

THERMODYNAMIC PROPERTIES OF AQUEOUS SODIUM
CHLORIDE SOLUTIONS FROM 32 TO 350 °F

By

JAMES CHIA-SAN CHOU

Bachelor of Science
National Institute of Technology
Chungking, China
1941

Master of Science
Georgia Institute of Technology
Atlanta, Georgia
1949

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of the Oklahoma State University
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Thesis Approved:

Allen M. Rowe

Thesis Adviser

A. Glomer

Robert H. Robinson, Jr.

J. A. Wittelt

O. N. Durhan

Dean of the Graduate College

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CHAPTER I

INTRODUCTION

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 interest. In ordinary sea water sodium and chloride ions constitute about 86 per cent of the dissociated ions, and they are also frequently the principal contaminants in brackish water. The properties of sodium chloride solutions are often used as first approximations to those of sea water in designing desalinating evaporators. It is desirable to have these properties available in convenient forms.

A great number of data have been collected on aqueous sodium chloride solutions in the last century. Many of the early experiments were carried out meticulously with a high degree of precision, even by the modern standards; however, the experimental data are scattered in the literature, usually limited to temperatures not over 100°C and recorded in metric units. In 1965 the M. W. Kellogg Company (31), under a contract with the Office of Saline Water, compiled an engineering data book which contains a few interesting charts covering some of the thermodynamic properties of sodium chloride solutions in English units. In this book one finds that the specific heats have been extrapolated from approximately 165 to 250°F without any justification and that the

densities are limited to a maximum temperature of 212°F at 1 atmosphere. Evidently an expansion of such work is needed to encompass a broader region.

The objective of this study is to obtain formulae by correlating the experimental data so that vapor pressures, specific volumes, enthalpies, entropies, and heats of vaporization can be readily computed for the unsaturated solutions at temperatures from 32 to 350°F. This temperature range corresponds to the vapor pressure range of pure water from 0.088 to 135 psia.

Among the most basic data required for the calculations of thermodynamic properties of solutions are the values of specific heats at various conditions and pressure-volume-temperature-concentration (P-v-T-x) relations. Since an insufficient number of direct measurements of specific heat, even below 75°C, has been made, the values of specific heats were calculated in this study with osmotic coefficient data, specific heat data for liquid water and solid salt, and concentration data for saturated solutions. The detailed calculations and the comparison of calculated results with experimental data are shown in Chapter III. The results appear quite reasonable.

As to the P-v-T-x relation, the data on specific volume in the literature are limited to solutions at one atmosphere or the vapor pressures. In order to account for the effect of pressure, solutions were compressed isothermally up to 5,000 psig with a calibrated positive-displacement pump, as reported in Chapter IV. Then, the experimental data were fitted into an equation to represent specific volume explicitly in terms of temperature, pressure, and concentration. This equation and its derivatives enable one to determine the pressure dependencies of

specific heat, specific volume, enthalpy and entropy.

Chapter V covers the calculations of enthalpy and entropy. The reference state for the water in solution is the same as that of pure water in current steam tables; thus, the values obtained in this study may be used in conjunction with the steam tables for heat balances. Heat of vaporization was computed from the activity of water in solution.

No equation can be found to represent the relations among the properties in an absolutely correct manner without understanding the fundamental nature of the substances and their interactions. However, an equation - even if it is empirical - which adequately represents the property relations can be used to interpolate the experimental data, to facilitate calculations involving integration and differentiation, and to provide a concise representation of a large mass of data. An efficient evaluation of the properties is nearly impossible without interpolation formulae. Some of the rather cumbersome equations developed in this study would have been impractical in the pre-computer days, but they present no difficulty today. The key formulae in this paper can be easily programmed for computing the properties in the range of interest.

CHAPTER II

VAPOR PRESSURE

Ideal Solution

From the viewpoint of the discrete nature of matter, the vapor pressure of a volatile component in solution reflects the probability that a molecule will or can escape from the solution into the surroundings. Raoult's law gives the vapor pressure p_i of a volatile component in an ideal solution as

$$p_i = x_i p_i^\circ$$

where p_i° is the vapor pressure of the pure liquid of that component at the same temperature and x_i is the mole fraction of the component in solution. If each ion of a dissociated 1-1 electrolyte in solution acts independently as if it were a molecule to the escaping probability, the vapor pressure lowering $(p_1^\circ - p_1)/p_1^\circ$ of the solvent of an ideal binary solution should be equal to two times the mole fraction x_2 of the electrolyte; since

$$p_1 = (1 - 2x_2)p_1^\circ,$$

one has

$$\frac{p_1^\circ - p_1}{p_1^\circ} = 2x_2.$$

This expression furnishes a basis to roughly approximate the vapor pressure of aqueous sodium chloride solutions from the vapor pressure p_1^0 of pure water. The deviations of the actual values at a few selected temperatures and concentrations are shown in Table I. One notes that the deviations vary nonuniformly and are exceedingly large in some cases.

Experimental Data and Graphical Representations

Many experimental data on vapor pressures of aqueous NaCl solutions have been reported in literature, but most of them were taken at conditions below the boiling-point temperature at one atmosphere. The results of early measurements from 0 to 100°C from 0 to 25% weight of salt have been compiled by Kracek as shown in International Critical Table (51) and have been reviewed by Badger and Baker (3). Emden and Tam-
mann's data are recorded in Tabellen (28). Recently, Fabuss and Korosi (7, 8) reported measurements with a modified isoteniscope over the temperature range of 75 to 150°C at 0.1, 1.0, 2.0, and 3.0 moles salt per 1,000 grams water. Keevil (21) measured the vapor pressures of saturated solutions from 150 to 650°C. The experimental data from the various sources are not in complete agreement among themselves. The values of vapor pressures derived from data on osmotic coefficients, which will be discussed later, are considered to be more precise than those reported in literature.

If the degree of accuracy is not critical, a graphical method may facilitate the interpolation and extrapolation of experimental data. Othmer (34) plotted the logarithms of the vapor pressures of several aqueous solutions against the logarithms of vapor pressures of water at

TABLE I
 VAPOR PRESSURE LOWERING RATIO,
 $(p_1^0 - p_1)/p_1^0 x_2$

Temp., °C	Salt Weight, gm/100 gm Solution						
	1.0	2.0	5.0	10.0	15.0	20.0	25.0
0	1.964	1.901	1.846	1.902	2.031	2.197	2.378
10	1.949	1.895	1.857	1.925	2.059	2.225	2.404
20	1.934	1.889	1.865	1.944	2.082	2.247	2.421
30	1.920	1.884	1.872	1.960	2.099	2.261	2.432
40	1.907	1.878	1.878	1.972	2.111	2.271	2.435
50	1.894	1.872	1.883	1.982	2.120	2.275	2.433
60	1.882	1.867	1.886	1.989	2.125	2.275	2.427
70	1.871	1.861	1.888	1.993	2.127	2.271	2.416
80	1.860	1.856	1.890	1.996	2.126	2.264	2.401
90	1.850	1.851	1.891	1.997	2.122	2.253	2.382
100	1.841	1.846	1.890	1.997	2.117	2.240	2.361
110	1.831	1.841	1.890	1.995	2.109	2.225	2.336
120	1.823	1.836	1.888	1.991	2.099	2.207	2.309
130	1.814	1.831	1.887	1.987	2.088	2.187	2.280
140	1.860	1.826	1.884	1.981	2.076	2.166	2.249
150	1.798	1.821	1.882	1.975	2.062	2.143	2.216
160	1.791	1.816	1.879	1.967	2.047	2.118	2.182
170	1.784	1.811	1.875	1.959	2.031	2.093	2.146
180	1.777	1.807	1.871	1.951	2.014	2.066	2.108

Note: Ratio of ideal solution = 2.0

the same temperatures to show that the data points fell on a family of straight lines which were substantially parallel. Baker and Waite (4) employed Dühring's rule (i.e., the ratios of the boiling points of two similar liquids have approximately the same value at all pressures) to plot the boiling points of aqueous solutions against the corresponding boiling points of water; and the points so obtained formed a family of approximately straight lines. Roehl (16) plotted the logarithms of the vapor pressures of saturated aqueous solutions against the reciprocals of absolute temperature and found the lines were also straight and parallel. Graphical approximations such as these mentioned may give reasonable estimates for certain applications, but they can rarely be used for precise computation. To improve the precision, interpolation formulae were developed in this study and are presented later in this chapter.

Activity of Water and Osmotic Coefficient

The difference in the Gibbs free energy of perfect gas, accompanying an isothermal change between two states, is given by

$$g - g_0 = RT \ln P/P_0.$$

A similar equation, originated by G. N. Lewis, may be arbitrarily written for an imperfect gas at a constant temperature T:

$$g - g_0 = RT \ln f/f_0$$

where f and f_0 are the fugacities at the pressures P and P_0 . The definition of fugacity is completed by specifying the condition that f/P

approaches unity as P approaches zero.

When a liquid is in equilibrium with its vapor, the molal free energy of the liquid must be the same as that of vapor. It follows that the fugacity of the liquid is equal to that of vapor with which it is in equilibrium. The ratio of fugacity in a given state to fugacity in the reference state is called the activity and is here represented by the letter a . Activity is dimensionless, while fugacity has the dimension of pressure. In dealing with a solution, it is necessary to use the partial molal free energy, or chemical potential, of each component. The partial molal free energy \bar{g}_i of i th component in a solution is defined as the rate of change of molal free energy of the solution with change in the number of moles of i th component, with the numbers of moles of all other components being held constant at constant temperature and pressure. The activity a_i of i th component is then related to its partial molal free energy by

$$\bar{g}_i - \bar{g}_i^\circ = RT \ln f_i / f_i^\circ = RT \ln a_i. \quad (2-1)$$

The reference state to which the partial molal free energy of the solvent in an electrolyte solution is referred is invariably the pure solvent at the same temperature and pressure of the solution.

For purely numerical reasons, another function ϕ , called the practical osmotic coefficient, is defined by the relation

$$\ln a_1 = -\phi \nu m M_1 / 1000 \quad (2-2)$$

where ν refers to the number of ions in solution per molecule of dissociated salt, m denotes the moles of salt per 1,000 grams of solvent, a_1 is the activity of solvent and M_1 is the molecular weight of solvent.

The osmotic coefficients of aqueous sodium chloride solution from 60 to 100°C and from 0.05 to 4 m have been determined with boiling point data by Smith (45). He considers his measurements of boiling points are consistent within $\pm 0.0002^\circ\text{C}$. Harned and Nims (14) determined the activity coefficients of sodium chloride from electromotive force measurements over a temperature range from 0 to 40°C. Smith and Hirtle (46) then calculated the osmotic coefficients with Harned and Nims' data. Scatchard, Hamer, and Wood (40) determined the osmotic coefficients from isopiestic vapor pressure measurements at 25°C for concentrations ranging from 0.1 to 6.0 m; their results are in good agreement with Harned and Nims'. Recently, Gardner, Jones and Nordwall (10) have designed a capacitance pressure transducer to translate vapor pressure into dry nitrogen pressure for the solution and solvent separately; they extended the osmotic coefficient data to 275°C at 1, 2, and 3 m from the measurements of vapor pressures.

The problem of using activities to calculate other properties is best regarded as that of finding a correct expression which describes activity as a function of composition, temperature, or other relevant variables. The Debye-Hückel theory explains the behavior of strong electrolytes in very dilute solution. Their limiting law points out that the ratio of activity of electrolytes to the square root of concentration approaches linearity at high dilution. Many papers have been written to examine the range of validity of Debye-Hückel equation, and it is agreed that this equation will not fit the experimental data accurately above 0.1 m. Several modified versions of the equation have been proposed for fitting the data at higher concentrations, and as a rule extra terms are added to the basic equation without theoretical

justification (37). The real nature of electrolyte solutions in regions of high salt concentration has yet to be discovered.

The activity a_1 of solvent, the activity a_2 of solute and the mole fraction x of solute are related by the Gibbs-Duhem relation

$$\left(\frac{\partial \ln a_1}{\partial x}\right)_{P,T} = -\frac{x}{1-x} \left(\frac{\partial \ln a_2}{\partial x}\right)_{P,T}$$

It follows that as x approaches zero, either

$$\left(\frac{\partial \ln a_1}{\partial x}\right)_{P,T} \rightarrow 0 \text{ or } \left(\frac{\partial \ln a_2}{\partial x}\right)_{P,T} \rightarrow \infty.$$

Guggenheim (13) points out that the first alternative applies to a non-electrolyte solution which is characterized by short-range forces between solute particles. In this case, if $\ln a_1$ is expressed in a series of integral powers of x , say

$$\ln a_1 = A'x^2 + B'x^3 + C'x^4 + \dots$$

where A' , B' , C' ... are parameters which depend on temperature and pressure, there can be no term lower than the second power of x . However, for an electrolyte solution the deviation from ideality is due to long range electrostatic interactions between ions in addition to short range forces, so the second alternative is valid. The series representation of $\ln a_2$ of electrolyte must include a term x^n where n is a fractional number as

$$\ln a_2 = A''x^n + B''x + C''x^2 + \dots$$

Thus, the lowest power of x in the expression of $\ln a_1$ is less than second power.

The logarithm of vapor pressure of a solution at a fixed concentration may be fitted into a three term polynomial, $a + b/T + c \ln T$, satisfactorily. Since $\ln a_1$ is approximately equal to the ratio of vapor pressure of water in solution to vapor pressure of pure water at the same temperature, the following equation is expected to fit the experimental values of $\ln a_1$ at constant pressure:

$$\begin{aligned} \ln a_1 = & Ax + Bx^{1.5} + Cx^2 + (Dx + Ex^{1.5} + Fx^2)/T \\ & + (Gx + Hx^{1.5} + Ix^2) \ln T \end{aligned} \quad (2-3)$$

where x is the mole fraction of salt and T is the temperature in degrees Kelvin. From the osmotic coefficient data reported in literature, the values of $\ln a_1$ have been calculated with Equation (2-2). The least squares method was then used to determine the best values of the coefficients of Equation (2-3) at 1 atmosphere from 0 to 100°C. The results are:

$$\begin{aligned} A = -0.072395368 & \quad B = -153.44684 \\ C = -25.984373 & \quad D = -401.49907 \\ E = 11212.309 & \quad F = -9402.7989 \\ G = -0.1201684 & \quad H = 21.082685 \\ I = 6.4225388. & \end{aligned}$$

Equation (2-3) is strictly an empirical equation, which does not describe the true nature of the relationship among the variables. However, it may be used as an interpolation formula. Table II shows the comparison between activities of water as calculated from osmotic coefficient data and as given by Equation (2-3). The derivatives of $\ln a_1$ are related to other thermal properties, and these relations must be

TABLE II
ACTIVITIES OF WATER AT 1 ATMOSPHERE

Molality	Temp., °C	Ln a_1 (Data)	Ln a_1 (Est.)	Data-Est.
				Data
0.10	0.0	-0.003351 (46)	-0.003617	-0.0793
0.20	0.0	-0.006630	-0.007008	-0.0570
0.50	0.0	-0.016359	-0.016774	-0.0254
1.00	0.0	-0.033005	-0.033027	-0.0007
1.50	0.0	-0.050373	-0.050121	0.0050
2.00	0.0	-0.068605	-0.068463	0.0021
2.50	0.0	-0.088098	-0.088237	-0.0016
3.00	0.0	-0.109177	-0.109525	-0.0032
3.50	0.0	-0.131913	-0.132360	-0.0034
0.10	20.0	-0.003351	-0.003542	-0.0571
0.20	20.0	-0.006644	-0.006924	-0.0421
0.50	20.0	-0.016539	-0.016837	-0.0180
1.00	20.0	-0.033618	-0.033610	0.0002
1.50	20.0	-0.051562	-0.051360	0.0039
2.00	20.0	-0.070839	-0.070382	0.0064
2.50	20.0	-0.091251	-0.090802	0.0049
3.00	20.0	-0.113068	-0.112668	0.0035
3.50	20.0	-0.136453	-0.135989	0.0034
0.10	25.0	-0.003358 (36)	-0.003524	-0.0495
0.20	25.0	-0.006666	-0.006902	-0.0354
0.30	25.0	-0.009956	-0.010227	-0.0272
0.50	25.0	-0.016611	-0.016839	-0.0137
0.70	25.0	-0.023381	-0.023497	-0.0050
1.00	25.0	-0.033798	-0.033708	0.0027
1.50	25.0	-0.051832	-0.051577	0.0049
2.00	25.0	-0.071055	-0.070719	0.0047
2.50	25.0	-0.091611	-0.091248	0.0040
3.00	25.0	-0.113501	-0.113202	0.0026
3.50	25.0	-0.136832	-0.136587	0.0018
4.00	25.0	-0.161712	-0.161385	0.0020
4.20	25.0	-0.171159	-0.171693	-0.0031
4.40	25.0	-0.181688	-0.182220	-0.0029
4.60	25.0	-0.192433	-0.192963	-0.0028
4.80	25.0	-0.203393	-0.203919	-0.0026
5.00	25.0	-0.214751	-0.215086	-0.0016
5.20	25.0	-0.226151	-0.226460	-0.0014
5.40	25.0	-0.237963	-0.238040	-0.0003
5.60	25.0	-0.250005	-0.249820	0.0007
5.80	25.0	-0.262277	-0.261800	0.0018
6.00	25.0	-0.274780	-0.273974	0.0029
0.10	40.0	-0.003347	-0.003472	-0.0371
0.20	40.0	-0.006666	-0.006833	-0.0250
0.50	40.0	-0.016611	-0.016816	-0.0124
1.00	40.0	-0.033906	-0.033903	0.0001
1.50	40.0	-0.052156	-0.052042	0.0022

