.7186	25.00	25.00
0.0324	-0.5304	25.01	25.01
0.0065	-0.2395	25.01	25.01
0.0032	-0.1711	25.01	25.01
0.0006	-0.0855	25.01	25.01

$$h_o = 25.015(1 - w) + 30.805561\ w^{1.5} - 161.50632\ w^2 + 79.059598\ w^{2.5} + 114.83149\ w^3 \qquad (3)$$

in which the respective units are calories per gram and grams salt per 100 grams water.

Enthalpy at Other Temperatures and Pressures

For a homogeneous system of invariable composition, the differential of enthalpy may be expressed in terms of the two independent properties, temperature and pressure, as

$$dh = \left(\frac{\partial h}{\partial T} \right)_P dT + \left(\frac{\partial h}{\partial P} \right)_T dP.$$

This leads to the expression

$$h = h_o + \int_{T_o}^{T} c_p dT + \int_{P_o}^{P} \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP. \qquad (4)$$

The pressure dependency of c_p may be determined by the relation

$$c_p = c_p^o - T \int_{P^o}^{P} \left(\frac{\partial^2 v}{\partial T^2} \right)_P dP. \qquad (5)$$

These equations provide a means to evaluate the enthalpies of solution at a fixed concentration if the values of specific heat and the P-v-T relation are known.

Since the experimental data on specific heat are not only scarce but also slightly inconsistent, Chou (1) determined the specific heats of unsaturated solutions from the osmotic coefficients, solubilities, specific heats of pure water, and specific heats of solid salt. The calculated values of c_p in relation to mole fraction x and temperature T in degrees Kelvin were fitted into the following interpolation formula:

$$
\begin{aligned}
c_p = {} & 1.3165380 - 8.9594831\, x + 23.807251\, x^2 \\
& - (0.20328368 \times 10^{-2} - 0.036271808\, x \\
& + 0.062168183\, x^2)\, T + (0.32218320 \times 10^{-5} \\
& - 0.61529617 \times 10^{-4} x + 0.10557408 \times 10^{-3}\, x^2)\, T^2 . \qquad (6)
\end{aligned}
$$

Based on the experimental evidence, he also found a formula, given below, to represent specific volume for temperatures ranging from 0 to 175°C, for concentrations ranging from 0 to 25% of salt weight in solution, and for pressures up to 300 atmospheres with maximum deviation 1.5 parts per thousand:

$$
\begin{aligned}
v = {} & A(T) - P \cdot B(T) - P^2 \cdot C(T) + w \cdot D(T) + w^2 \cdot E(T) \\
& - wP \cdot F(T) - w^2 P \cdot G(T) - \tfrac{1}{2} wP^2 \cdot H(T) \qquad (7)
\end{aligned}
$$

where w is the concentration in grams salt per 100 grams solution, v is the specific volume in cm^3 per gram, T is the temperature in degrees Kelvin, and the temperature functions are:

$$
\begin{aligned}
A(T) = {} & 5.916365 - 0.010357941\, T \\
& + 0.92700482 \times 10^{-5}\, T^2 - 1127.5221/T \\
& + 100674.1/T^2 , \\
B(T) = {} & 0.52049144 \times 10^{-2} - 0.10482101 \times 10^{-4}\, T \\
& + 0.83285321 \times 10^{-8}\, T^2 - 1.1702939/T \\
& + 102.27831/T^2 , \\
C(T) = {} & 0.11854697 \times 10^{-7} - 0.65991434 \times 10^{-10}\, T , \\
D(T) = {} & -2.5166005 + 0.011176552\, T - 0.17055209 \times 10^{-4}\, T^2 , \\
E(T) = {} & 2.8485101 - 0.015430471\, T + 0.22398153 \times 10^{-4}\, T^2 , \\
F(T) = {} & -0.0013949422 + 0.77922822 \times 10^{-5}\, T - 0.17736045 \times 10^{-7}\, T^2 , \\
G(T) = {} & 0.0024223209 - 0.13698670 \times 10^{-4}\, T + 0.20303356 \times 10^{-7}\, T^2 ,
\end{aligned}
$$

$$H(T) = 0.55541298 \times 10^{-6} - 0.36241535 \times 10^{-8}T + 0.60444040 \times 10^{-11}\ T^2.$$

Furthermore, an equation which fits the experimental data on vapor pressure precisely was found as follows:

$$\ln p = (1 - 0.61430798\ x + 1.2470136\ x^2) \cdot (71.024449 - 7381.6477/T - 9.0993037\ \ln T + 0.0070831558\ T) - x\ (2.0278886 - 1.4908968\ x + 77.008083\ x^2) \qquad (8)$$

where p is the vapor pressure in atmospheres, T is the temperature in degrees Kelvin, and x is the mole fraction of salt.