TABLE II - Continued

Molality	Temp., °C	Ln a_1 (Data)	Ln a_1 (Est.)	<u>Data-Est.</u> Data
2.00	40.0	-0.071704	-0.071444	0.0036
2.50	40.0	-0.092512	-0.092188	0.0035
3.00	40.0	-0.114257	-0.114296	-0.0003
3.50	40.0	-0.137462	-0.137760	-0.0022
0.05	50.0	-0.001694	-0.001740	-0.00274
0.10	50.0	-0.003340	-0.003437	-0.00291
0.14	50.0	-0.004666	-0.004781	-0.00247
0.20	50.0	-0.006637	-0.006785	-0.00223
0.30	50.0	-0.009934	-0.010111	-0.0178
0.40	50.0	-0.013274	-0.013439	-0.0124
0.50	50.0	-0.016629	-0.016781	-0.0092
0.60	50.0	-0.020041	-0.020148	-0.0054
0.70	50.0	-0.023482	-0.023546	-0.0027
0.80	50.0	-0.026952	-0.026978	-0.0010
1.00	50.0	-0.034014	-0.033962	0.0015
0.05	60.0	-0.001694 (45)	-0.001720	-0.0154
0.10	60.0	-0.003347	-0.003404	-0.0169
0.20	60.0	-0.006637	-0.006736	-0.0150
0.30	60.0	-0.009934	-0.010056	-0.0123
0.40	60.0	-0.013274	-0.013385	-0.0083
0.50	60.0	-0.016629	-0.016733	-0.0062
0.60	60.0	-0.020041	-0.020108	-0.0033
0.70	60.0	-0.023482	-0.023516	-0.0014
0.80	60.0	-0.026952	-0.026960	-0.0003
1.00	60.0	-0.034014	-0.033971	0.0013
1.50	60.0	-0.052318	-0.052292	0.0005
2.00	60.0	-0.071992	-0.071840	0.0021
2.50	60.0	-0.092873	-0.092658	0.0023
3.00	60.0	-0.114690	-0.114748	-0.0005
3.50	60.0	-0.137714	-0.138090	-0.0027
4.00	60.0	-0.162865	-0.162650	0.0013
0.05	70.0	-0.001692	-0.001700	-0.0049
0.10	70.0	-0.003340	-0.003371	-0.0092
0.20	70.0	-0.006623	-0.006687	-0.0097
0.30	70.0	-0.009912	-0.009998	-0.0087
0.40	70.0	-0.013245	-0.013323	-0.0059
0.50	70.0	-0.016593	-0.016671	-0.0047
0.60	70.0	-0.019998	-0.020049	-0.0026
0.70	70.0	-0.023406	-0.023462	-0.0024
0.80	70.0	-0.026923	-0.026912	0.0004
1.00	70.0	-0.033942	-0.033937	0.0002
1.50	70.0	-0.052318	-0.052286	0.0006
2.00	70.0	-0.071920	-0.071834	0.0012
2.50	70.0	-0.092692	-0.092613	0.0009
3.00	70.0	-0.114474	-0.114615	-0.0012
3.50	70.0	-0.137462	-0.137816	-0.0026
4.00	70.0	-0.162432	-0.162180	0.0016

TABLE II - Continued

Molality	Temp., °C	Ln a_1 (Data)	Ln a_1 (Est.)	Data-Est. Data
0.05	80.0	-0.001690	-0.001681	0.0052
0.10	80.0	-0.003337	-0.003339	-0.0007
0.20	80.0	-0.006615	-0.006637	-0.0032
0.30	80.0	-0.009902	-0.009937	-0.0036
0.40	80.0	-0.013217	-0.013255	-0.0029
0.50	80.0	-0.016575	-0.016599	-0.0015
0.60	80.0	-0.019955	-0.019976	-0.0011
0.70	80.0	-0.023381	-0.023388	-0.0003
0.80	80.0	-0.026837	-0.026838	-0.0001
1.00	80.0	-0.033870	-0.033863	0.0002
1.50	80.0	-0.052210	-0.052204	0.0001
2.00	80.0	-0.071704	-0.071713	-0.0001
2.50	80.0	-0.092422	-0.092410	0.0001
3.00	80.0	-0.114257	-0.114279	-0.0002
3.50	80.0	-0.136958	-0.137294	-0.0025
4.00	80.0	-0.161423	-0.161415	0.0001
0.05	100.0	-0.001684	-0.001645	0.0232
0.10	100.0	-0.003326	-0.003277	0.0147
0.20	100.0	-0.006587	-0.006535	0.0078
0.30	100.0	-0.009848	-0.009806	0.0042
0.40	100.0	-0.013144	-0.013102	0.0032
0.50	100.0	-0.016485	-0.016428	0.0034
0.60	100.0	-0.019846	-0.019789	0.0029
0.70	100.0	-0.023230	-0.023186	0.0019
0.80	100.0	-0.026693	-0.026622	0.0026
1.00	100.0	-0.033690	-0.033616	0.0022
1.50	100.0	-0.051886	-0.051848	0.0007
2.00	100.0	-0.071055	-0.071174	-0.0017
2.50	100.0	-0.091521	-0.091595	-0.0008
3.00	100.0	-0.113285	-0.113085	0.0018
3.50	100.0	-0.135823	-0.135611	0.0016
4.00	100.0	-0.159261	-0.159133	0.0008

Note: Data based on osmotic coefficients by Robinson et al. (36) and Smith et al. (45,46).

taken into consideration when determining the form of the interpolation formula for $\ln a_1$. Equation (2-3) was adopted after having tried several other forms of formulae.

The rate of change of the activity with pressure at a given temperature may be evaluated from partial molal volumes. Differentiation of $\ln a_1$ in Equation (2-1) gives

$$\left(\frac{\partial \ln a_1}{\partial P}\right)_{T,x} = \frac{1}{RT} (\bar{v}_1 - \bar{v}_1^0) \quad (2-4)$$

If $(\bar{v}_1 - \bar{v}_1^0)$ is taken as a constant at its mean value over the given range of pressure, and if the activity at the reference pressure P_0 is known, the value of activity at the pressure P may be approximated by the equation

$$\ln a_1 = \ln a_{1(P_0)} + \frac{\bar{v}_1 - \bar{v}_1^0}{RT} (P - P_0).$$

The activities of water at 10 atmospheres have been calculated from the partial molal volumes derived from Equation (4-13). For $\ln a_1$ at 10 atmospheres from 0 to 125°C the best coefficients of Equation (2-3) were found with multiple regression to be:

$$\begin{aligned} A &= -2.5509192 & B &= -99.476802 \\ C &= -254.95580 & D &= -294.59634 \\ E &= 8729.2130 & F &= 1316.7006 \\ G &= 0.25187398 & H &= 13.070179 \\ I &= 40.304140. \end{aligned}$$

The largest error in fitting the data at 10 atmospheres occurs at very

low salt concentrations; it appears similar to the result shown in Table II for activities at 1 atmosphere. As the value of activity a_1 approaches unity, its logarithm becomes very sensitive to error; for example, $\ln a_1 = -0.0101$ for $a_1 = 0.990$ as compared to $\ln a_1 = -0.0091$ for $a_1 = 0.991$. An interpolation formula with more terms can lower the relative errors, but the improved accuracy may not be warranted by the uncertainty in the experimental data. Table III shows the estimated values of $\ln a_1$ by Equation (2-3) for temperatures above 100°C are in good agreement with the data derived from osmotic coefficients given by Gardner, Jones and Nordwall (10). The effects of temperature and concentration on the negative values of $\ln a_1$ are shown in Figure 1. The slopes of the curves vary with temperature and concentration; after each minimum point, $\ln a_1$ increases monotonically with temperature.

Vapor Pressure Equations

The fugacity of a solvent in equilibrium with its vapor is equal to its vapor pressure if the solvent vapor behaves as a perfect gas. Since water vapor deviates from the ideal condition, one should consider it as an imperfect gas for the calculation of fugacity. For convenience, the difference in the volumes of vapor between real and perfect conditions is defined as follows:

$$\alpha = \frac{RT}{P} - v.$$

The partial derivative of Gibbs free energy with respect to pressure at constant temperature is equal to the volume. Then, from the definition of fugacity, one may write

TABLE III
ACTIVITIES OF WATER AT 10 ATMOSPHERES

$t, ^\circ\text{C}$	Molality	$-\ln a_1$ (Data)	$-\ln a_1$ (Est.)	<u>Data-Est.</u> Data
125	1.0	0.033081	0.033155	-0.0022
150	1.0	0.032432	0.032578	-0.0045
175	1.0	0.031673	0.031908	-0.0074
125	2.0	0.070061	0.070014	0.0007
150	2.0	0.068690	0.068467	0.0033
175	2.0	0.067025	0.066622	0.0060
125	3.0	0.110395	0.110558	-0.0015
150	3.0	0.107151	0.107389	-0.0022
175	3.0	0.103353	0.103680	-0.0032

Note: Data based on osmotic coefficients by Gardner et al. (10).

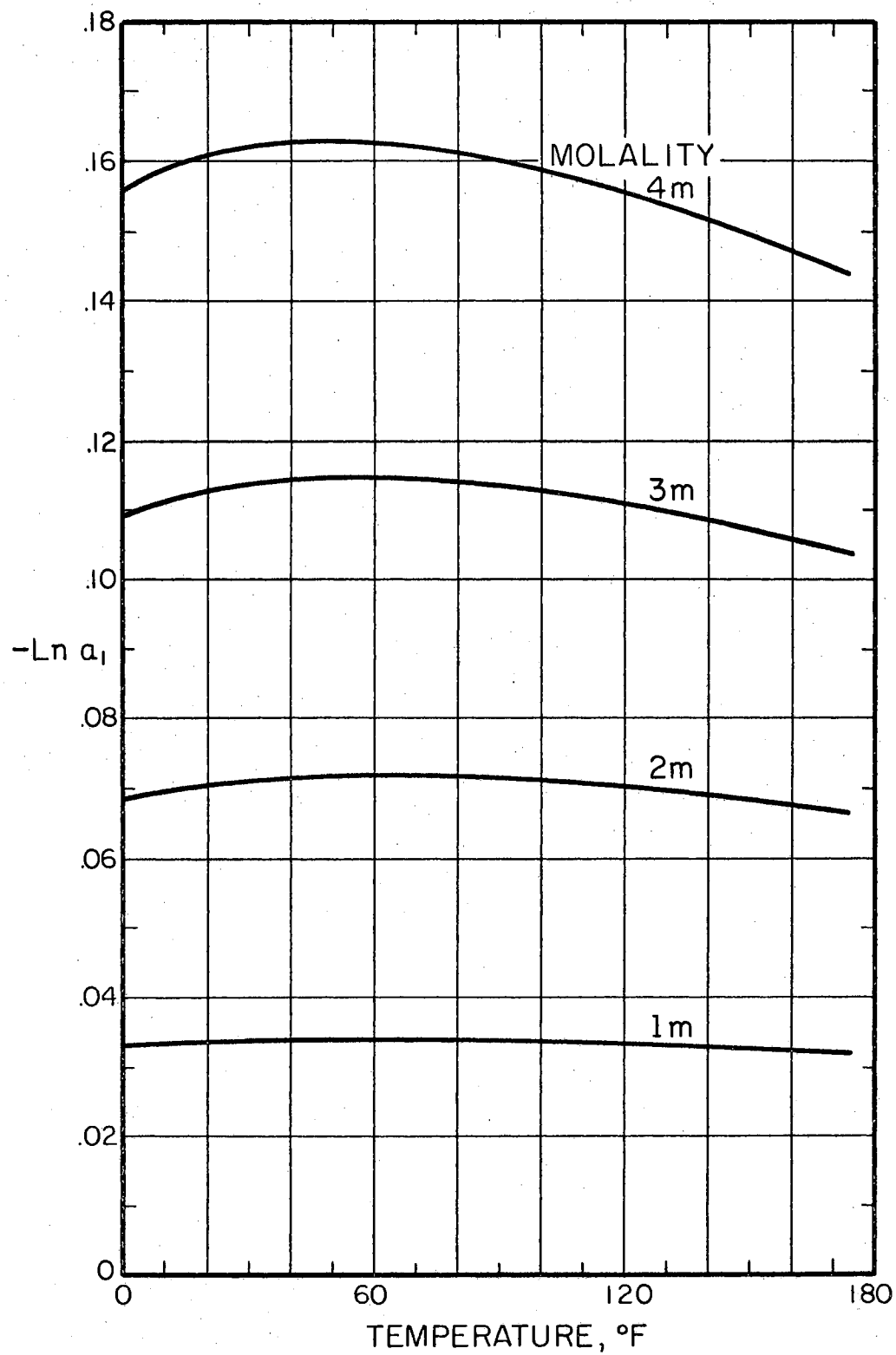


Figure 1. Logarithm of Activity of Water in Solution at 10 atm., Calculated from Osmotic Coefficient

$$RT \, d \ln f - v dP = RT \frac{dP}{P} - \alpha dP.$$

Integration between virtually zero pressure to a given pressure P_1 gives

$$\ln f_1 = \ln P_1 - \frac{1}{RT} \int_0^{P_1} \alpha dP,$$

or

$$f_1 = P_1 \exp\left(-\frac{1}{RT} \int_0^{P_1} \alpha dP\right).$$

From the interpolation formula for P-v-T relation of water vapor by Keyes, Smith and Gerry (45), it follows that

$$-\frac{1}{RT} \int_0^{P_1} \alpha dP = \frac{1}{RT} \left[B_0 P_1 + B_0^2 G_1 \frac{P_1^2}{2T} + B_0^4 G_2 \frac{P_1^4}{4T^3} + B_0^{13} G_3 \frac{P_1^{13}}{13T^{12}} \right] \quad (2-5)$$

where P_1 is the pressure of water vapor in atmospheres and T is the temperature in degrees Kelvin. The values of the parameters are:

$$B_0 = 1.89 - 2641.62 \times 10^{80870/T^2} / T,$$

$$G_1 = 82.546/T - 1.2697 \times 10^5 / T^2,$$

$$G_2 = 0.21828 - 1.2697 \times 10^5 / T^2,$$

$$G_3 = 3.635 \times 10^{-4} - 6.768 \times 10^{64} / T^{24}.$$

When the liquid phase of a solution is in equilibrium with its vapor phase, the numerical value of the fugacity of any component in the solution is equal to that in the vapor phase over the solution. Hence, the activity of water in solution may be determined from the vapor pressure p_1 of solution and the vapor pressure p_1° of pure water by the relation

$$\ln a_1 = \ln \frac{f_1}{f_1^\circ} = \ln \frac{p_1}{p_1^\circ} - \frac{1}{RT} \int_{p_1^\circ}^{p_1} \alpha dp. \quad (2-6)$$

The values of $\ln a_1$ using the vapor pressure data given by Fabuss (7), Kracek (51) and Tammann (28) have been calculated with Equations (2-5) and (2-6). Figures 2, 3, and 4 show the comparisons of the $\ln a_1$ as calculated from vapor pressure data and as determined by Equation (2-3), which is based on osmotic coefficient data. The vapor pressure data from other sources (3, 28) have also been tried for the determination of $\ln a_1$, but the results were even more inconsistent than those shown in the graphs. Hence, it is believed that in general the osmotic coefficient data are more accurate than the vapor pressure data for determining activity.

The values of the second term on the right side of Equation (2-6) are relatively unimportant as shown in Table IV. This does not mean the water vapor behaves as a perfect gas. The reason for the second term being negligible is that the correction factor for nonideality of water vapor is practically the same for the solution as for pure water since the vapor pressures of the solution and pure water vary approximately in the same manner.

By making use of Equations (2-3) and (2-6), the values of $\ln p_1/p_1^\circ$,

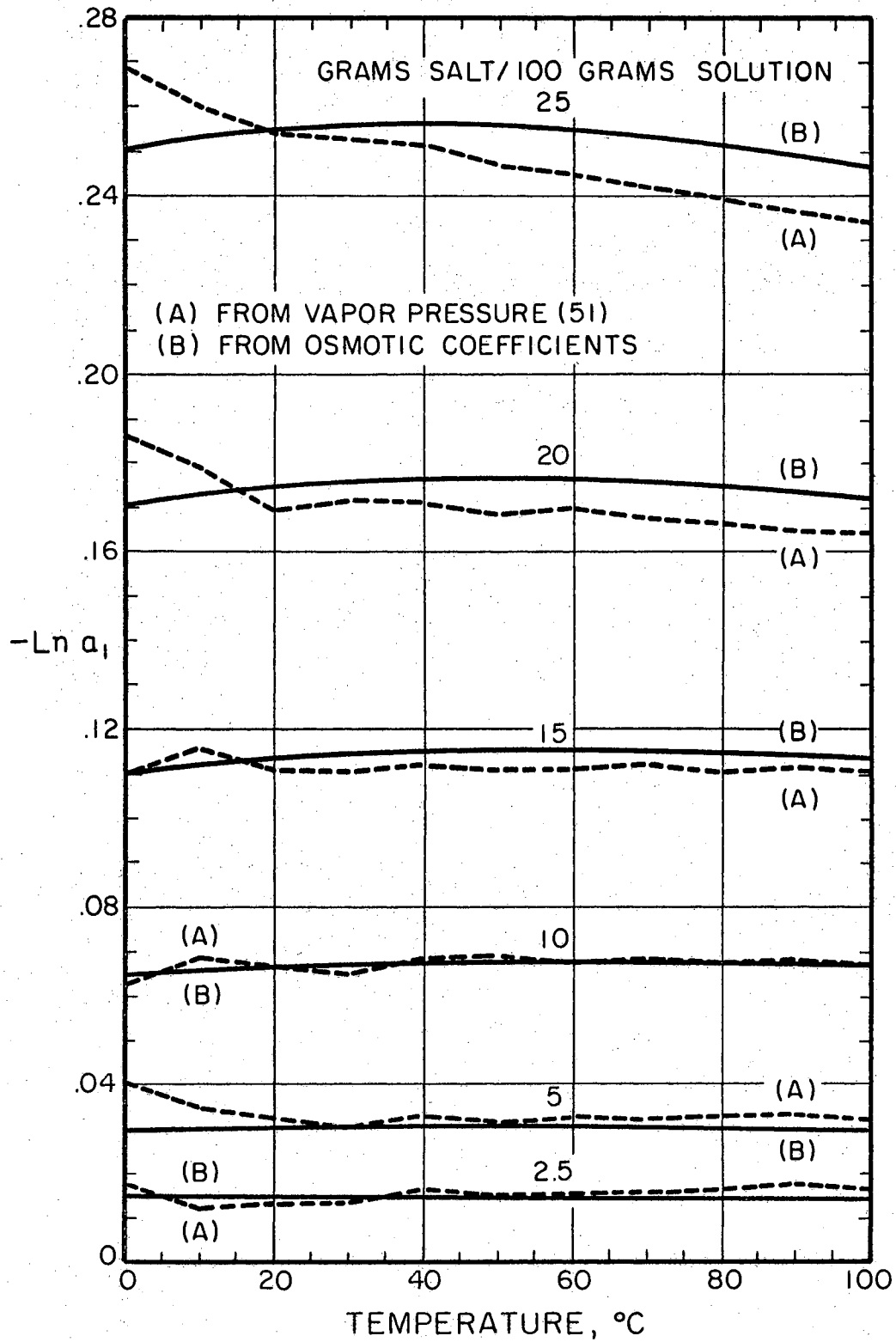


Figure 2. Logarithm of Activity of Water

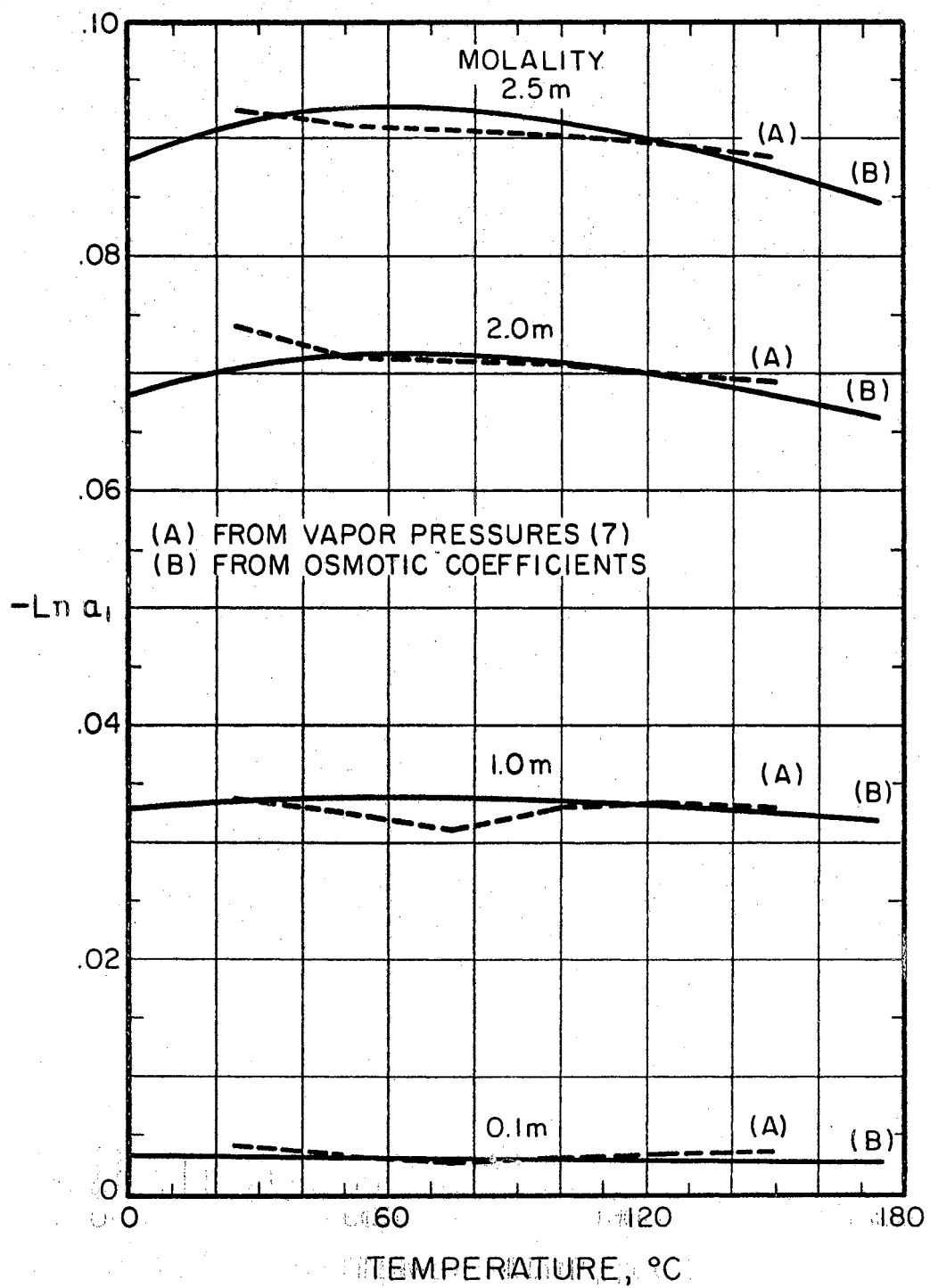


Figure 4. Logarithm of Activity of Water

TABLE IV
 ACTIVITIES OF WATER AS DETERMINED FROM
 VAPOR PRESSURE DATA

Salt Wt., %	t, °C	$-\ln \left(\frac{p_1}{p_1^0} \right)$	$-\frac{1}{RT} \int_{p_1^0}^{p_1} \alpha dp$	$-\ln a_1$ (at 1 atm.)
5.00	0.0	0.03987610	0.00002183	0.03988292
5.00	10.0	0.03423858	0.00002946	0.03423339
5.00	20.0	0.03127062	0.00004078	0.03125053
5.00	30.0	0.02965304	0.00005675	0.02961407
5.00	40.0	0.03194690	0.00008709	0.03187524
5.00	50.0	0.03117022	0.00011811	0.03106560
5.00	60.0	0.03167531	0.00016290	0.03152421
5.00	80.0	0.03279920	0.00029178	0.03251544
5.00	100.0	0.03208832	0.00045906	0.03162978
10.00	0.0	0.06286561	0.00003402	0.06289102
10.00	10.0	0.06852764	0.00005798	0.06852003
10.00	20.0	0.06720263	0.00008609	0.06715948
10.00	30.0	0.06590086	0.00012389	0.06581391
10.00	40.0	0.06803820	0.00018219	0.06788809
10.00	50.0	0.06865332	0.00025537	0.06842607
10.00	60.0	0.06753151	0.00034121	0.06721497
10.00	80.0	0.06830589	0.00059714	0.06772587
10.00	100.0	0.06805347	0.00095662	0.06709910
15.00	0.0	0.11049366	0.00005841	0.11052785
15.00	10.0	0.11615568	0.00009599	0.11613819
15.00	20.0	0.11082327	0.00013896	0.11075128
15.00	30.0	0.11050516	0.00020323	0.11035957
15.00	40.0	0.11152330	0.00029233	0.11128111
15.00	50.0	0.11121291	0.00040513	0.11085183
15.00	60.0	0.11143030	0.00055103	0.11091807
15.00	80.0	0.11138947	0.00095351	0.11046349
15.00	100.0	0.11122563	0.00153102	0.10970022
20.00	0.0	0.18647957	0.00009500	0.18651305
20.00	10.0	0.17906952	0.00014352	0.17903494
20.00	20.0	0.16985679	0.00020694	0.16974283
20.00	30.0	0.17200735	0.00030700	0.17178046
20.00	40.0	0.17189544	0.00043753	0.17152774
20.00	50.0	0.16965091	0.00060069	0.16911173
20.00	60.0	0.17074689	0.00082038	0.16998099
20.00	80.0	0.16799311	0.00139918	0.16663362
20.00	100.0	0.16717372	0.00223992	0.16494518
25.00	0.0	0.26871765	0.00013159	0.26875345
25.00	10.0	0.26019508	0.00020056	0.26013651
25.00	20.0	0.25441414	0.00029758	0.25423784
25.00	30.0	0.25360600	0.00043522	0.25327542
25.00	40.0	0.25229586	0.00061782	0.25176943

TABLE IV - Continued

Salt Wt., %	t, °C	$-\ln \left(\frac{p_1}{p_1^0} \right)$	$-\frac{1}{RT} \int_{p_1^0}^{p_1} \alpha dp$	$-\ln a_1$ (at 1 atm.)
25.00	50.0	0.24820092	0.00084625	0.24743547
25.00	60.0	0.24656571	0.00114230	0.24549538
25.00	80.0	0.24258757	0.00194955	0.24069215
25.00	100.0	0.23805684	0.00308357	0.23499366

Note: Vapor pressure data from International Critical Tables (51).

based on osmotic coefficient data, were calculated and incorporated into the following interpolation formula for temperatures ranging from 0 to 175°C:

$$\begin{aligned} \ln \frac{p_1}{p_1^0} = & -1.2275791x + 15.026523x^{1.5} - 574.51650x^2 \\ & - (331.63222x - 3322.7702x^{1.5} - 16390.844x^2)/T \\ & + (0.040568938x - 3.8316690x^{1.5} + 87.479492x^2) \ln T \end{aligned} \quad (2-7)$$

where x is the mole fraction of sodium chloride and T is the temperature in degrees Kelvin. It has the same form as the equation for $\ln a_1$; the different coefficients were again determined by multiple regression. The relative errors between actual and calculated values are about the same as those for $\ln a_1$.

Regarding the vapor pressure of pure water p_1^0 , the Third International Conference on Steam Tables (48) agreed upon a skeleton table together with tolerances which constitute a criterion to judge the reliability of a steam table. Many interpolation formulae have been developed for the vapor pressure of water and some of them are extremely complicated (33, 44). The true relation between vapor pressure and temperature is still unknown so far. An equation which fits the data given by the Third International Conference on Steam Tables from 0 to 175°C is as follows:

$$\ln p_1^0 = 71.0571369 - 7381.6477/T - 9.0993037 \ln T + 0.0070831558T \quad (2-8)$$

where p_1^0 is the pressure in kilograms per square centimeter and T is the temperature in degrees Kelvin. If the first coefficient is changed to 71.024449, the pressure unit becomes atmosphere. The form of this

equation was originally suggested by Nernst (32) from the fact that the heat of vaporization may be expressed in the form of a power series.

Table V shows how well Equation (2-8) fits the experimental data.

Among many different empirical forms of equation for vapor pressure, another interesting one is the Antoine equation (49),

$$\ln p_1^{\circ} = A + \frac{B}{C + T} \quad (2-9)$$

This equation does not fit the data (Table VI) as accurately as the Nernst equation, but it has the advantage of expressing temperature explicitly in terms of pressure. In order to use a linear least-square computer program to determine the coefficients, it is necessary to make the following substitutions:

$$A = A', \quad B = -(A'C' + B'), \quad C = -C'$$

so that

$$T \ln p_1^{\circ} = B' + A'T + C' \ln p_1^{\circ}$$

where the undetermined coefficients are now in linear form. The best values of the coefficients for fitting the vapor pressure data of water from 0 to 175°C are:

$$A = 11.767794 \quad B = -3884.5791$$

$$C = -43.107355$$

where pressure is in atmospheres and temperature in degrees Kelvin.

Experience from curve fitting indicates that the vapor pressure of solution may be expressed as a function of mole fraction x and vapor

TABLE V
VAPOR PRESSURE OF WATER

t, °C	Vapor Pressure, kg/cm ²		Difference	Tolerance (+ or -)
	(Data)	(Est.)		
0.0	0.006228	0.006227	0.000001	0.000006
10.0	0.012513	0.012515	-0.000002	0.000010
20.0	0.023829	0.023837	-0.000008	0.000020
30.0	0.043254	0.043268	-0.000014	0.000030
40.0	0.075204	0.075224	-0.000020	0.000038
50.0	0.125780	0.125799	-0.000019	0.00006
60.0	0.203120	0.203126	-0.000006	0.00010
70.0	0.317750	0.317735	0.000015	0.00016
80.0	0.482920	0.482882	0.000038	0.00024
90.0	0.714910	0.714856	0.000054	0.00036
100.0	1.033230	1.033230	-0.000000	NIL
110.0	1.460900	1.461054	-0.000154	0.0010
120.0	2.024500	2.024989	-0.000489	0.0013
130.0	2.754400	2.755366	-0.000966	0.0016
140.0	3.684800	3.686188	-0.001388	0.0021
150.0	4.853500	4.855065	-0.001565	0.0032
160.0	6.302300	6.303094	-0.000794	0.0042
170.0	8.076400	8.074694	0.001706	0.0053
180.0	10.225000	10.217400	0.007600	0.007

Note: Data recommended by the Third International Conference on Steam Tables (48).

TABLE VI
 COMPARISON OF EXPERIMENTAL DATA ON VAPOR
 PRESSURE WITH CALCULATED VALUES

Molality	Temp., °C	Vapor Pressure, mm Hg		
		Data	Eq. (2-9,10)	Eq. (2-7,8)
0.1	25.0	23.70	23.75	23.67
0.1	50.0	92.20	92.48	92.21
0.1	75.0	288.20	288.22	288.13
0.1	100.0	757.50	756.13	757.48
0.1	125.0	1734.80	1731.77	1735.63
0.1	150.0	3557.60	3556.58	3559.71
1.0	25.0	23.00	23.08	22.97
1.0	50.0	89.50	89.85	89.44
1.0	75.0	280.00	279.94	279.40
1.0	100.0	734.60	734.27	734.44
1.0	125.0	1682.40	1681.39	1682.83
1.0	150.0	3450.10	3452.58	3451.63
2.0	25.0	22.10	22.23	22.13
2.0	50.0	86.10	86.56	86.12
2.0	75.0	269.10	269.70	268.93
2.0	100.0	707.30	707.40	706.94
2.0	125.0	1619.90	1619.84	1620.26
2.0	150.0	3322.00	3326.20	3324.89
2.5	25.0	21.70	21.77	21.68
2.5	50.0	84.40	84.76	84.34
2.5	75.0	263.80	264.10	263.37
2.5	100.0	693.40	692.76	692.47
2.5	125.0	1588.00	1586.40	1587.71
2.5	150.0	3256.70	3257.66	3259.78

Note: Data by Fabuss (7).

pressure p_1° of pure water without directly specifying the temperature by the following equation:

$$\ln p_1 = (1 + ax + bx^{1.5} + ex^2) \ln p_1^\circ + (cx + dx^{1.5} + ex^2) \quad (2-10)$$

where $\ln p_1^\circ$ may be either in the form of Nernst equation or Antoine equation. When the Antoine equation is used to represent $\ln p_1^\circ$, Equation (2-10) may be rearranged into the form

$$T = \frac{C(\ln p_1 - cx + dx^{1.5} - ex^2) - (AC + B)(1 + ax + bx^{1.5})}{A(1 + ax + bx^{1.5}) + (cx + dx^{1.5} + ex^2 - \ln p_1)} \quad (2-11)$$

which expresses temperature explicitly. Thus, the boiling temperature of solution can be readily computed. Based on osmotic coefficient data, the values of coefficients with temperature in degrees Kelvin and pressure in atmospheres were found to be:

$$a = -0.033204655 \quad b = 0.13635246$$

$$c = -1.9203617 \quad d = 3.2750375$$

$$e = -19.866438.$$

Comparisons of the experimental data on vapor pressure reported by Fabuss (7) and the values calculated from Equations (2-7), (2-8), (2-9), and (2-10) are shown in Table VI. Although the difference could hardly be detected by ordinary vapor pressure gages, Equations (2-7) and (2-8) are recommended for precise work. The development of Equation (2-7) is based on osmotic coefficient data which appear more consistent and more precise than vapor pressure data given in the literature. In Figure 5, the variations of vapor pressure lowering with temperature and concentration are illustrated.

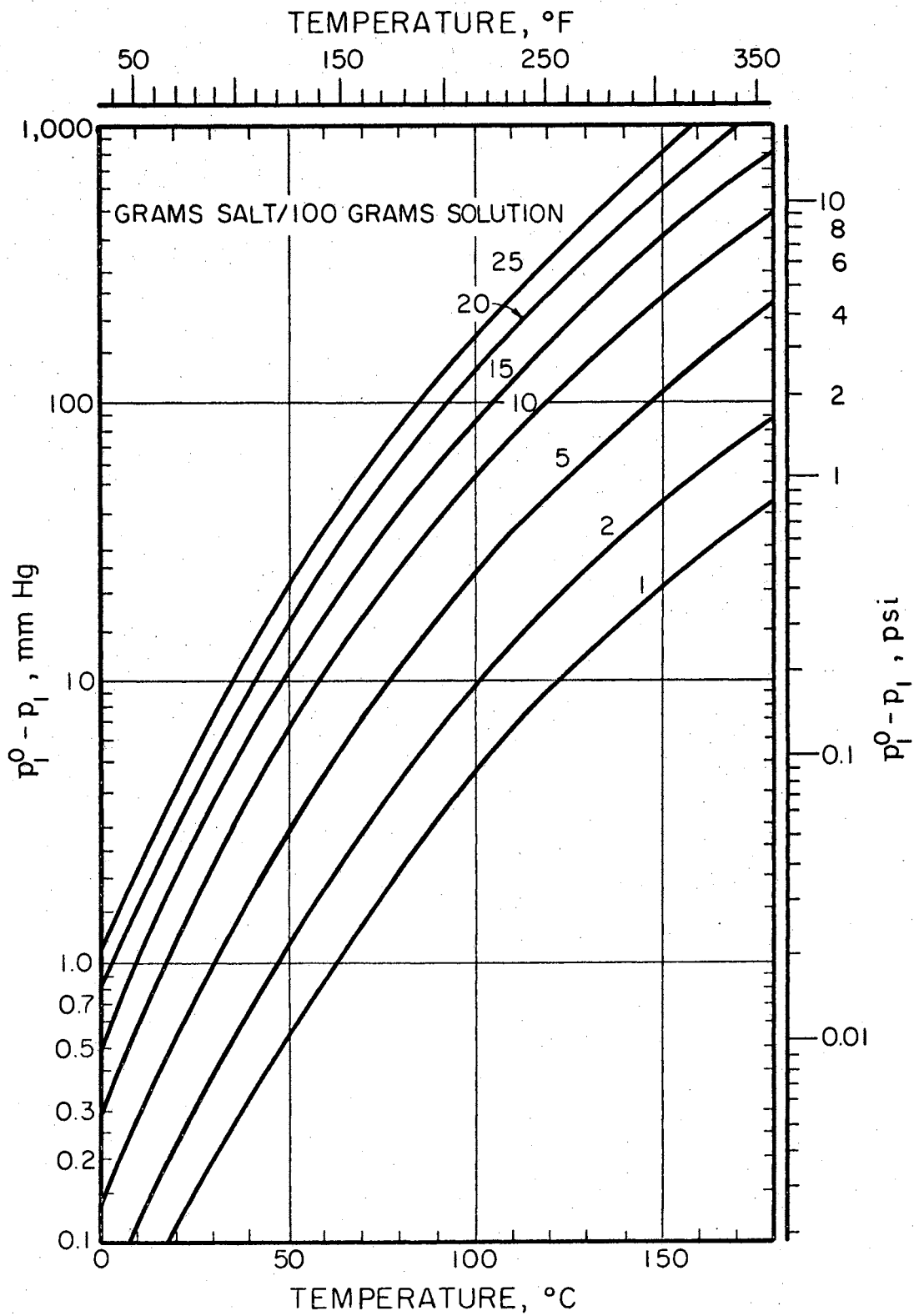


Figure 5. Vapor Pressure Lowering Obtained from Equations (2-7) and (2-8)

CHAPTER III

SPECIFIC HEAT

Relation of Activity to Specific Heat

The specific heat of a solution may be related to the activities of the components through the concept of partial molal properties. For a solution containing n_1 moles of solvent and n_2 moles of solute at pressure P and temperature T , the differential of any extensive property $Y(P, T, n_1, n_2)$ may be written in the form

$$dY = \left(\frac{\partial Y}{\partial T}\right)_{P, n_1, n_2} dT + \left(\frac{\partial Y}{\partial P}\right)_{T, n_1, n_2} dP + \left(\frac{\partial Y}{\partial n_1}\right)_{T, P, n_2} dn_1 + \left(\frac{\partial Y}{\partial n_2}\right)_{T, P, n_1} dn_2.$$

If the solution is at a constant temperature and pressure, this equation reduces to

$$dY = \bar{y}_1 dn_1 + \bar{y}_2 dn_2 \quad (3-1)$$

where $\bar{y}_1 = (\partial Y / \partial n_1)_{T, P, n_2}$ and $\bar{y}_2 = (\partial Y / \partial n_2)_{T, P, n_1}$; they are called partial molal properties of the respective components. The nature of an extensive property is such that if the amounts of all the components are changed in the same proportion at constant T and P , the value of the dependent property changes in that proportion also. Letting $dn_1 = n_1 dr$, and $dn_2 = n_2 dr$ where dr is an infinitesimal proportioning factor, one has $dY = Ydr$ so that

$$Y dr = \bar{y}_1 n_1 dr + \bar{y}_2 n_2 dr.$$

After cancelling out dr , this equation becomes

$$Y = n_1 \bar{y}_1 + n_2 \bar{y}_2. \quad (3-2)$$

Therefore, an extensive property of a solution may be determined from the numbers of moles and the partial molal properties of the components at a given temperature and pressure. Moreover, this relation is equally valid if the unit of quantity is taken to be a unit of mass instead of mole. Differentiation of Equation (3-2) gives

$$dY = n_1 d\bar{y}_1 + \bar{y}_1 dn_1 + n_2 d\bar{y}_2 + \bar{y}_2 dn_2. \quad (3-3)$$

Combination of Equations (3-1) and (3-3) leads to another equation valid only at constant temperature and pressure,

$$n_1 d\bar{y}_1 + n_2 d\bar{y}_2 = 0, \quad (3-4)$$

which is a generalized form of the Gibbs-Duhem relation.