By using Equations (3), (4), (5), (6), (7) and (8), the values of enthalpy at temperatures and pressures other than 25°C and 1 atmosphere have been calculated. The computations can be easily carried out with a computer, although the equations seem long and cumbersome. Table II shows some of the calculated values of enthalpy at the vapor pressures of solutions and at pressures in the subcooled region of 1,000, 2,000, 3,000, 4,000, and 5,000 psia. Figure 1 shows the trends of variations of enthalpy with temperature and concentration at 10 atmospheres.

Comparison

The enthalpies of water in Keenan and Keyes' steam table (4) agree with the calculated enthalpies at zero salt concentration to 1.5 parts per thousand. The enthalpies of sodium chloride solutions have also been calculated by Jessup (3) and Kusunoki (5). However, the scope of Jessup's work is limited to less than 80°F, and in his computation the enthalpies of solid salt in solution and pure water were taken as 200 BTU per pound each at 32°F. Kusunoki's work covers a wider range, from 0 to 100°C at 1 atmosphere, but unfortunately the

TABLE II

ENTHALPY IN BTU PER POUND

Temp, °F	Salt Weight, gm/100 gm Solution 0	5	10	15	20	25
(At vapor pressure)						
32	-0.00	0.13	-0.41	-1.58	-3.27	-5.40
35	3.00	2.98	2.29	0.99	-0.82	-3.03
40	8.01	7.72	6.79	5.27	3.28	0.93
45	13.01	12.46	11.28	9.54	7.37	4.88
50	18.01	17.19	15.77	13.81	11.45	8.84
55	23.01	21.92	20.25	18.08	15.54	12.79
60	28.00	26.65	24.74	22.34	19.62	16.74
65	32.99	31.37	29.22	26.61	23.71	20.69
70	37.98	36.10	33.70	30.87	27.79	24.64
75	42.96	40.82	38.18	35.13	31.87	28.58
80	47.95	45.54	42.65	39.39	35.94	32.52
85	52.93	50.26	47.12	43.64	40.02	36.46
90	57.91	54.98	51.60	47.90	44.09	40.40
95	62.89	59.69	56.07	52.15	48.16	44.34
100	67.87	64.41	60.54	56.40	52.23	48.27
105	72.85	69.12	65.00	60.65	56.29	52.20
110	77.83	73.83	69.47	64.90	60.36	56.13
115	82.81	78.55	73.94	69.14	64.42	60.05
120	87.79	83.26	78.40	73.39	68.48	63.98
125	92.77	87.97	82.86	77.63	72.54	67.69
130	97.76	92.68	87.33	81.87	76.59	71.81
135	102.74	97.39	91.79	86.11	80.64	75.72
140	107.72	102.11	96.25	90.35	84.69	79.63
145	112.71	106.82	100.71	94.58	88.74	83.54
150	117.69	111.54	105.17	98.82	92.78	87.44
155	122.68	116.25	109.63	103.05	96.82	91.34
160	127.68	120.97	114.09	107.28	100.86	95.23
165	132.67	125.68	118.56	111.51	104.90	99.12
170	137.67	130.40	123.02	115.74	108.93	103.01
175	142.67	135.13	127.48	119.97	112.97	106.89
180	147.67	139.85	131.94	124.20	116.99	110.77
185	152.68	144.57	136.40	128.42	121.02	114.64
190	157.69	149.30	140.86	132.65	125.04	118.51
195	162.71	154.03	145.33	136.87	129.06	122.37
200	167.73	158.76	149.79	141.09	133.08	126.23
205	172.76	163.50	154.26	145.31	137.09	130.09
210	177.79	168.24	158.72	149.54	141.10	133.94
212	179.80	170.13	160.51	151.22	142.71	135.48
215	182.82	172.98	163.19	153.76	145.11	137.78
220	187.87	177.72	167.66	157.97	149.12	141.62
225	192.91	182.47	172.13	162.19	153.12	145.45
230	197.97	187.23	176.60	166.41	157.12	149.28
235	203.03	191.98	181.07	170.63	161.11	153.11
240	208.09	196.74	185.55	174.84	165.11	156.92
245	213.17	201.51	190.02	179.06	169.10	160.74

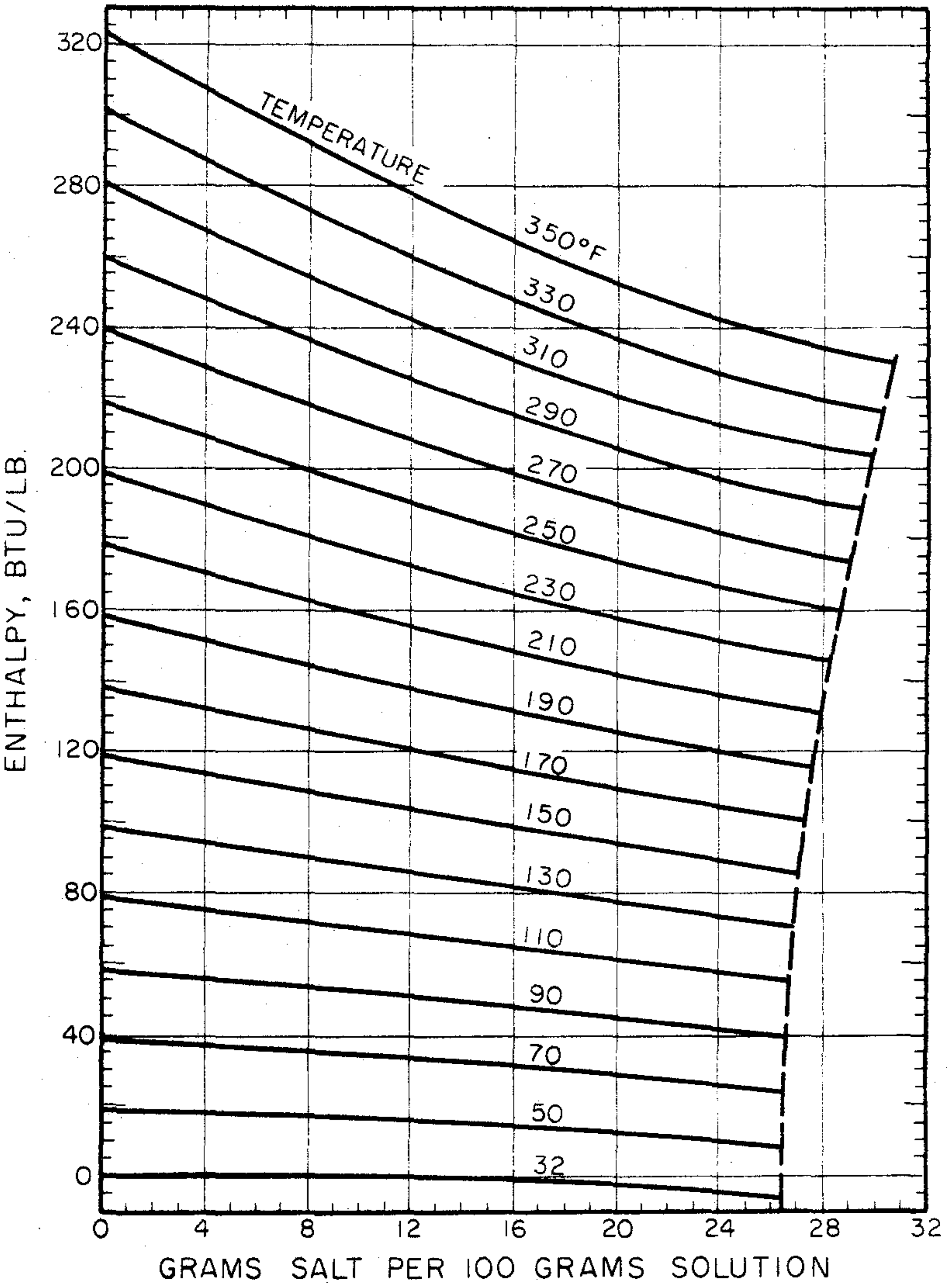
TABLE II - Continued

Temp, °F	Salt Weight, gm/100 gm Solution					
	0	5	10	15	20	25
(At vapor pressure)						
250	218.25	206.28	194.50	183.27	173.08	164.54
255	223.33	211.05	198.98	187.48	177.07	168.34
260	228.43	215.83	203.47	191.70	181.05	172.14
265	233.53	220.62	207.95	195.91	185.02	175.92
270	238.64	225.41	212.44	200.12	188.99	179.71
275	243.76	230.20	216.93	204.33	192.96	183.48
280	248.89	235.00	221.42	208.55	196.93	187.25
285	254.03	239.81	225.92	212.76	200.89	191.01
290	259.18	244.62	230.42	216.97	204.85	194.77
295	264.33	249.44	234.92	221.18	208.81	198.52
300	269.50	254.27	239.42	225.39	212.76	202.26
305	274.67	259.10	243.93	229.60	216.71	205.99
310	279.86	263.94	248.44	233.81	220.65	209.72
315	285.05	268.79	252.96	238.02	224.59	213.44
320	290.26	273.64	257.47	242.23	228.53	217.16
325	295.48	278.50	262.00	246.44	232.46	220.86
330	300.70	283.36	266.52	250.65	236.39	224.56
335	305.94	288.24	271.05	254.85	240.32	228.25
340	311.19	293.12	275.58	259.06	244.24	231.93
345	316.46	298.01	280.12	263.27	248.16	235.61
350	321.73	302.91	284.66	267.48	252.07	239.28
(Pressure = 1,000 PSIA)						
50	20.89	19.91	18.34	16.26	13.79	11.07
100	70.51	66.92	62.94	58.70	54.43	50.39
150	120.14	113.90	107.46	101.03	94.93	89.52
200	169.98	160.98	151.97	143.23	135.18	128.29
250	220.26	208.31	196.54	185.30	175.11	166.55
300	271.22	256.05	241.26	227.26	214.65	204.16
350	323.08	304.37	286.22	269.11	253.75	240.99