Since the partial molal properties are derived from extensive properties by differentiating with respect to one of the mole numbers, any thermodynamic relation among extensive properties holds for the corresponding partial molal properties. Differentiating the equation $G = H - TS$ with respect to n_1 at constant temperature, pressure and number of moles of the other component establishes the following relationship among partial molal properties as

$$\bar{g}_1 = \bar{h}_1 - T\bar{s}_1.$$

This equation may be transformed to the Gibbs-Helmholtz equation by

applying the Maxwell relation,

$$\bar{g}_1 - T \left(\frac{\partial \bar{g}_1}{\partial T} \right)_{P, n_1, n_2} = \bar{h}_1.$$

After dividing through both sides by T^2 , the derivative may be rearranged to take the form

$$\left(\frac{\partial (\bar{g}_1/T)}{\partial T} \right)_{P, n_1, n_2} = - \frac{\bar{h}_1}{T^2}.$$

Then, from Equation (2-1) one has

$$\left(\frac{\partial \ln a_1}{\partial T} \right)_{P, n_1, n_2} = - \frac{\bar{h}_1 - \bar{h}_1^{\circ}}{RT^2}. \quad (3-5)$$

For an aqueous solution, \bar{h}_1° is equal to the molal enthalpy of pure water at the temperature T since the reference state of water is the state of an infinitely diluted solution. An equation analogous to Equation (3-5) may be written for solute as

$$\left(\frac{\partial \ln a_2}{\partial T} \right)_{P, n_1, n_2} = - \frac{\bar{h}_2 - \bar{h}_2^{\circ}}{RT^2}. \quad (3-6)$$

Substituting \bar{h}_1 and \bar{h}_2 from Equations (3-5) and (3-6) into Equation (3-2), one may express the enthalpy per mole of solution as

$$h = (1 - x) \left[\bar{h}_1^{\circ} - RT^2 \left(\frac{\partial \ln a_1}{\partial T} \right)_{P, x} \right] + x \left[\bar{h}_2^{\circ} - RT^2 \left(\frac{\partial \ln a_2}{\partial T} \right)_{P, x} \right] \quad (3-7)$$

where x is the mole fraction of solute.

The definitions of fugacity and activity may be applied to a pure substance in the solid phase. If a_s is the activity of pure solid of solute in terms of the reference state identical to the one

conventionally adopted for the solute in solution, it is possible to write

$$g_s - \bar{g}_2^{\circ} = RT \ln a_s \quad (3-8)$$

where g_s is the molal free energy of solid solute and \bar{g}_2° refers to the partial molal free energy of the solute in solution at the same temperature at infinite dilution. Following procedures applied to the derivation of Equation (3-5), one may obtain an expression to relate the derivative $\left(\frac{\partial \ln a_s}{\partial T}\right)_P$ to molal enthalpy difference of the solute between the solid state and the reference state, $h_s - \bar{h}_2^{\circ}$,

$$\left(\frac{\partial \ln a_s}{\partial T}\right)_P = - \frac{h_s - \bar{h}_2^{\circ}}{RT^2} \quad (3-9)$$

The fugacity of the solid solute in saturated solution is identical to the fugacity of the solute dissolved in solution when the system is in equilibrium. Consequently, the activity a_s in Equation (3-9) may be substituted by the activity a_{2s} of the dissolved solute in a saturated solution since a common reference state has been assigned. Because the value of an extensive property of electrolyte in solution depends on the values of the properties of ions, the definition of mean ionic activity, denoted by a_{\pm} , is introduced as $a_2 = a_{\pm}^{\nu}$ where ν is the number of ions into which a formula unit of an electrolyte dissociates and a_2 is the activity of solute; for 1 - 1 strong electrolyte such as sodium chloride, $\nu = 2$ by assuming complete dissociation. Combining Equation (3-9) and the definition of mean ionic activity, one may rewrite Equation (3-7) as

$$h = (1 - x) \left[\bar{h}_1^{\circ} - RT^2 \left(\frac{\partial \ln a_1}{\partial T} \right)_{P,x} \right] + x \left[h_s + 2RT^2 \left(\frac{\partial \ln a_{\pm s}}{\partial T} \right)_P - 2RT^2 \left(\frac{\partial \ln a_{\pm}}{\partial T} \right)_{P,x} \right] \quad (3-10)$$

where $a_{\pm s}$ denotes the mean ionic activity of solute in the saturated solution. The constant-pressure specific heat c_p may be derived from Equation (3-10) by taking partial differentiation with respect to temperature at constant P and x .

$$c_p = (1 - x) \left[c_{p,w} - 2RT \left(\frac{\partial \ln a_1}{\partial T} \right)_{P,x} - RT^2 \left(\frac{\partial^2 \ln a_1}{\partial T^2} \right)_{P,x} \right] + x \left[c_{p,s} + 4RT \left(\frac{\partial \ln a_{\pm s}}{\partial T} \right)_P + 2RT^2 \left(\frac{\partial^2 \ln a_{\pm s}}{\partial T^2} \right)_P - 4RT \left(\frac{\partial \ln a_{\pm}}{\partial T} \right)_{P,x} - 2RT^2 \left(\frac{\partial^2 \ln a_{\pm}}{\partial T^2} \right)_{P,x} \right] \quad (3-11)$$

This indicates the possibility of evaluating the specific heat of solution from the specific heat of pure water $c_{p,w}$, the specific heat of solid salt $c_{p,s}$ and the derivatives of activities when the calorimetric measurements of c_p for a solution are not available.

Specific Heats of Water and Solid

Sodium Chloride

The values of enthalpy of saturated water from 0 to 180°C in the Third International Skeleton Steam Tables (48) were satisfactorily fitted into the following interpolation formula, as shown in Table VII:

$$h_f = 1.0031519T - 0.12638365 \times 10^{-3}T^2 + 0.97645145 \times 10^{-6}T^3$$

where h_f is the enthalpy of saturated water in international steam-table

TABLE VII
ENTHALPY OF SATURATED WATER

Temp., °C	Enthalpy, cal/gm		Difference	Tolerance (+ or -)
	(Data)	(Est.)		
0.0	0.00	0.00	0.00	0.00
10.0	10.04	10.02	0.02	0.01
20.0	20.03	20.02	0.01	0.02
30.0	30.00	30.01	-0.01	0.02
40.0	39.98	39.99	-0.01	0.02
50.0	49.95	49.96	-0.01	0.03
60.0	59.94	59.95	-0.01	0.03
70.0	69.93	69.94	-0.01	0.03
80.0	79.95	79.94	0.01	0.04
90.0	89.98	89.97	0.01	0.05
100.0	100.04	100.03	0.01	0.05
110.0	110.12	110.12	0.00	0.06
120.0	120.25	120.25	0.00	0.06
130.0	130.42	130.42	0.00	0.07
140.0	140.64	140.64	0.00	0.07
150.0	150.92	150.92	0.00	0.08
160.0	161.25	161.27	-0.02	0.08
170.0	171.68	171.68	0.00	0.09
180.0	182.18	182.17	0.01	0.09

Note: Data recommended by the Third International Conference on Steam Tables (48).

calories per gram and T is the temperature in degrees Kelvin. Differentiating h_f with respect to temperature gives the amount of heat required per unit rise of temperature to heat water along the saturated line which is denoted here by subscript f . To relate the specific heat c_f of the saturated water with the constant-pressure specific heat $c_{p,w}$ for the subcooled state, the temperature T and pressure P were selected as the independent variables of entropy s so that

$$ds = \left(\frac{\partial s}{\partial P}\right)_T dP + \left(\frac{\partial s}{\partial T}\right)_P dT. \quad (3-13)$$

From the Maxwell relation and the definition of specific heat, it follows that

$$ds = - \left(\frac{\partial v}{\partial T}\right)_P dP + \frac{c_{p,w}}{T} dT.$$

To evaluate the specific heat along the saturation line, one may write

$$c_f = T \left(\frac{\partial s}{\partial T}\right)_f = \left[c_{p,w} - T \left(\frac{\partial v}{\partial T}\right)_P \frac{dP}{dT} \right]_f. \quad (3-14)$$

Since the differentials in Equation (3-13) are exact, it follows that

$$- \left(\frac{\partial^2 v}{\partial T^2}\right)_P = \frac{1}{T} \left(\frac{\partial c_{p,w}}{\partial P}\right)_T. \quad (3-15)$$

Thus, the variation of specific heat with pressure may be determined from an appropriate P - v - T relation. In Table VIII are the constant-pressure specific heats of water from 0 to 180°C at 10 atmospheres, as calculated by the following equation:

TABLE VIII
SPECIFIC HEAT OF WATER

Temp., °C	Specific Heat, cal/gm °C			
	c_f	c_p (1 atm)	c_p (10 atm) Eq. (3-16)	c_p (10 atm) Eq. (3-17)
0.0	1.0039	1.0039	1.0029	1.0035
10.0	1.0017	1.0017	1.0009	1.0011
20.0	1.0000	1.0000	0.9994	0.9993
30.0	0.9990	0.9990	0.9984	0.9982
40.0	0.9985	0.9986	0.9981	0.9977
50.0	0.9986	0.9987	0.9983	0.9979
60.0	0.9993	0.9995	0.9991	0.9987
70.0	1.0006	1.0009	1.0005	1.0002
80.0	1.0025	1.0029	1.0025	1.0023
90.0	1.0049	1.0056	1.0051	1.0050
100.0	1.0080	1.0088	1.0084	1.0084
110.0	1.0116		1.0123	1.0125
120.0	1.0158		1.0168	1.0172
130.0	1.0206		1.0221	1.0225
140.0	1.0260		1.0281	1.0285
150.0	1.0320		1.0348	1.0351
160.0	1.0385		1.0422	1.0424
170.0	1.0457		1.0505	1.0503
180.0	1.0534		1.0596	1.0589

$$c_{p,w} = \frac{dh_f}{dT} + \frac{T}{J} \left[\left(\frac{\partial v}{\partial T} \right)_P \frac{dP}{dT} \right]_f - \frac{1}{J} \int_{P_f}^{10} T \left(\frac{\partial^2 v}{\partial T^2} \right)_P dP \quad (3-16)$$

where J is the Joule's constant and P_f denotes the vapor pressure. The data for the P-v-T relation were obtained from the Third International Skeleton Steam Tables. To facilitate the calculations of specific heats for solutions, the values of $c_{p,w}$ at 10 atmospheres were fitted into the following interpolation formula by the least square method:

$$c_{p,w} = 4.1986279 - 0.11428663 \times 10^{-2}t + 0.13498960 \times 10^{-4}t^2 \quad (3-17)$$

where $c_{p,w}$ is in joules per gram per degree and t is in degrees centigrade.

The enthalpies of solid sodium chloride, h_s , from 298 to 1,073°K have been determined by Kelly (24) from his spectroscopic observations. The following equation fits the data within 1% accuracy:

$$h_s = h_s(25^\circ\text{C}) + 10.98T + 1.95 \times 10^{-3}T^2 - 3.447.$$

From this equation one finds that the specific heat increases linearly with temperature as follows:

$$c_{p,s} = 10.98 + 3.90 \times 10^{-3}T \quad (3-18)$$

where $c_{p,s}$ is in calories per mole per degree and T is in degrees Kelvin. The coefficients of volume expansion of solid sodium chloride are 124.34×10^{-6} at 100°C, 127.48×10^{-6} at 150°C and 130.58×10^{-6} at 200°C at atmospheric pressure according to Kaufmann's compilation (19). The available data on coefficients of expansion are insufficient for

meaningful evaluation of the pressure dependence of specific heats. However, the specific heat of a solid, it is believed, is extremely insensitive to pressure changes, although the temperature dependence is of importance. No allowance was made in this study for the effect of pressure on the specific heat of solid sodium chloride.

Specific Heat at 10 Atmospheres

from 0 to 175°C

The evaluations of the partial derivatives of activities are necessary in order to use Equation (3-11) to calculate the specific heats. Equation (2-3) was proposed to represent the activities of water in solution at a constant pressure; the values of the corresponding coefficients at 10 atmospheres were reported in Chapter II. From Equation (2-3) the first and second derivatives of $\ln a_1$ may be found in terms of mole fraction of sodium chloride and absolute temperature as follows:

$$\left(\frac{\partial \ln a_1}{\partial T}\right)_{P,x} = -(Dx + Ex^{1.5} + Fx^2)/T^2 + (Hx + Ix^{1.5} + Jx^2)/T, \quad (3-19)$$

$$\left(\frac{\partial^2 \ln a_1}{\partial T^2}\right)_{P,x} = 2(Dx + Ex^{1.5} + Fx^2)/T^3 - (Hx + Ix^{1.5} + Jx^2)/T^2. \quad (3-20)$$

The Gibbs-Duhem relation provides a means to determine the activities of solute from the known activities of solvent. Considering the partial molal property in Equation (3-4) to be the partial molal Gibbs free energy, one has an expression valid at a constant temperature and pressure,

$$(1 - x)d(\ln a_1) + xd(\ln a_{\pm}^2) = 0.$$

After dividing by dx and rearranging the terms, one finds that

$$\left(\frac{\partial \ln a_{\pm}}{\partial x}\right)_{T,P} = -\frac{1-x}{2x} \left(\frac{\partial \ln a_1}{\partial x}\right)_{T,P}. \quad (3-21)$$

Then, at a constant pressure, the change of $\ln a_{\pm}$ between the two states may be found by integration as

$$\ln a_{\pm}'' - \ln a_{\pm}' = \frac{1}{2} \int_{x'}^{x''} \frac{x-1}{x} \left(\frac{\partial \ln a_1}{\partial x}\right)_{T,P} dx + F(T). \quad (3-22)$$

When x diminishes, the activity coefficient approaches unity regardless of the value of temperature. For this reason, every term in a series representing a_{\pm} should be associated with x , and the function $F(T)$ resulting from integration must be equal to zero. The partial derivative of $\ln a_1$ with respect to x may be readily obtained from Equation (2-3). Upon integrating from the mole fraction of saturated solution, denoted by subscript s , one has

$$\begin{aligned} \ln a_{\pm} - \ln a_{\pm s} &= \frac{1}{2}[Ax + Bx^{1.5} + Cx^2 + (Dx + Ex^{1.5} + Fx^2)/T \\ &+ (Gx + Hx^{1.5} + Ix^2)\ln T]_{x_s}^x - \frac{1}{2}[A \ln x + 3Bx^{0.5} + 2Cx \\ &+ (D \ln x + 3Ex^{0.5} + 2Fx)/T + (G \ln x + 3Hx^{0.5} + 2Ix)\ln T]_{x_s}^x. \end{aligned} \quad (3-23)$$

The mole fraction x_s for the saturated condition varies with temperature and pressure. Adams and Hall (1) measured the electrical resistance of solution and thus determined that the increase of dissolved sodium chloride due to changes in pressure (1 to 2,000 bars) was 1 gram per 100 grams of solution at 29.93°C. Evidently, the value of x_s is insensitive

to a small variation of pressure. The experimental data on solubility at various temperatures are not in complete agreement. An interpolation formula has been arbitrarily determined as follows to fit the data reported by Sidell (42) and Schroeder, et al. (41) above 100°C, and by Gillespie (51) below 100°C:

$$x_s = -0.22195188 + 3.5536043/\sqrt{T} + .38955142 \times 10^{-6}T \quad (3-24)$$

where x_s is the mole fraction of sodium chloride and T is the temperature in degrees Kelvin. The differences between the data and the calculated values using Equation (3-24) are shown in Table IX.

Equation (3-24) gives the temperature dependence of mole fraction at a saturated condition, by which one may evaluate the following derivatives from Equation (3-23):

$$\begin{aligned} \left(\frac{\partial \ln a_{\pm}}{\partial T} \right)_{P,x} - \left(\frac{\partial \ln a_{\pm s}}{\partial T} \right)_P &= \frac{1}{2T^2} [-(Dx + Ex^{1.5} + Fx^2) \\ &+ (Dx_s + Ex_s^{1.5} + Fx_s^2) + (D \ln x + 3Fx^{0.5} + 2Fx) \\ &- (D \ln x_s + 3Ex_s^{0.5} + 2Fx_s)] + \frac{1}{2T} [(Gx + Hx^{1.5} + Ix^2) \\ &- (Gx_s + Hx_s^{1.5} + Ix_s^2) - (G \ln x + 3Hx^{0.5} + 2Ix) \\ &+ (G \ln x_s + 3x_s^{0.5} + 2Ix_s)] + \frac{1}{2} \left(\frac{\partial x_s}{\partial T} \right)_P (1 - x_s) \left[\frac{A}{x_s} + \right. \\ &\left. + 1.5Bx_s^{-0.5} + \frac{1}{T} \left(\frac{D}{x_s} + 1.5x_s^{-0.5} \right) + \ln T \left(\frac{G}{x_s} + 1.5x_s^{-0.5} \right) \right], \quad (3-25) \end{aligned}$$

TABLE IX
 CONCENTRATION OF SODIUM CHLORIDE IN
 SATURATED SOLUTION

Temp., °C	Salt Weight, %		Difference
	(Data)	(Est.)	
0.0	26.34 (51)	26.38	-0.04
10.0	26.35	26.39	-0.04
20.0	26.43	26.45	-0.02
25.0	26.48	26.50	-0.02
30.0	26.56	26.55	0.01
40.0	26.71	26.68	0.03
50.0	26.89	26.84	0.05
60.0	27.09	27.04	0.05
70.0	27.30	27.26	0.04
80.0	27.53	27.51	0.02
90.0	27.80	27.28	0.02
100.0	28.12	28.07	0.05
107.0	28.39	28.29	0.10
150.0	29.57 (42)	29.79	-0.22
173.0	30.36	30.69	-0.33
200.0	31.60	31.81	-0.21
225.0	33.19	32.91	0.28
118.0	28.46 (41)	28.64	-0.18
140.0	29.62	29.41	0.21
160.0	30.36	30.17	0.19
180.0	30.98	30.97	0.01

Note: Data by Schroeder et al. (41) and Seidell (42), and from International Critical Tables (51).