(Pressure = 2,000 PSIA)						
50	23.75	22.62	20.91	18.69	16.11	13.30
100	73.14	69.43	65.33	61.00	56.64	52.52
150	122.59	116.27	109.75	103.25	97.08	91.61
200	172.26	163.22	154.17	145.39	137.30	130.36
250	222.35	210.41	198.64	187.39	177.18	168.60
300	273.08	257.97	243.22	229.25	216.66	206.17
350	324.68	306.08	288.01	270.97	255.66	242.93
(Pressure = 3,000 PSIA)						
50	26.59	25.31	23.46	21.12	18.42	15.51
100	75.76	71.93	67.73	63.29	58.84	54.64
150	125.03	118.63	112.04	105.47	99.23	93.70

TABLE II - Continued

Temp, °F	Salt Weight, gm/100 gm Solution					
	0	5	10	15	20	25
(Pressure = 3,000 PSIA)						
200	174.54	165.46	156.37	147.55	139.41	132.43
250	224.44	212.51	200.74	189.49	179.26	170.65
300	274.96	259.91	245.20	231.25	218.67	208.18
350	326.30	307.81	289.83	272.85	257.58	244.87
(Pressure = 4,000 PSIA)						
50	29.41	27.98	25.99	23.53	20.73	17.72
100	78.36	74.42	70.11	65.58	61.04	56.76
150	127.47	120.99	114.33	107.69	101.38	95.78
200	176.82	167.70	158.57	149.71	141.53	134.51
250	226.55	214.62	202.84	191.58	181.33	172.70
300	276.86	261.86	247.18	233.26	220.69	210.20
350	327.97	309.57	291.66	274.75	259.52	246.83
(Pressure = 5,000 PSIA)						
50	32.21	30.63	28.52	25.94	23.02	19.92
100	80.96	76.90	72.49	67.86	63.24	58.87
150	129.91	123.35	116.61	109.90	103.53	97.87
200	179.10	169.94	160.77	151.87	143.65	136.58
250	228.67	216.73	204.95	193.68	183.41	174.76
300	278.78	263.83	249.18	235.28	222.72	212.22
350	329.66	311.35	293.52	276.66	261.47	248.80