$$\begin{aligned}
\frac{\partial}{\partial T} \left[\left(\frac{\partial \ln a_{\pm}}{\partial T} \right)_{P,x} - \left(\frac{\partial \ln a_{\pm s}}{\partial T} \right)_P \right] &= - \frac{1}{T^2} [-(Dx + Ex^{1.5} + Fx^2) \\
&+ (Dx_s + Ex_s^{1.5} + Fx_s^2) + (D \ln x + 3Ex^{0.5} + 2Fx) \\
&- (D \ln x_s + 3Ex_s^{0.5} + 2Fx_s)] - \frac{1}{2T^2} [(Gx + Hx^{1.5} + Ix^2) \\
&- (Gx_s + Hx_s^{1.5} + Ix_s^2) - (G \ln x + 3Hx^{0.5} + 2Ix) \\
&+ (G \ln x_s + 3Hx_s^{0.5} + 2Ix_s)] + \left(\frac{\partial x_s}{\partial T} \right)_P (1 - x_s) \\
\left[- \frac{1}{T^2} \left(\frac{D}{x_s} + 1.5Ex_s^{-0.5} + 2F \right) + \frac{1}{T} \left(\frac{G}{x_s} + 1.5Hx_s^{-0.5} + 2I \right) \right. \\
&- \left. \frac{1}{2} \left(\frac{\partial x_s}{\partial T} \right)_P \left(\frac{A}{x_s^2} + 0.75Bx_s^{-1.5} \right) \right] - \frac{1}{2} \left(\frac{\partial x_s}{\partial T} \right)_P^2 (1 - x_s) \\
&\left[\frac{1}{T} \left(\frac{D}{x_s^2} + 0.75Ex_s^{-1.5} \right) + \ln T \left(\frac{G}{x_s^2} + 0.75Hx_s^{-1.5} \right) \right] \\
&+ \frac{1}{2} \left[\left(\frac{\partial^2 x_s}{\partial T^2} \right)_P (1 - x_s) - \left(\frac{\partial x_s}{\partial T} \right)_P^2 \right] \left[\frac{A}{x_s} + 1.5Bx_s^{-0.5} + 2C \right. \\
&\left. + \frac{1}{T} \left(\frac{D}{x_s} + 1.5Ex_s^{-0.5} + 2F \right) + \ln T \left(\frac{G}{x_s} + 1.5Hx_s^{-0.5} + 2I \right) \right]. \quad (3-26)
\end{aligned}$$

Substituting Equations (3-17), (3-18), (3-19), (3-20), (3-25), and (3-26) into Equation (3-11) yields the specific heat of the solution; the results of calculations are presented in Table X and Figure 6. The forms of interpolation formulae exercise a great influence on the final results of the calculation; and the higher the concentration or the temperature, the greater the influence. This shows that the probable error resulting from using the empirical formulae increases with the increase of temperature or concentration. Several other types of formulae have been tried to test the validity of the calculation procedures. Experience indicates that the fluctuations of the results are within $\pm 1\%$ of

TABLE X
 CONSTANT-PRESSURE SPECIFIC HEAT OF SOLUTION
 AT 10 ATMOSPHERES IN CALORIES PER GRAM
 PER DEGREE CENTIGRADE

Temp., °C	Salt Weight, gm/100 gm Solution						
	1.0	2.0	5.0	10.0	15.0	20.0	25.0
0	.991	.979	.946	.896	.854	.817	.787
10	.988	.977	.944	.896	.853	.818	.788
20	.987	.975	.943	.895	.853	.818	.789
30	.986	.974	.942	.894	.852	.817	.788
40	.985	.974	.941	.893	.851	.816	.787
50	.985	.974	.941	.892	.850	.814	.785
60	.986	.974	.941	.892	.849	.812	.782
70	.987	.975	.942	.891	.847	.810	.779
80	.989	.977	.942	.891	.846	.807	.775
90	.991	.979	.944	.891	.845	.805	.771
100	.995	.982	.946	.891	.844	.802	.767
110	.998	.985	.948	.892	.842	.799	.762
120	1.003	.989	.951	.893	.842	.796	.758
130	1.008	.994	.954	.894	.841	.794	.753
140	1.013	.999	.958	.896	.840	.791	.748
150	1.019	1.004	.962	.898	.840	.788	.743
160	1.026	1.011	.967	.900	.840	.786	.739
170	1.033	1.018	.973	.903	.841	.784	.734
180	1.041	1.025	.979	.907	.841	.782	.729

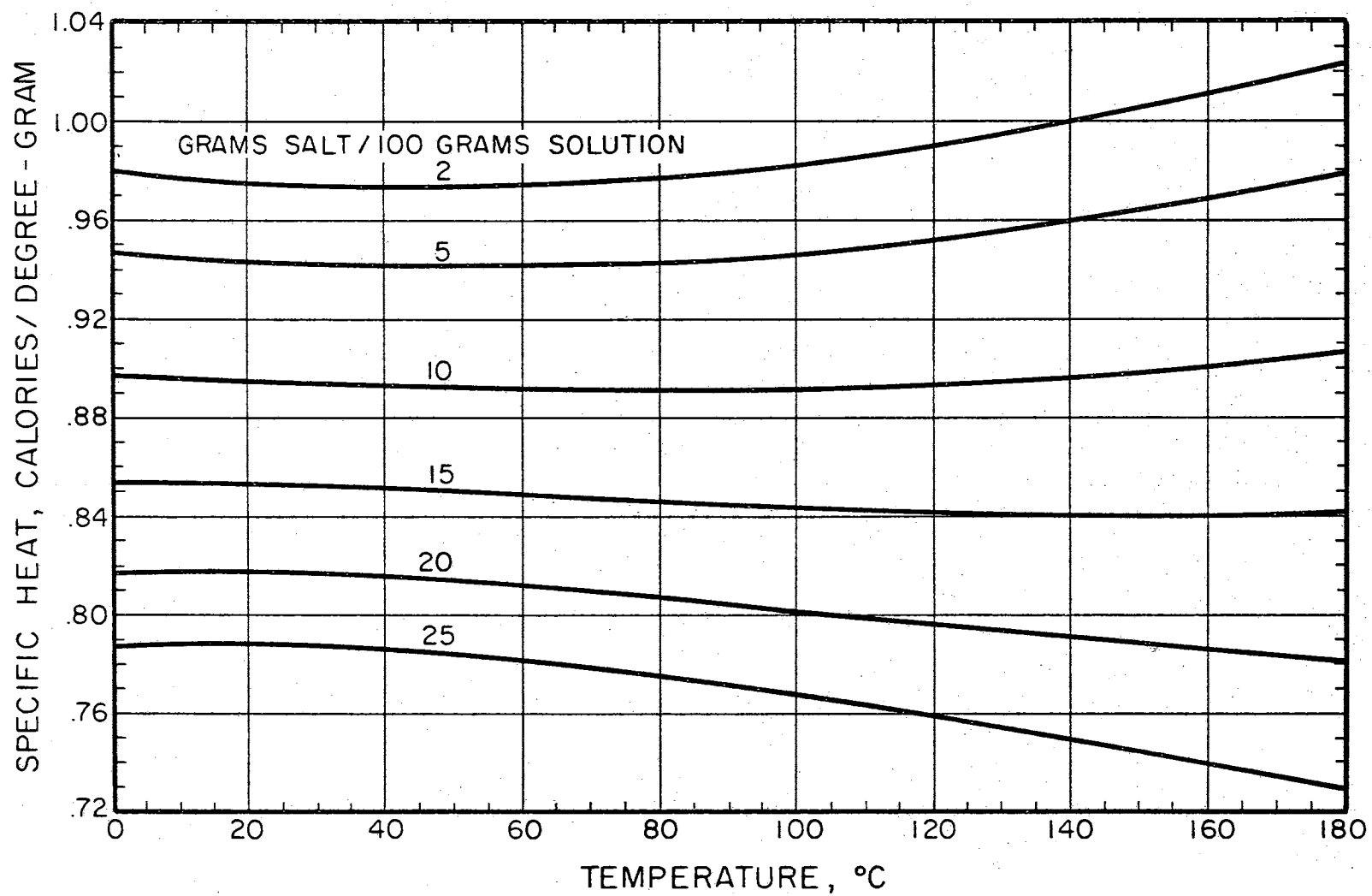


Figure 6. Constant-Pressure Specific Heat at 10 Atmospheres

c_p for concentrations up to 12% of sodium chloride and for temperatures less than 100°C for a combination of any reasonable formulae.

The method of multiple regression gives the following formula for calculating the values of specific heats in calories per gram per degree as given in Table X in terms of concentration in mole fraction and temperature in degrees Kelvin with maximum deviation of less than four parts per thousand:

$$c_p = 1.3165380 - 8.9594831x + 23.807251x^2 - (0.20328368 \times 10^{-5} - 0.036271808x + 0.062168183x^2)T + (0.32218320 \times 10^{-8} - 0.61529617 \times 10^{-4}x + 0.10557408 \times 10^{-6}x^2)T^2. \quad (3-27)$$

Experimental Data

Randall and Rossini (35) measured the specific heats at 25°C with twin calorimeters. Lipsett, Johnson, and Maas (29) determined the specific heats at 20 and 25°C from heats of solution, using a rotating calorimeter. Some of the early experimental data are tabulated in the International Critical Tables (50,52). The highest temperature for the experimental values recorded in literature is 75°C (39). Some discrepancies among the measured data, illustrated in Figure 7, exist at high concentrations. Table XI shows the measured data are in fair agreement with the calculated values from Equation (3-27). All of these measurements were taken at one atmosphere. The differences in specific heats between 1 atmosphere and 10 atmospheres are considered to be negligible in this comparison. It is desirable to have experimental data at high temperatures to verify the calculated values.

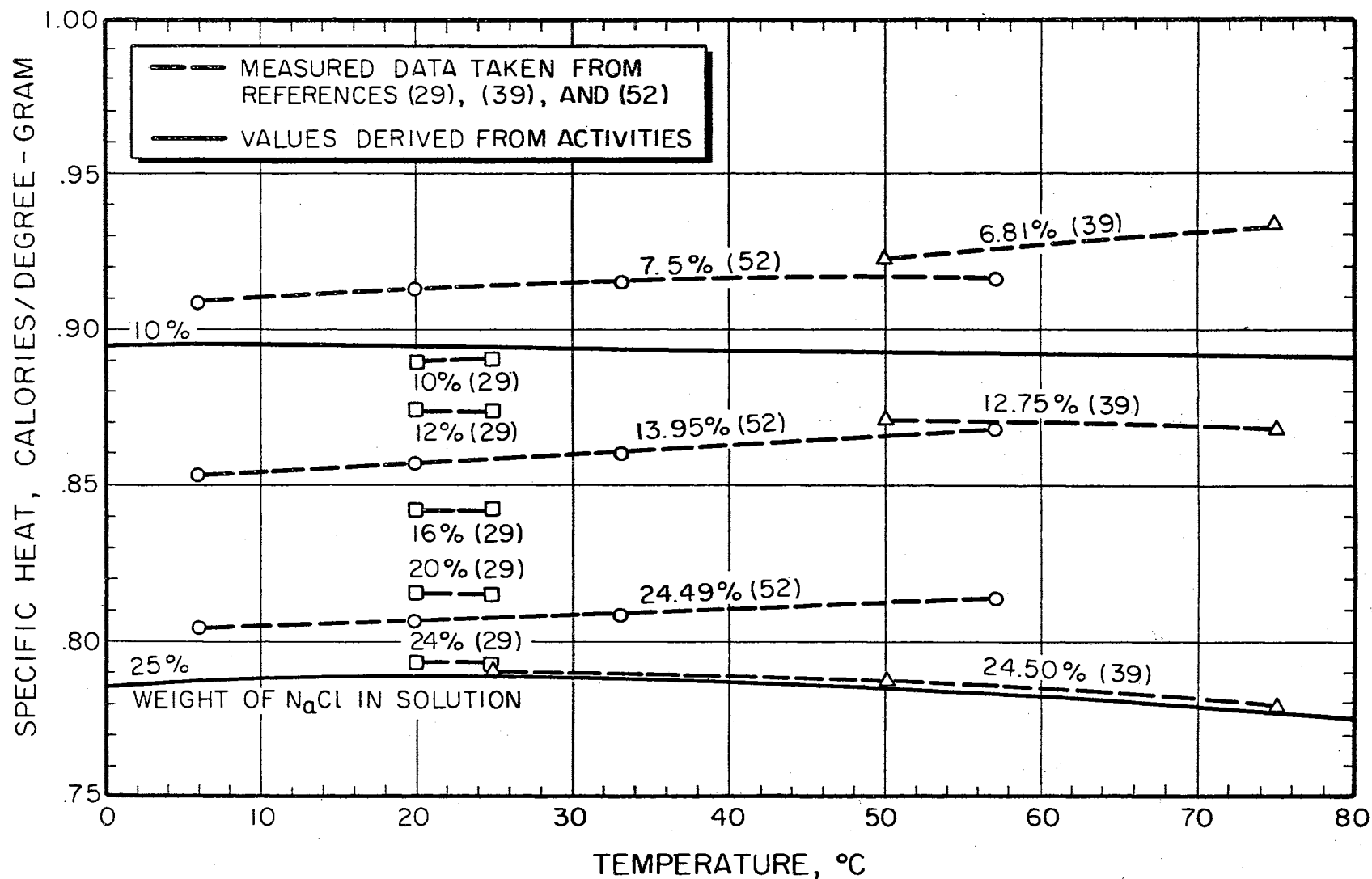


Figure 7. Comparison of Specific Heats at High Concentrations

TABLE XI
 COMPARISON OF MEASURED VALUES OF SPECIFIC
 HEAT WITH CALCULATED VALUES

t, °C	Salt, %	c _p , cal/gm °C		Data-Est. Data
		(Data)	(Est.)	
25	24.50	0.790 (39)	0.791	-0.0012
50	1.16	0.984	0.983	0.0006
50	2.84	0.965	0.965	-0.0008
50	6.81	0.924	0.924	-0.0005
50	12.75	0.871	0.868	0.0037
50	24.50	0.787	0.786	0.0008
75	1.16	0.988	0.986	0.0018
75	2.84	0.969	0.967	0.0013
75	6.81	0.936	0.925	0.0117
75	12.75	0.869	0.866	0.0040
75	24.50	0.780	0.780	-0.0000
6	24.49	0.805 (52)	0.793	0.0148
6	17.78	0.826	0.833	-0.0087
6	13.95	0.853	0.863	-0.0114
6	7.50	0.910	0.922	-0.0132
6	5.13	0.934	0.946	-0.0125
6	3.88	0.948	0.959	-0.0111
6	3.14	0.958	0.966	-0.0086
6	2.11	0.968	0.977	-0.0092
6	1.59	0.978	0.983	-0.0054
20	24.49	0.807	0.792	0.0196
20	17.78	0.828	0.831	-0.0034
20	13.95	0.858	0.861	-0.0031
20	7.50	0.913	0.920	-0.0072
20	5.13	0.937	0.943	-0.0069
20	3.88	0.951	0.956	-0.0057
20	3.14	0.960	0.964	-0.0037
20	2.11	0.970	0.975	-0.0046
20	1.59	0.978	0.980	-0.0028
20	1.07	0.983	0.986	-0.0034
20	0.80	0.989	0.989	0.0002
33	24.49	0.810	0.790	0.0248
33	17.78	0.829	0.829	-0.0001
33	13.95	0.861	0.859	0.0019
33	7.50	0.916	0.918	-0.0025
33	5.13	0.940	0.942	-0.0022
33	3.88	0.953	0.955	-0.0022
33	3.14	0.961	0.963	-0.0020
33	2.11	0.972	0.973	-0.0017
33	1.59	0.978	0.979	-0.0012
57	24.49	0.815	0.785	0.0365
57	17.78	0.841	0.826	0.0176
57	13.95	0.870	0.857	0.0147

TABLE XI - Continued

t, °C	Salt, %	c _p , cal/gm °C		Data-Est. Data
		(Data)	(Est.)	
57	7.50	0.917	0.917	0.0004
20	0.20	0.997 (29)	0.995	0.0016
20	0.40	0.994	0.993	0.0010
20	0.60	0.991	0.991	0.0005
20	0.80	0.989	0.989	0.0001
20	1.00	0.986	0.987	-0.0003
20	1.20	0.984	0.985	-0.0006
20	1.40	0.981	0.982	-0.0009
20	2.00	0.974	0.976	-0.0020
20	3.00	0.962	0.965	-0.0030
20	4.00	0.951	0.955	-0.0044
20	6.00	0.929	0.935	-0.0058
20	8.00	0.909	0.915	-0.0061
20	10.00	0.891	0.896	-0.0058
20	12.00	0.873	0.878	-0.0050
20	14.00	0.857	0.861	-0.0039
20	16.00	0.842	0.845	-0.0028
20	18.00	0.828	0.830	-0.0017
20	20.00	0.816	0.816	-0.0004
20	22.00	0.804	0.804	-0.0001
20	24.00	0.793	0.794	-0.0009
20	26.00	0.783	0.785	-0.0029
25	0.20	0.996	0.995	0.0016
25	0.40	0.994	0.993	0.0012
25	0.60	0.991	0.990	0.0008
25	0.80	0.989	0.988	0.0005
25	1.00	0.986	0.986	0.0004
25	1.20	0.984	0.984	0.0000
25	1.40	0.981	0.982	-0.0002
25	2.00	0.974	0.975	-0.0009
25	3.00	0.963	0.965	-0.0019
25	4.00	0.952	0.954	-0.0029
25	6.00	0.930	0.934	-0.0038
25	8.00	0.910	0.914	-0.0040
25	10.00	0.892	0.895	-0.0035
25	12.00	0.875	0.877	-0.0026
25	14.00	0.859	0.860	-0.0014
25	16.00	0.843	0.844	-0.0006
25	18.00	0.829	0.829	-0.0003
25	20.00	0.817	0.816	0.0015
25	22.00	0.805	0.804	0.0015
25	24.00	0.794	0.793	0.0005
25	26.00	0.783	0.785	-0.0018
15	0.06	0.999 (15)	9.998	0.0018
25	0.06	0.997	0.996	0.0009
35	0.06	0.997	0.995	0.0012

TABLE XI - Continued

t, °C	Salt, %	c _p , cal/gm. °C		Data-Est. Data
		(Data)	(Est.)	
45	0.06	0.997	0.995	-0.0021
15	0.29	0.996	0.995	0.0011
25	0.29	0.994	0.994	0.0006
35	0.29	0.994	0.993	0.0008
45	0.29	0.995	0.993	0.0027
15	0.41	0.994	0.994	0.0005
25	0.41	0.993	0.992	0.0004
35	0.41	0.992	0.992	0.0007
45	0.41	0.994	0.991	0.0022
15	0.58	0.992	0.992	0.0000
25	0.58	0.990	0.991	-0.0002
35	0.58	0.990	0.990	0.0002
45	0.58	0.992	0.990	0.0021
15	1.72	0.977	0.980	-0.0032
25	1.72	0.976	0.978	-0.0021
35	1.72	0.976	0.977	-0.0011
45	1.72	0.978	0.977	0.0008
15	4.00	0.949	0.956	-0.0068
25	4.00	0.950	0.954	-0.0044
35	4.00	0.951	0.953	-0.0023
45	4.00	0.952	0.953	-0.0012
15	5.69	0.930	0.938	-0.0091
25	5.69	0.932	0.937	-0.0055
35	5.69	0.933	0.936	-0.0027
45	5.69	0.935	0.935	-0.0008

Note: Data by Hess et al. (15), Lipsett et al. (29) and Rutskov (39), and from International Critical Tables (52).

CHAPTER IV

SPECIFIC VOLUME

Specific Volume of Water from 0 to 150°C

Liquids have neither the rigid geometrical structure of solids nor the complete randomness of gases. The scientific understanding of the liquid state has lagged behind the basic knowledge of both the solid and gaseous states. The theory of the behavior of a liquid is not well developed because there is no clear-cut limiting cases, such as the crystalline phase at the absolute zero temperature for solid and the perfect gas for the real gas. Numerous equations of state have been developed over the years, but most of them can be applied only to gases. To deal with liquids, tables, graphs or power series are usually used in place of an equation of state. The behavior of water is further complicated since it exhibits a peculiarity of thermal expansion in the low temperature region. Of the many interpolation formulae that may be found in literature for the specific volume of water (6), none is simple even in a small range of temperature. Kell (22) recently used a seven-term series for the precise representation of the specific volume from 0 to 110°C at 1 atmosphere.

In 1893 Amagat (2) reported experimental values of densities and compressibilities for water, which are considered precise even by modern standards. Since then, many experiments have been carried out to a very

high degree of precision. Over the range 0 to 40°C, values of densities are often published to one part in 10 million. In this study the values of specific volume of water are based on those recommended by the Third International Conference on Steam Tables (48). The following mathematical expression was arbitrarily chosen to fit these data:

$$v = A(T) - P \cdot B(T) - P^2 \cdot C(T) \quad (4-1)$$

where 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:

$$A(T) = 5.916365 - 0.010357941T + 0.92700482 \times 10^{-6}T^2 \\ - 1127.5221/T + 100674.1/T^2,$$

$$B(T) = 0.52049144 \times 10^{-3} - 0.10482101 \times 10^{-4}T + 0.83285321 \times 10^{-8}T^2 \\ - 1.1702939/T + 102.27831/T^2,$$

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

The values calculated from Equation (4-1) with the accepted values are compared in Table XII. The deviations of the calculated values from the data are within the tolerances accepted by the Third International Conference on Steam Tables. The function $A(T)$ may be interpreted as the specific volume in a hypothetical state of zero pressure. Since the compressibilities of liquids are in the order of 10^{-6} per atmosphere, $A(T)$ is approximately equal to the specific volume at the vapor pressure if the temperature is not over 150°C.

TABLE XII
SPECIFIC VOLUME OF WATER

$t, ^\circ\text{C}$	$P, \text{kg/cm}^2$	Sp. Vol., cm^3/gm (Data)	Sp. Vol., cm^3/gm (Est.)	Diff.	Tolerance + or -
0	0.006	1.00021	1.00021	-0.00000	0.00005
10	0.013	1.00035	1.00036	-0.00001	0.0001
20	0.024	1.00184	1.00183	0.00001	0.0001
30	0.043	1.00442	1.00439	0.00003	0.0001
40	0.075	1.00789	1.00787	0.00002	0.0001
50	0.126	1.01210	1.01214	-0.00004	0.0002
60	0.203	1.01710	1.01712	-0.00002	0.0002
70	0.318	1.02280	1.02276	0.00004	0.0002
80	0.483	1.02900	1.02903	-0.00003	0.0002
90	0.715	1.03590	1.03592	-0.00002	0.0002
100	1.033	1.04350	1.04341	0.00009	0.0002
110	1.461	1.05150	1.05153	-0.00003	0.0004
120	2.025	1.06030	1.06029	0.00001	0.0004
130	2.754	1.06970	1.06971	-0.00001	0.0004
140	3.685	1.07980	1.07980	-0.00000	0.0004
150	4.854	1.09060	1.09061	-0.00001	0.0004
160	6.302	1.10210	1.10214	-0.00004	0.0004
170	8.076	1.11440	1.11443	-0.00003	0.0004
180	10.225	1.12750	1.12749	0.00001	0.0004
0	1.000	1.00016	1.00016	-0.00000	0.00005
0	5.000	0.99990	0.99996	-0.00006	0.0002
0	10.000	0.99970	0.99972	-0.00002	0.0002
0	25.000	0.99890	0.99898	-0.00008	0.0002
0	50.000	0.99770	0.99775	-0.00005	0.0002
0	75.000	0.99650	0.99653	-0.00003	0.0002
0	100.000	0.99520	0.99532	-0.00012	0.0002
0	125.000	0.99400	0.99412	-0.00012	0.0002
0	150.000	0.99290	0.99292	-0.00002	0.0002
0	200.000	0.99050	0.99056	-0.00006	0.0002
0	250.000	0.98820	0.98822	-0.00002	0.0002
0	300.000	0.98590	0.98591	-0.00001	0.0002
0	350.000	0.98370	0.98364	0.00006	0.0002
0	400.000	0.98140	0.98139	0.00001	0.0002
50	1.000	1.01210	1.01210	-0.00000	0.0002
50	5.000	1.01190	1.01192	-0.00002	0.0002
50	10.000	1.01170	1.01169	0.00001	0.0002
50	25.000	1.01100	1.01102	-0.00002	0.0002
50	50.000	1.00990	1.00991	-0.00001	0.0002
50	75.000	1.00880	1.00881	-0.00001	0.0002
50	100.000	1.00770	1.00772	-0.00002	0.0002
50	125.000	1.00670	1.00664	0.00006	0.0002
50	150.000	1.00560	1.00557	0.00003	0.0002
50	200.000	1.00350	1.00347	0.00003	0.0002
50	250.000	1.00150	1.00142	0.00008	0.0002

TABLE XII - Continued

$t, ^\circ\text{C}$	$P, \text{kg/cm}^2$	Sp. Vol., cm^3/gm		Diff.	Tolerance + or -
		(Data)	(Est.)		
50	300.000	0.99950	0.99942	0.00008	0.0002
50	350.000	0.99750	0.99747	0.00003	0.0002
50	400.000	0.99560	0.99556	0.00004	0.0002
100	5.000	1.04320	1.04321	-0.00001	0.0002
100	10.000	1.04310	1.04295	0.00015	0.0002
100	25.000	1.04220	1.04219	0.00001	0.0002
100	50.000	1.04090	1.04092	-0.00002	0.0002
100	75.000	1.03970	1.03968	0.00002	0.0002
100	100.000	1.03850	1.03845	0.00005	0.0002
100	125.000	1.03720	1.03723	-0.00003	0.0002
100	150.000	1.03600	1.03603	-0.00003	0.0002
100	200.000	1.03370	1.03368	0.00002	0.0002
100	250.000	1.03140	1.03139	0.00001	0.0002
100	300.000	1.02910	1.02917	-0.00007	0.0002
100	350.000	1.02690	1.02701	-0.00011	0.0002
100	400.000	1.02470	1.02492	-0.00022	0.0002
150	5.000	1.09060	1.09060	0.00000	0.0002
150	10.000	1.09020	1.09027	-0.00007	0.0002
150	25.000	1.08930	1.08928	0.00002	0.0002
150	50.000	1.08770	1.08766	0.00004	0.0002
150	75.000	1.08610	1.08605	0.00005	0.0002
150	100.000	1.08450	1.08447	0.00003	0.0002
150	125.000	1.08290	1.08290	-0.00000	0.0002
150	150.000	1.08140	1.08136	0.00004	0.0002
150	200.000	1.07840	1.07833	0.00007	0.0002
150	250.000	1.07550	1.07538	0.00012	0.0002
150	300.000	1.07260	1.07251	0.00009	0.0002
150	350.000	1.06980	1.06972	0.00008	0.0002
150	400.000	1.06700	1.06701	-0.00001	0.0002
200	25.000	1.15560	1.15518	0.00042	0.0003
200	50.000	1.15320	1.15288	0.00032	0.0003
200	75.000	1.15080	1.15061	0.00019	0.0003
200	100.000	1.14850	1.14837	0.00013	0.0003
200	125.000	1.14620	1.14614	0.00006	0.0003
200	150.000	1.14390	1.14394	-0.00004	0.0003
200	200.000	1.13950	1.13962	-0.00012	0.0003
200	250.000	1.13530	1.13539	-0.00009	0.0003
200	300.000	1.13120	1.13126	-0.00006	0.0003
200	350.000	1.12720	1.12722	-0.00002	0.0003
200	400.000	1.12340	1.12329	0.00011	0.0003

TABLE XII - Continued

Note: Data given by the Third International Conference on Steam Tables (48).

Experimental Determination of the Derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$

A survey of literature indicated the lack of experimental data on compressibility of sodium chloride solutions at temperatures above 40°C. Measurements were therefore made to obtain the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ for temperatures ranging from 0 to 180°C, for concentrations ranging from 0 to 25% salt weight in solution, and for pressures up to 5,000 psig; the results were used to derive an appropriate P-v-T-x relation. In this investigation, the change in volume as a function of pressure for a constant temperature was measured by utilizing a calibrated positive-displacement pump.

The apparatus is shown schematically in Figure 8. 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 electrical 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 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

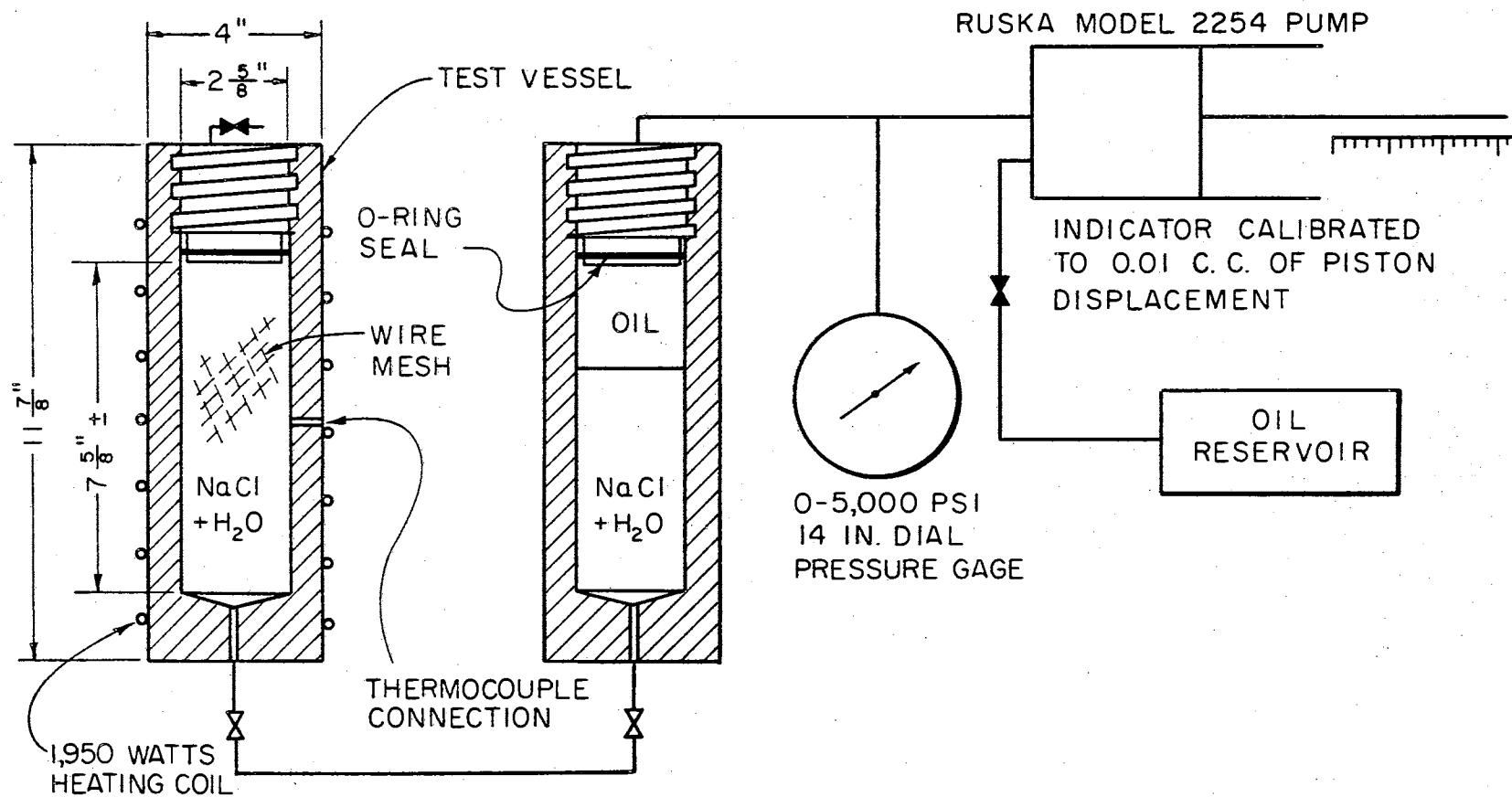


Figure 8. Arrangement of Apparatus for Determining Derivative $\left(\frac{\partial V}{\partial P}\right)_{T,x}$

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. A layer of light oil was floating above the solution in the second vessel to separate the pump and the pressure gage from the solution. The 14" dial bourdon 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 together 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 crystal sodium chloride of reagent grade 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, the entrained air was carefully 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 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; it was necessary to raise the current through the heating coil for maintaining a constant temperature. To control the variation of temperature within 0.2 °F throughout the test was not too difficult. After the pressure was lowered to 185 psig, the valve underneath the vessel which contained only solution 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 lowered, and the readings of piston displacement were repeated for every 250 psi. These two sets of data, first with the valve open and then with the valve closed, were needed to account for the volume changes attributed to the vessel which contained only solution. Under normal operation, the time required to complete the test of a solution was about six hours for one temperature.

The fundamental measurements made in this experiment are 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 9. The difference between the two piston displacements taken at the same pressure gives the change in volume of test vessel and its contents. The results of these measurements are tabulated in Table XIII. A very slight nonlinearity of the data is evident. For simplicity, the differences of the volume changes for the two valve positions were assumed to be linear with the mean values of pressure, and the data were fitted by the least square method to the equation

$$\Delta V = a + bP. \quad (4-2)$$

In this equation ΔV is the difference of the volume change in cubic centimeter and P is the pressure in psia. The smoothed values of the

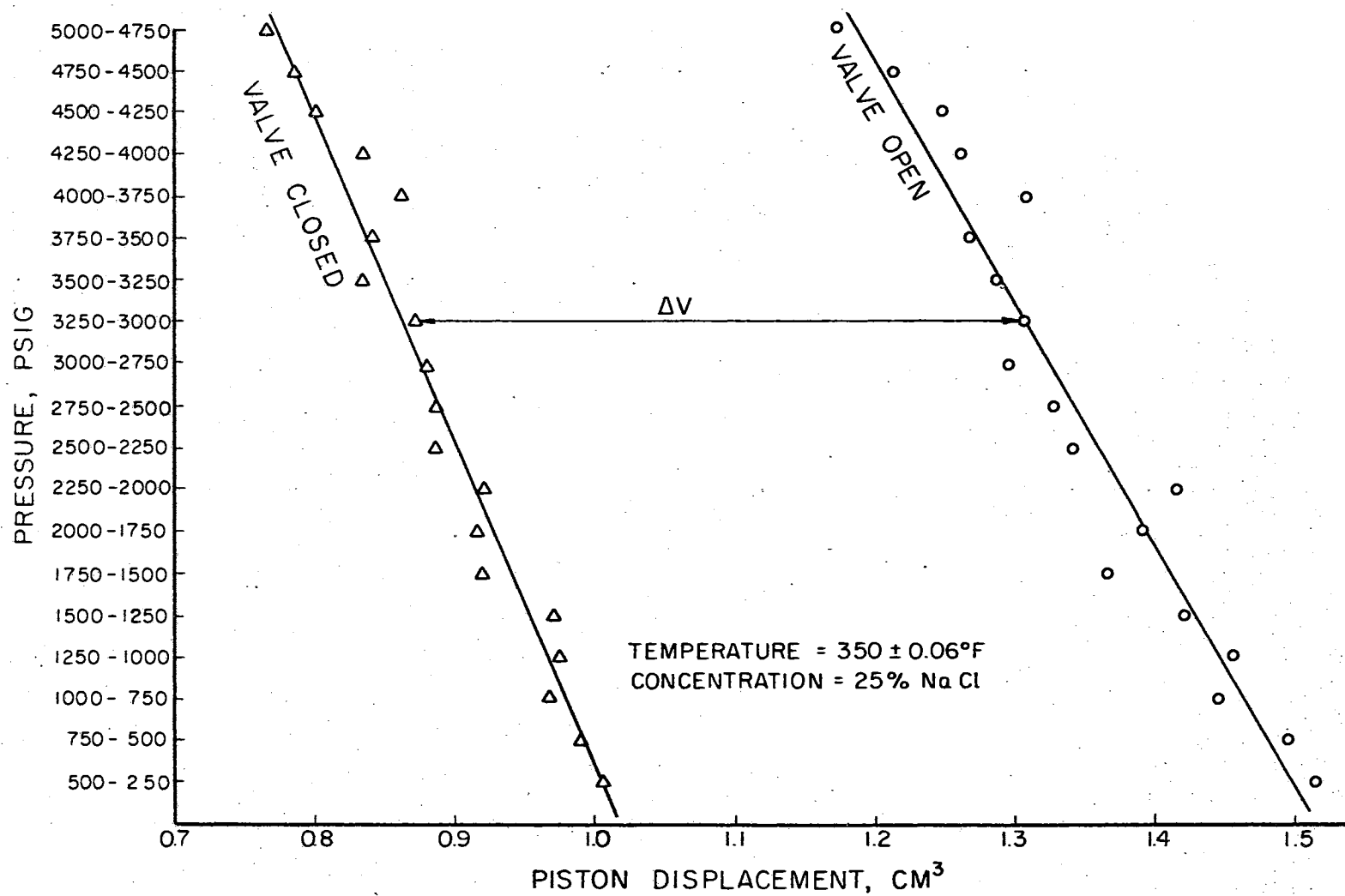


Figure 9. Typical Measurements of Piston Displacement for Compression Test

TABLE XIII

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

TABLE XIII - Continued

Pressure, psig	Salt Weight, gm/100 gm Solution					
	0	5	10	15	20	25
(Temperature = 125 F)						
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
(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

TABLE XIII - Continued

Pressure, psig	Salt Weight, gm/100 gm Solution					
	0	5	10	15	20	25
(Temperature = 250 F)						
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
(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

TABLE XIII - Continued

Pressure, psig	Salt Weight, gm/100 gm Solution					
	0	5	10	15	20	25
(Temperature = 350 F)						
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

coefficients a and b are summarized in Table XIV.