Figure 1. Enthalpy at 10 Atmospheres


TEMPERATURE
350°F
330
310
290
270
250
230
210
190
170
150
130
110
90
70
50
32
ENTHALPY, BTU/LB.
320
280
240
200
160
120
80
40
0
0
4
8
12
16
20
24
28
32
GRAMS SALT PER 100 GRAMS SOLUTION

results are published in a small graph. Kusunoki assumes the enthalpies of liquid water and crystalline salt to be zero at 0°C. In this study the enthalpy of dissolved salt in an infinitely dilute solution at 25°C is taken as zero. If this is the case, the enthalpy of crystalline salt at 25°C has a value of -15.9 calories per gram according to the heats of formation given by Rossini (7). After making proper adjustment of the datum values, the calculated values of this study fall on the lines of Kusunoki's graph. Taking the enthalpy of each component, solid salt and pure water, to be 200 BTU per pound at 32°F, the agreement between the enthalpies computed from equations of this study and those by Jessup is better than 4.5 parts in a thousand.

Heat of Vaporization

From the definition of activity one has

$$\left(\frac{\partial \ln a_1}{\partial T}\right)_{P,x} = -\frac{\bar{h}_1 - \bar{h}_1^o}{RT^2} \tag{9}$$

By adding $\bar{h}_g$, the molal enthalpy of water vapor at T, to both sides of Equation (9) and rearranging terms, the heat of vaporization of water for a given solution may be determined by the heat of vaporization at infinite dilution and the activity as shown in the equation

$$\bar{h}_g - \bar{h}_1 = \bar{h}_g - \bar{h}_1^o + RT^2\left(\frac{\partial \ln a_1}{\partial T}\right)_{P,x}. \tag{10}$$

The last term of this equation may be interpreted as the difference between the heat of vaporization of water from solution and the latent heat of pure water at the same temperature. The following discussion describes how this equation was evaluated. In accordance with the data established by the Third International Conference on Steam Tables (10), the latent heat of pure water in BTU per pound can be given by the following equation with a maximum deviation of two parts per ten thousand:

$$\bar{h}_g - \bar{h}_1^o = 1093.3254 - 0.57909483t + 0.228937 \times 10^{-3} t^2 - 0.11130559 \times 10^{-5} t^3 \quad (11)$$

where t is the temperature in degrees Fahrenheit. In general $\ln a_1$ is a function of temperature, pressure, and concentration. The variation of $\ln a_1$ with pressure can be determined by the relation

$$\ln a_1 = \ln a_1 (P_o) + \frac{1}{RT} \int_{P_o}^{P} (\bar{v}_1 - \bar{v}_1^o) dP \quad (12)$$

where $\ln a_1 (P_o)$ is a function of T and x at the fixed pressure P_o; $\bar{v}_1$ and $\bar{v}_1^o$ are respectively the partial volume at the concentration to which the activity a_1 refers and the partial volume at infinite dilution. The partial volumes can be easily evaluated from the specific volume of the solution given by Equation (7) by the relation

$$\bar{v}_1 = v - x \left(\frac{\partial v}{\partial x} \right)_{T,P}.$$

Based on the values of activity from osmotic coefficients given by Gardner, et al. (2), Robinson and Stokes (6), and Smith and Hirtle (8, 9), the differences between $(\bar{h}_g - \bar{h}_1)$ and $(\bar{h}_g - \bar{h}_1^o)$ for solutions from 0 to 350°F have been calculated; the results are tabulated in Table III.

The sum of the value in this table and the heat of vaporization of pure water, which may be found in a steam table or calculated from Equation (11), is the heat required for the phase transition of water in solution from liquid to vapor phase at a constant temperature and composition.