The term ΔV in Equation (4-2) represents the total volume change of the isolated solution and of the vessel containing only solution with the pressure change ΔP at a constant temperature. 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

$$-\left(\frac{\partial v}{\partial P}\right)_{T,x} \cong \frac{\Delta V - \Delta V_e}{M\Delta P} \quad (4-3)$$

where M is the mass of solution isolated from the system after the closing of the valve and ΔV_e is the dilation of the vessel subjected to the internal pressure change 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 of the volume of the vessel due to the thermal expansion of metal at temperature t . Then, Equation (4-3) can be written as

$$-\left(\frac{\partial v}{\partial P}\right)_{T,x} \cong \frac{v_i(\Delta V - \Delta V_e)}{(V_o + V_t)\Delta P} \quad (4-4)$$

TABLE XIV
 COEFFICIENTS a AND b OF EQUATION (4-2)

Salt, %	Temperature, °F					
	72	125	180	250	300	350
(Coefficient a)						
0	0.5567	0.5483	0.5671	0.6324	0.7153	0.8293
5	0.5100	0.5065	0.5208	0.5734	0.6383	0.7174
10	0.4704	0.4691	0.4843	0.5268	0.5758	0.6382
15	0.4370	0.4393	0.4537	0.4885	0.5285	0.5776
20	0.4082	0.4137	0.4269	0.4552	0.4874	0.5266
25	0.3845	0.3927	0.4019	0.4263	0.4539	0.4852
(Coefficient b) x (-0.0001)						
0	0.1232	0.1328	0.1534	0.2041	0.2414	0.3239
5	0.1062	0.1112	0.1242	0.1519	0.1859	0.2364
10	0.1165	0.1178	0.1262	0.1438	0.1637	0.1903
15	0.1212	0.1224	0.1256	0.1337	0.1438	0.1575
20	0.1273	0.1216	0.1197	0.1218	0.1269	0.1350
25	0.1289	0.1212	0.1166	0.1148	0.1171	0.1222

The value of ΔV_e , according to the usual theory of elasticity (25), may be computed by the equation

$$\Delta V_e = \frac{V\Delta P[3(1 - 2\sigma)r_i^3 + 2(1 + \sigma)r_o^3]}{E(r_o^3 - r_i^3)} \quad (4-5)$$

where σ is Poisson's ratio, E is Young's modulus, r_i is the inside radius, r_o is the outside radius, and V is the internal volume of the vessel. For $E = 30,000,000$ psi and $\sigma = 0.3$, which are the typical values for stainless steel, the value of ΔV_e is equal to 0.0304 cubic centimeter for 250 psi of pressure change with the geometrical dimensions as shown in Figure 8.

The increase of volume with pressure as determined above was checked experimentally by weighing the overflow of water from the top of the vessel in the following manner. The valve under the vessel was closed at a desired pressure, and the valve on the top was then opened to drop the pressure to atmospheric pressure. The temperatures of water were observed before and after the expansion of water. From the P-v-T relation of water as given by Equation (4-1), the volume increase ΔV_e was computed. The observed data at room temperature are given in Table XV, and the results may be represented by the equation

$$\Delta V_e = 0.05215 + 0.0001287P \quad (4-6)$$

where ΔV_e is in cubic centimeter and P is in psig. The value of ΔV_e as calculated by Equation (4-6) for 250 psi increment of pressure change is 0.0322 cubic centimeter, which compares very closely to the value obtained from Equation (4-5).

The moduli of elasticity of metals typically drop by about 0.03%

TABLE XV
 DILATION OF VESSEL SUBJECTED TO INTERNAL
 PRESSURE AT 72 °F

P, psig	w, gm	t_1 , °F	t_2 , °F	ΔV_e , cm ³
5,020	10.726	73.13	72.13	0.7028
4,510	9.658	72.92	72.02	0.6313
4,010	8.635	72.74	71.94	0.5717
3,510	7.590	72.74	72.04	0.5033
3,010	6.533	72.64	72.04	0.4315
2,505	5.477	72.54	72.04	0.3801
2,010	4.406	72.50	72.10	0.3033
1,510	3.335	72.39	72.09	0.2466
1,015	2.255	72.26	72.06	0.1799
505	1.139	72.16	72.06	0.1173
253	0.589	72.16	72.11	0.0919

where ΔV_e = dilation of vessel
 $= v_2 w + 661.1(v_2/v_1 - 1)$
 v_1 = specific volume of water at t_1 and P
 v_2 = specific volume of water at t_2 and 1 atm
 t_1 = temperature before expansion
 t_2 = temperature after expansion
P = internal pressure
w = overflow of mass from the top
661.1 cm³ = volume of vessel at 72 °F and 1 atm.

per 1°C temperature rise (30). The variation of Poisson's ratio with temperature is smaller than modulus of elasticity, and Equation (4-5) is quite insensitive to the variation of Poisson's ratio. For this reason, the value ΔV_e at temperatures above the room temperature for pressure increment of 250 psi is taken to be

$$\Delta V_e = 0.0322 \div (1.012 - 0.000167t) \quad (4-7)$$

where ΔV_e is in cubic centimeter per 250 psi 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. From repeated measurements, the value of V_o was ascertained to be 661.1 ± 0.2 cubic centimeters.

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 250 psig pressure. The data, shown in Table XVI, were taken when the water and vessel reached the conditions of thermal equilibrium. The values of V_t in cubic centimeters were then calculated from specific volumes given by Equation (4-1). The results were fitted into the following interpolation formula:

$$V_o + V_t = 661.741245 - 0.0209182t + 0.172507 \times 10^{-6}t^2 \quad (4-8)$$

where t is in degrees Fahrenheit.

The data on densities in grams per cubic centimeter in the region

TABLE XVI
THERMAL EXPANSION OF VESSEL

$t, ^\circ\text{F}$	$v, \text{cm}^3/\text{gm}$	$\Delta V_{\text{pd}}, \text{cm}^3$	V_t, cm^3
124.58	1.01198	6.180	0.76
182.37	1.03053	16.600	2.58
240.67	1.05572	30.250	5.57
294.91	1.08535	45.920	9.45
343.25	1.11740	62.720	13.81

where V_t = vessel expansion at temperature above 72°F

$$V_t = 661.13(v/v_o - 1) - \Delta V_{\text{pd}}$$

v = specific volume of water at temperature t and 250 psig

v_o = specific volume of water at 72°F and 250 psig

ΔV_{pd} = piston displacement

661.13 cm^3 = vessel volume at 72°F and 250 psig.

from 0 to 100°C and from 1 to 26 grams of salt per 100 grams of solution at 1 atmosphere are given in International Critical Tables (51). From these data and the data obtained by Fabuss (7) 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 as

$$v_i = A(T) + x \cdot D(T) + x^2 \cdot E(T), \quad (4-9)$$

where

$$D(T) = -2.573475 + 0.01153566T - 0.17617526 \times 10^{-4}T^2,$$

$$E(T) = 3.1262732 - 0.017185204T + 0.25147256 \times 10^{-4}T^2,$$

and the function $A(T)$ is the same as that of Equation (4-1). The data and the estimated values from Equation (4-9) are shown in Table XVII. 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 changes of v_i with 185 psi of pressure change are about 0.00101 to 0.00025 cubic centimeter per gram. The error caused by using Equation (4-9) to represent v_i at 185 psi in Equation (4-4) may not be excessive in comparison with other experimental uncertainties.

By using Equation (4-4) together with Equations (4-2), (4-7), (4-8), (4-9) and (4-1), 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 tabulated in Table XVIII. The comparison of the experimental values obtained in this work with those calculated from Smith and Keyes' formula (43) and Equation (4-1) is illustrated in Figure 10. The comparison is for pure water only. In considering the values derived from the

TABLE XVII
SPECIFIC VOLUME OF SOLUTION

t, °C	Salt, %	Sp. Vol., cm ³ /gm		Difference
		(Data)	(Est.)	
0	0.0100	0.9926 (51)	0.9929	-0.0003
0	0.0200	0.9851	0.9856	-0.0005
0	0.0400	0.9705	0.9712	-0.0007
0	0.0600	0.9563	0.9571	-0.0009
0	0.0800	0.9423	0.9432	-0.0009
0	0.1000	0.9287	0.9296	-0.0009
0	0.1200	0.9154	0.9162	-0.0008
0	0.1400	0.9023	0.9031	-0.0008
0	0.1600	0.8895	0.8902	-0.0007
0	0.1800	0.8770	0.8776	-0.0006
0	0.2000	0.8646	0.8652	-0.0006
0	0.2200	0.8524	0.8530	-0.0006
0	0.2400	0.8403	0.8411	-0.0008
0	0.2600	0.8284	0.8294	-0.0010
10	0.0100	0.9930	0.9932	-0.0002
10	0.0200	0.9858	0.9861	-0.0003
10	0.0400	0.9716	0.9720	-0.0004
10	0.0600	0.9578	0.9582	-0.0004
10	0.0800	0.9442	0.9446	-0.0003
10	0.1000	0.9309	0.9312	-0.0002
10	0.1200	0.9179	0.9180	-0.0001
10	0.1400	0.9051	0.9050	0.0000
10	0.1600	0.8924	0.8923	0.0001
10	0.1800	0.8799	0.8798	0.0002
10	0.2000	0.8676	0.8675	0.0002
10	0.2200	0.8555	0.8554	0.0001
10	0.2400	0.8435	0.8436	-0.0001
10	0.2600	0.8316	0.8319	-0.0004
20	0.0100	0.9947	0.9948	-0.0001
20	0.0200	0.9877	0.9878	-0.0001
20	0.0400	0.9739	0.9740	-0.0001
20	0.0600	0.9604	0.9604	-0.0000
20	0.0800	0.9471	0.9470	0.0001
20	0.1000	0.9340	0.9338	0.0002
20	0.1200	0.9211	0.9207	0.0004
20	0.1400	0.9084	0.9079	0.0005
20	0.1600	0.8959	0.8953	0.0006
20	0.1800	0.8835	0.8829	0.0006
20	0.2000	0.8712	0.8707	0.0006
20	0.2200	0.8591	0.8586	0.0005
20	0.2400	0.8472	0.8468	0.0004
20	0.2600	0.8353	0.8352	0.0001
40	0.0100	1.0009	1.0010	-0.0001
40	0.0200	0.9941	0.9942	-0.0001

TABLE XVII - Continued

$t, ^\circ\text{C}$	Salt, %	Sp. Vol., cm^3/gm		Difference
		(Data)	(Est.)	
40	0.0400	0.9806	0.9807	-0.0000
40	0.0600	0.9673	0.9673	0.0000
40	0.0800	0.9542	0.9541	0.0001
40	0.1000	0.9413	0.9411	0.0002
40	0.1200	0.9285	0.9283	0.0002
40	0.1400	0.9159	0.9156	0.0003
40	0.1600	0.9034	0.9031	0.0004
40	0.1800	0.8911	0.8907	0.0004
40	0.2000	0.8789	0.8786	0.0004
40	0.2200	0.8669	0.8666	0.0003
40	0.2400	0.8549	0.8547	0.0002
40	0.2600	0.8431	0.8431	0.0000
60	0.0100	1.0101	1.0103	-0.0002
60	0.0200	1.0033	1.0035	-0.0002
60	0.0400	0.9898	0.9900	-0.0002
60	0.0600	0.9765	0.9767	-0.0002
60	0.0800	0.9633	0.9635	-0.0002
60	0.1000	0.9503	0.9505	-0.0002
60	0.1200	0.9375	0.9376	-0.0001
60	0.1400	0.9248	0.9249	-0.0001
60	0.1600	0.9122	0.9123	-0.0001
60	0.1800	0.8998	0.8999	-0.0001
60	0.2000	0.8875	0.8877	-0.0002
60	0.2200	0.8753	0.8756	-0.0003
60	0.2400	0.8633	0.8636	-0.0004
60	0.2600	0.8513	0.8518	-0.0005
80	0.0100	1.0220	1.0221	-0.0001
80	0.0200	1.0150	1.0152	-0.0002
80	0.0400	1.0012	1.0015	-0.0003
80	0.0600	0.9877	0.9879	-0.0003
80	0.0800	0.9743	0.9745	-0.0003
80	0.1000	0.9611	0.9613	-0.0002
80	0.1200	0.9480	0.9482	-0.0003
80	0.1400	0.9351	0.9353	-0.0002
80	0.1600	0.9223	0.9225	-0.0002
80	0.1800	0.9097	0.9099	-0.0002
80	0.2000	0.8972	0.8974	-0.0002
80	0.2200	0.8847	0.8851	-0.0004
80	0.2400	0.8724	0.8730	-0.0006
80	0.2600	0.8601	0.8610	-0.0008
100	0.0100	1.0362	1.0363	-0.0001
100	0.0200	1.0289	1.0291	-0.0002
100	0.0400	1.0147	1.0149	-0.0002
100	0.0600	1.0006	1.0009	-0.0003
100	0.0800	0.9868	0.9871	-0.0003
100	0.1000	0.9731	0.9734	-0.0003

TABLE XVII - Continued

t, °C	Salt, %	Sp. Vol., cm ³ /gm		Difference
		(Data)	(Est.)	
100	0.1200	0.9597	0.9599	-0.0002
100	0.1400	0.9465	0.9466	-0.0001
100	0.1600	0.9334	0.9334	-0.0000
100	0.1800	0.9205	0.9205	0.0000
100	0.2000	0.9077	0.9077	0.0000
100	0.2200	0.8951	0.8950	0.0001
100	0.2400	0.8825	0.8826	-0.0000
100	0.2600	0.8702	0.8703	-0.0001
25	0.0058	0.9989 (7)	0.9989	-0.0000
25	0.0552	0.9652	0.9651	0.0001
25	0.1047	0.9327	0.9323	0.0004
25	0.1275	0.9181	0.9176	0.0005
45	0.0058	1.0059	1.0059	0.0000
45	0.0552	0.9728	0.9726	0.0001
45	0.1047	0.9406	0.9403	0.0003
45	0.1275	0.9260	0.9257	0.0003
65	0.0058	1.0157	1.0159	-0.0001
65	0.0552	0.9825	0.9825	0.0000
65	0.1047	0.9500	0.9500	-0.0000
65	0.1275	0.9353	0.9354	-0.0001
75	0.0058	1.0216	1.0218	-0.0003
75	0.0552	0.9878	0.9882	-0.0003
75	0.1047	0.9551	0.9554	-0.0003
75	0.1275	0.9405	0.9406	-0.0002
100	0.0058	1.0387	1.0393	-0.0005
100	0.0552	1.0037	1.0043	-0.0005
100	0.1047	0.9696	0.9703	-0.0006
100	0.1275	0.9545	0.9549	-0.0004
125	0.0058	1.0598	1.0606	-0.0008
125	0.0552	1.0224	1.0232	-0.0008
125	0.1047	0.9869	0.9871	-0.0002
125	0.1275	0.9710	0.9708	0.0001
150	0.0058	1.0845	1.0860	-0.0015
150	0.0552	1.0443	1.0453	-0.0010
150	0.1047	1.0063	1.0062	0.0001
150	0.1275	0.9896	0.9888	0.0008
175	0.0058	1.1137	1.1161	-0.0024
175	0.0552	1.0692	1.0710	-0.0018
175	0.1047	1.0285	1.0282	0.0003
175	0.1275	1.0106	1.0092	0.0014

Note: Data by Fabuss et al. (7) and from International Critical Tables (51).

TABLE XVIII

VALUES OF $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ 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	0.4470	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

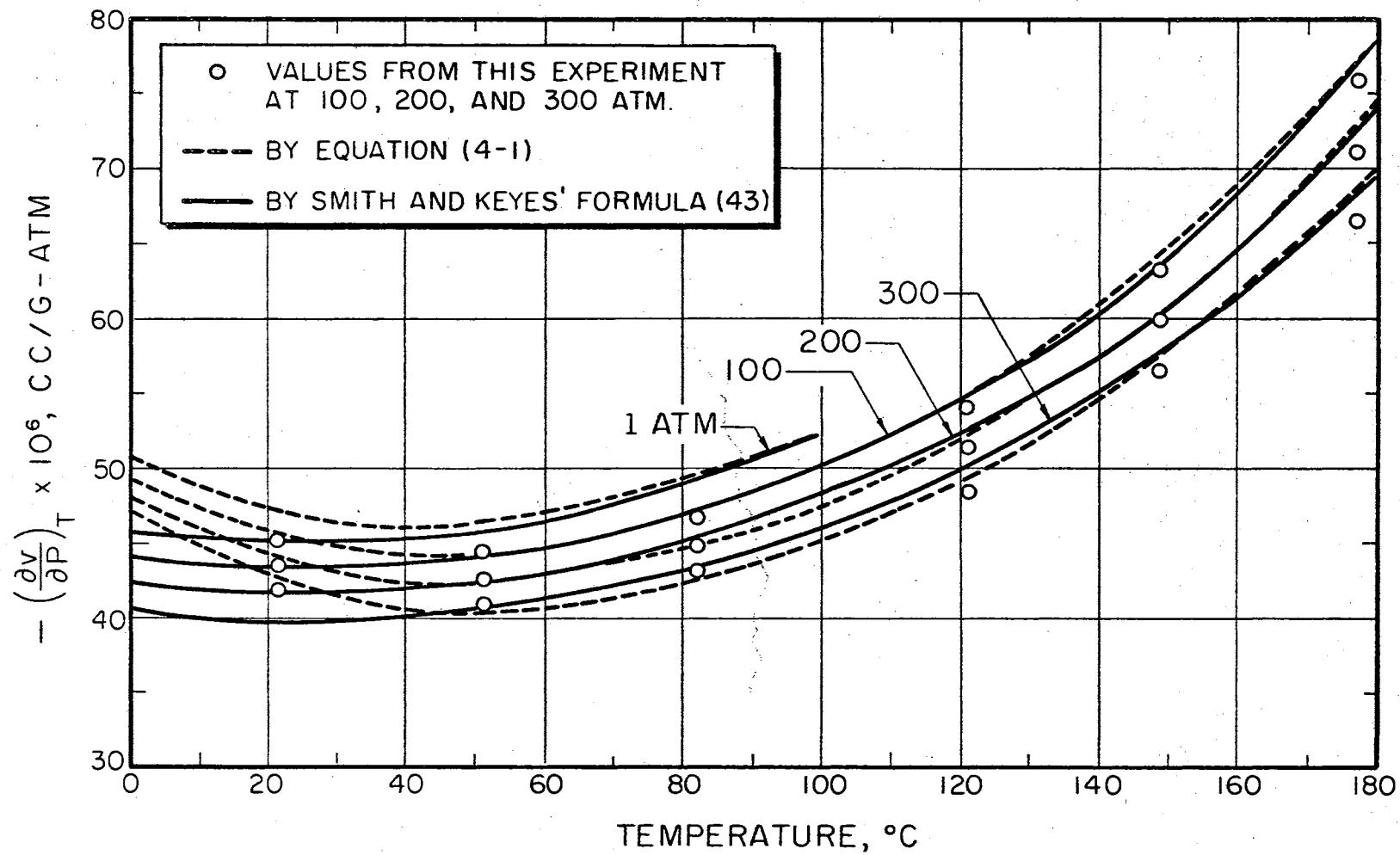


Figure 10. Comparison of $\left(\frac{\partial v}{\partial P}\right)_T$ of Water

compressibilities of Kelly and Whalley's recent investigation at one atmosphere (23), given below:

Temp., °C	0.00	10.00	20.00	40.00
$-\left(\frac{\partial v}{\partial P}\right)_T \times 10^6$, cc/g-atm	51.67	48.49	46.58	45.25.