TABLE III

HEAT OF VAPORIZATION OF SOLUTION MINUS LATENT HEAT OF PURE WATER IN BTU PER POUND

Temp, °F	Salt Weight, gm/100 gm Solution					
	1	5	10	15	20	25
32	0.07	-0.40	-1.65	-3.10	-4.52	-5.65
35	0.07	-0.39	-1.58	-3.01	-4.36	-5.38
40	0.07	-0.36	-1.51	-2.86	-4.10	-4.97
45	0.08	-0.34	-1.44	-2.71	-3.84	-4.56
50	0.08	-0.32	-1.37	-2.56	-3.58	-4.15
55	0.08	-0.30	-1.30	-2.41	-3.32	-3.74
60	0.08	-0.28	-1.23	-2.26	-3.06	-3.33
65	0.08	-0.25	-1.16	-2.11	-2.80	-2.92
70	0.08	-0.23	-1.08	-1.96	-2.54	-2.51
75	0.09	-0.21	-1.01	-1.81	-2.28	-2.10
80	0.09	-0.19	-0.94	-1.66	-2.02	-1.69
85	0.09	-0.17	-0.87	-1.51	-1.76	-1.28
90	0.09	-0.15	-0.80	-1.36	-1.50	-0.88
95	0.09	-0.12	-0.73	-1.21	-1.24	-0.47
100	0.09	-0.10	-0.66	-1.06	-0.98	-0.06
105	0.10	-0.08	-0.58	-0.91	-0.72	0.35
110	0.10	-0.06	-0.51	-0.76	-0.46	0.76
115	0.10	-0.04	-0.44	-0.62	-0.20	1.17
120	0.10	-0.01	-0.37	-0.47	0.06	1.58
125	0.10	0.01	-0.30	-0.32	0.32	1.99
130	0.11	0.03	-0.23	-0.17	0.58	2.40
135	0.11	0.05	-0.16	-0.02	0.84	2.81
140	0.11	0.07	-0.09	0.13	1.10	3.22
145	0.11	0.09	-0.01	0.28	1.36	3.63
150	0.11	0.12	0.06	0.43	1.62	4.04
155	0.11	0.14	0.13	0.58	1.88	4.45
160	0.12	0.16	0.20	0.73	2.14	4.86
165	0.12	0.18	0.27	0.88	2.40	5.27
170	0.12	0.20	0.34	1.03	2.66	5.68
175	0.12	0.23	0.41	1.18	2.92	6.08
180	0.12	0.25	0.49	1.33	3.18	6.49
185	0.12	0.27	0.56	1.48	3.44	6.90
190	0.13	0.29	0.63	1.63	3.70	7.31
195	0.13	0.31	0.70	1.77	3.96	7.72
200	0.13	0.33	0.77	1.92	4.22	8.13
205	0.13	0.36	0.84	2.07	4.48	8.54
210	0.13	0.38	0.91	2.22	4.74	8.95
212	0.13	0.39	0.94	2.28	4.85	9.11
215	0.14	0.40	0.98	2.37	5.00	9.36
220	0.14	0.42	1.06	2.52	5.26	9.77
225	0.14	0.44	1.13	2.67	5.52	10.18
230	0.14	0.46	1.20	2.82	5.78	10.59
235	0.14	0.49	1.27	2.97	6.04	11.00
240	0.14	0.51	1.34	3.12	6.30	11.40

TABLE III - Continued

Temp, °F	Salt Weight, gm/100 gm Solution					
	1	5	10	15	20	25
245	0.15	0.53	1.41	3.27	6.56	11.81
250	0.15	0.55	1.48	3.42	6.82	12.22
255	0.15	0.57	1.55	3.57	7.08	12.63
260	0.15	0.60	1.63	3.72	7.34	13.04
265	0.15	0.62	1.70	3.87	7.60	13.45
270	0.15	0.64	1.77	4.02	7.86	13.86
275	0.16	0.66	1.84	4.16	8.12	14.27
280	0.16	0.68	1.91	4.31	8.39	14.68
285	0.16	0.71	1.98	4.46	8.65	15.09
290	0.16	0.73	2.06	4.61	8.91	15.50
295	0.16	0.75	2.13	4.76	9.17	15.91
300	0.17	0.77	2.20	4.91	9.43	16.32
305	0.17	0.79	2.27	5.06	9.69	16.73
310	0.17	0.82	2.34	5.21	9.95	17.14
315	0.17	0.84	2.42	5.35	10.21	17.54
320	0.17	0.86	2.49	5.52	10.47	17.95
325	0.18	0.88	2.56	5.67	10.73	18.36
330	0.18	0.91	2.63	5.82	10.99	18.77
335	0.18	0.93	2.71	5.97	11.25	19.[illegible]8
340	0.18	0.95	2.78	6.12	11.52	19.60
345	0.18	0.98	2.85	6.27	11.78	20.01
350	0.19	1.00	2.93	6.42	12.04	20.42

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