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 (9) and by Hubbard and Loomis (17). With Laplace's assumption that the changes taking place in the medium traversed by the sound wave are adiabatic, the velocity of sound u can be related to the derivatives $\left(\frac{\partial v}{\partial P}\right)_T$ and $\left(\frac{\partial v}{\partial T}\right)_P$, and to temperature T , specific heat c_p and specific volume v by the relation (53),

$$\left(\frac{\partial v}{\partial P}\right)_T = \frac{v}{u^2} + \frac{Tv}{c_p} \left(\frac{\partial v}{\partial T}\right)_P^2. \quad (4-10)$$

The values of $\left(\frac{\partial v}{\partial T}\right)_P$ and v at one atmosphere may be determined from Equation (4-9). In Chapter III, an interpolation formula for c_p was given. According to the sound velocity measured by Freyer, the values of the derivative $\left(\frac{\partial v}{\partial P}\right)_T$ at 20°C and 1 atmosphere were calculated with Equation (4-10); the results are tabulated as follows:

x	1	6	10	16	20	24
u	1497.0	1554.5	1600.6	1673.0	1722.5	1771.5
$-\left(\frac{\partial v}{\partial P}\right)_T \times 10^6$	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 11 and compared with the values at 72°F from this experiment. The disagreement between the two sets of data increases with increasing salt concentration. A careful review of the testing procedures gave no reasonable explanation to account for such large discrepancies at high salt concentrations. Equation (4-10) is based on the assumption that 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. The electrostatic forces that exist between ions in the crystal of a salt are weakened by the presence of the water dipoles adjacent to the ions, and thus the crystal dissolves. These dissolved ions, being charged, orient the electrical dipoles of the water around them, a positive ion pulling the negatively charged oxygen end of water molecule toward it, a negative ion pulling the positively charged hydrogen end. The field of ions exercises large electrostatic pressure on the water dipoles to produce a strong compression of the aqueous medium. Each ion is, therefore, surrounded by a little sphere within which both the specific heat and the compressibility of water are reduced by pressure. This qualitative explanation of the behavior of water in electrolytic solution was first pointed out by Tammann. Later, Gucker and Rubin (12) determined from the experimental data at 25°C that the effect of one gram NaCl per 100 grams of solution is analogous to a rise of pressure to about 500 atmospheres.

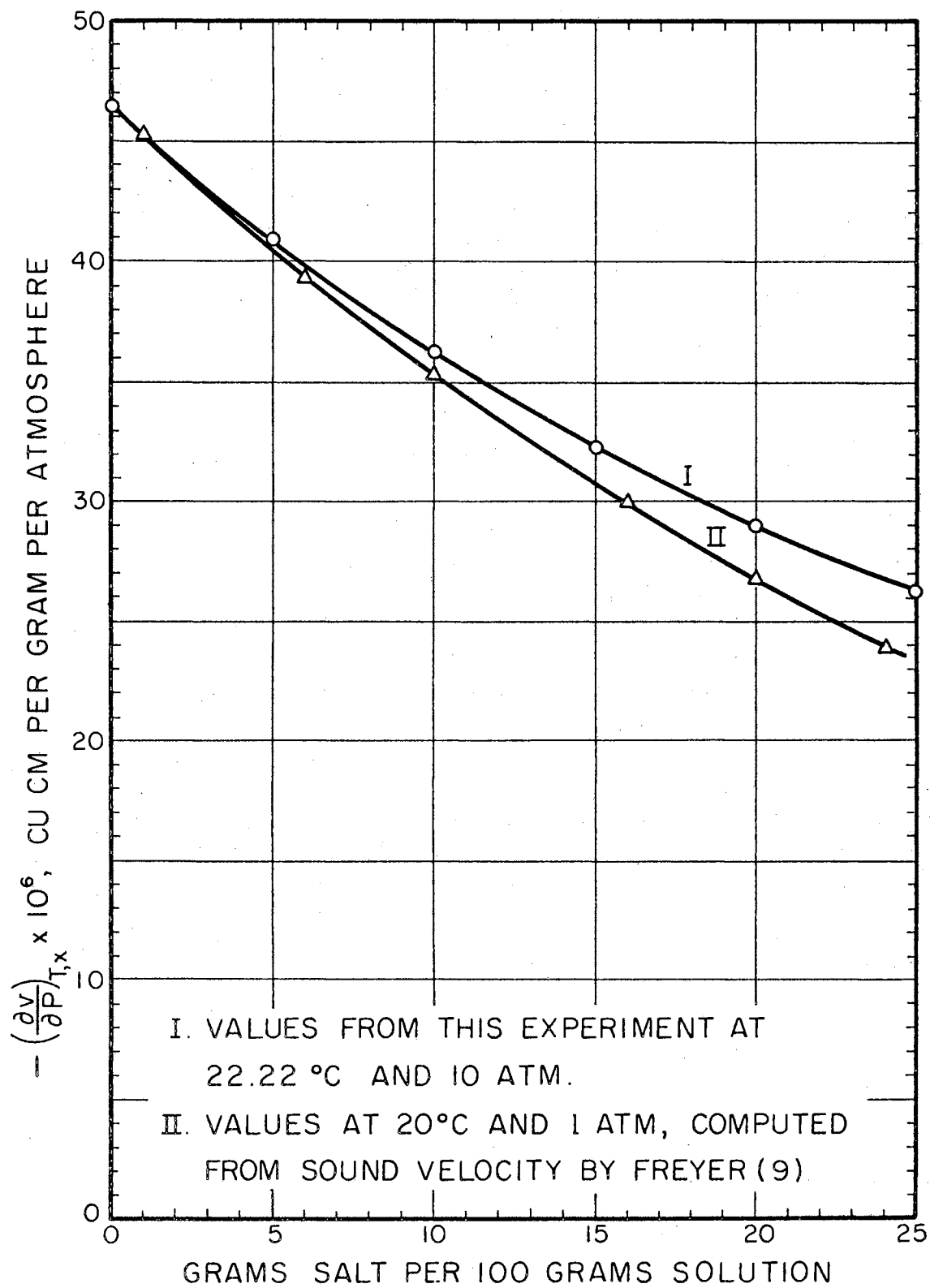


Figure 11. Comparison of $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ of Solution

Literature data are often reported in terms of mean isothermal compressibility k_m , defined as

$$k_m = \frac{(v_1 - v_p)}{v_1 (P - 1)} \quad (4-11)$$

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 (47) 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

$$k_m = \frac{0.00186}{(36 + P + x)} \quad (4-12)$$

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 (4-13), which fits the experimental results of this study. The disagreement between the values by Tait's formula and by Equations (4-13) and (4-11) is less than 2%, as shown in Table XIX.

Insufficient accuracy of the calibration of piston displacement and inability of maintaining thermal equilibrium exactly during a test are thought to be the principal causes of experimental error. The other sources of error include the static and dynamic errors of pressure gage and thermocouple recordings, and the possible nonuniformity of the temperature of solution in the vessel. The extent of each of these sources

TABLE XIX

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 (4-11) and (4-13).

(b) By Tait's equation (47).

of error was not determined. However, many repeated tests were made, and the deviation in results was less than one per cent of the average value of the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$. The comparisons of results with data on water from other sources show that the probable errors of the derivatives obtained from this experiment are within the limits of $\pm 4.5\%$ of the true values.

Pressure-Volume-Temperature-Concentration

Relation

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

$$v = A(T) - P \cdot B(T) - P^2 \cdot C(T) + x \cdot D(T) + x^2 \cdot E(T) \\ - xP \cdot F(T) - x^2P \cdot G(T) - \frac{1}{2}xP^2 \cdot H(T). \quad (4-13)$$

If the concentration x of salt in solution is zero, Equation (4-13) is reduced to Equation (4-1), of which the functions $A(T)$, $B(T)$, and $C(T)$ have already been determined. For a solution in a hypothetical state of zero pressure, Equation (4-13) becomes

$$v = A(T) + x \cdot D(T) + x^2 \cdot E(T). \quad (4-14)$$

Since the data given in International Critical Tables (51) and by Fabuss (7) are not at zero pressure, it was necessary to adjust these data to zero pressure with the information on compression in the previous section. The adjusted values were then fitted into Equation (4-14) for the determination of the functions $D(T)$ and $E(T)$. For v in cubic centimeters per gram, T in degrees Kelvin and x in grams salt per 100 grams solutions, the functions $D(T)$ and $E(T)$ can be adequately represented by

the formulae,

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

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

Equation (4-14) fits the data accurately to three decimal places.

From Equation (4-13), it follows that

$$\left(\frac{\partial v}{\partial P}\right)_{T,x=0} - \left(\frac{\partial v}{\partial P}\right)_{T,x} = x \cdot F(T) + x^2 \cdot G(T) + xP \cdot H(T). \quad (4-15)$$

The experimental values of the derivatives from the preceding section were fitted to Equation (4-15) with the quadratic forms of three temperature functions, found by multiple regression as

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

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

$$H(T) = 0.55541298 \times 10^{-5} - 0.36241535 \times 10^{-8}T + 0.60444040 \times 10^{-11}T^2.$$

with pressure p in kilograms per square centimeter. The maximum difference between the data and the estimated values by Equation (4-15) is 2.7% of the value of $\left(\frac{\partial v}{\partial P}\right)_{T,x=0}$. Since the magnitude of the derivative is in the order of 10^{-5} , five percent of relative error on the estimated value of the derivative would induce an error of approximately 0.0004 to 0.0006 cubic centimeter per gram in the specific volume at 300 atmospheres. The estimated maximum deviation of the experimental data on specific volume from Equation (4-13) with the respective temperature functions is less than 1.5 parts per thousand in the region from 0 to 150°C for concentrations ranging from 0 to 25% of salt weight in

solution and for pressures up to 300 atmospheres. The specific volumes at 10 atmospheres are plotted in Figure 12.

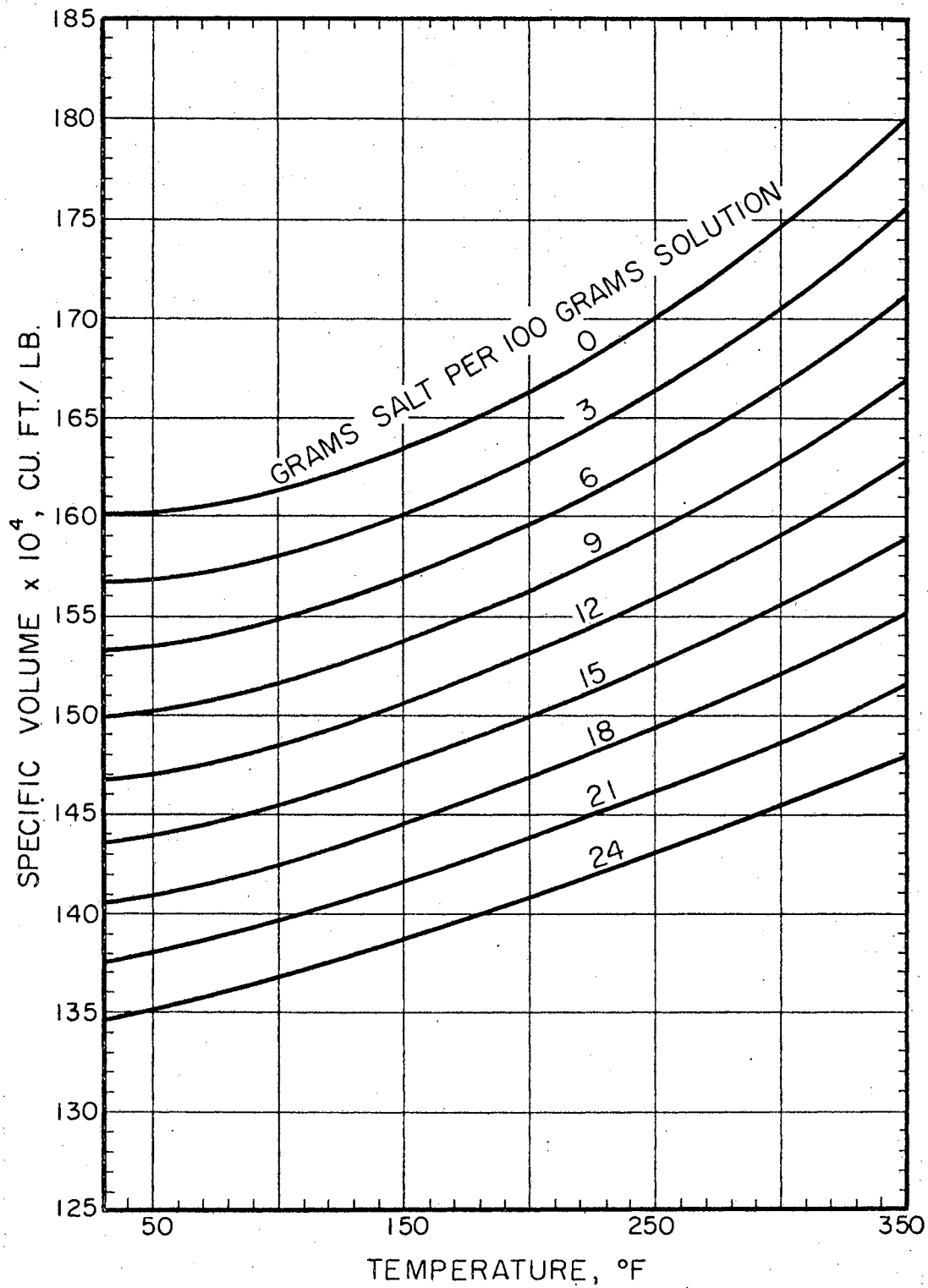


Figure 12. Specific Volume at 10 Atmospheres

CHAPTER V

ENTHALPY, ENTROPY AND HEAT OF VAPORIZATION

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 contains initially 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 then as follows:

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

where the superscript $^\circ$ denotes infinite dilution, since 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,

$$q_d = \frac{n_1}{n_2} (\bar{h}_1^\circ - \bar{h}_1) + (\bar{h}_2^\circ - \bar{h}_2). \quad (5-1)$$

If the infinite dilution is chosen as the reference state for the enthalpy of solute, \bar{h}_2° 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

$$h = (1 - x)\bar{h}_1^0 - xq_d. \quad (5-2)$$

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 (38). The minimum value of heat of formation is at 400 moles water per mole salt, so the heat of dilution when diluting beyond this concentration is negative, i.e., heat is evolved. In order to be consistent with the values in the steam tables, the value of \bar{h}_1^0 is based on the convention of zero enthalpy for the saturated water at 0°C and taken to be 25.015 calories per gram at 25°C and 1 atmosphere. The values of enthalpy have been calculated from Equation (5-2) 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 XX and may be adequately represented by the interpolation formula,

$$h = 25.015(1 - x) + 30.805561 x^{1.5} - 161.50632 x^2 + 79.059598 x^{2.5} + 114.83149 x^3, \quad (5-3)$$

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

Enthalpy Table

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

TABLE XX
 ENTHALPY AT 25 °C AND 1 ATMOSPHERE

Salt, %	Heat of Dilution cal/gm Salt	Enthalpy, cal/gm Solution	
		Eq. (5-2)	Eq. (5-3)
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

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

This leads to the expression

$$h = h_o + \int_{T_o}^T c_p dT + \int_{P_o}^P \left[v - T \left(\frac{\partial v}{\partial T}\right)_P \right] dP. \quad (5-4)$$

Using Equation (5-4) provides 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. In Chapter III, an interpolation formula was given for the constant-pressure specific heat at 10 atmospheres, and the pressure dependency of c_p may be determined by the relation

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

Equation (4-13) serves as the P-v-T-x relation of the solution at various concentrations. For convenience, it is here rewritten with new notations for the coefficients as

$$\begin{aligned} v = & A_{v1} + A_{v2}T + A_{v3}T^2 + A_{v4}/T + A_{v5}/T^2 \\ & - (B_{v1} + B_{v2}T + B_{v3}T^2 + B_{v4}/T + B_{v5}/T^2)P \\ & - (C_{v1} + C_{v2})P^2 + (D_{v1} + D_{v2}T + D_{v3}T^2)x \\ & + (E_{v1} + E_{v2}T + E_{v3}T^2)x^2 - (F_{v1} + F_{v2}T \\ & + F_{v3}T^2)Px - (F_{v1} + G_{v2}T + G_{v3}T^2)Px^2 \\ & - 0.5(H_{v1} + H_{v2}T + H_{v3}T^2)P^2x \end{aligned} \quad (5-6)$$

so that the integrals in Equations (5-4) and (5-5) may be readily found.

$$\begin{aligned}
 \int_{P_0}^P \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP = & [A_{v1} - A_{v3} T^2 + 2A_{v4}/T + 3A_{v5}/T^2 + (D_{v1} - D_{v3} T^2)x \\
 & + (E_{v1} - E_{v3} T^2)x^2](P - P_0) - 0.5[B_{v1} - B_{v3} T^2 + 2B_{v4}/T + 3B_{v5}/T^2] \\
 & - (F_{v1} - F_{v3} T^2)x - (G_{v1} - G_{v3} T^2)x^2](P^2 - P_0^2) - \frac{1}{3} [C_{v1} \\
 & + 0.5(H_{v1} - H_{v3} T^2)x](P^3 - P_0^3).
 \end{aligned}$$

$$\begin{aligned}
 \int_{T_0}^T \int_{P_0}^P T \left(\frac{\partial^2 v}{\partial T^2} \right)_P dPdT = & (T^2 - T_0^2) [(P - P_0)(A_{v3} + D_{v3}x + E_{v3}x^2) - \frac{1}{2}(P^2 - P_0^2) \\
 & (B_{v3} + F_{v3}x + G_{v3}x^2) - \frac{1}{6}(P^3 - P_0^3)H_{v3}x] - \left(\frac{1}{T} - \frac{1}{T_0} \right) [2(P - P_0)A_{v4} \\
 & - (P^2 - P_0^2)B_{v4}] - \left(\frac{1}{T^2} - \frac{1}{T_0^2} \right) [3(P - P_0)A_{v5} - 1.5(P^2 - P_0^2)B_{v5}].
 \end{aligned}$$

By utilizing these equations, the values of enthalpy at temperatures and pressures other than 25°C and 1 atmosphere may be calculated since the coefficients for specific heat and specific volume have already been determined. In Table XXI are the calculated values of enthalpy at the vapor pressures, and at 1,000, 2,000, 3,000, 4,000 and 5,000 psia. The variations of enthalpy with temperature and concentration at 10 atmospheres are illustrated in Figure 13. The enthalpies of water in Keenan and Keyes' steam table (20) 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 (18) and Kusunoki (27). However, the scope of Jessup's work is limited to less than 60°F, and in his computation the enthalpies of the hexahydrate and pure water have been taken as 200 BTU per pound each at 32°F. Kusunoki's work covers a wider range, from 0 to 100°C at 1

TABLE XXI

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	44.01	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	67.89
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

TABLE XXI - Continued

Temp, °F	Salt Weight, gm/100 gm Solution					
	0	5	10	15	20	25
(At vapor pressure)						
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
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

TABLE XXI - Continued

Temp, °F	Salt Weight, gm/100 gm Solution					
	0	5	10	15	20	25
(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
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	233.29	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

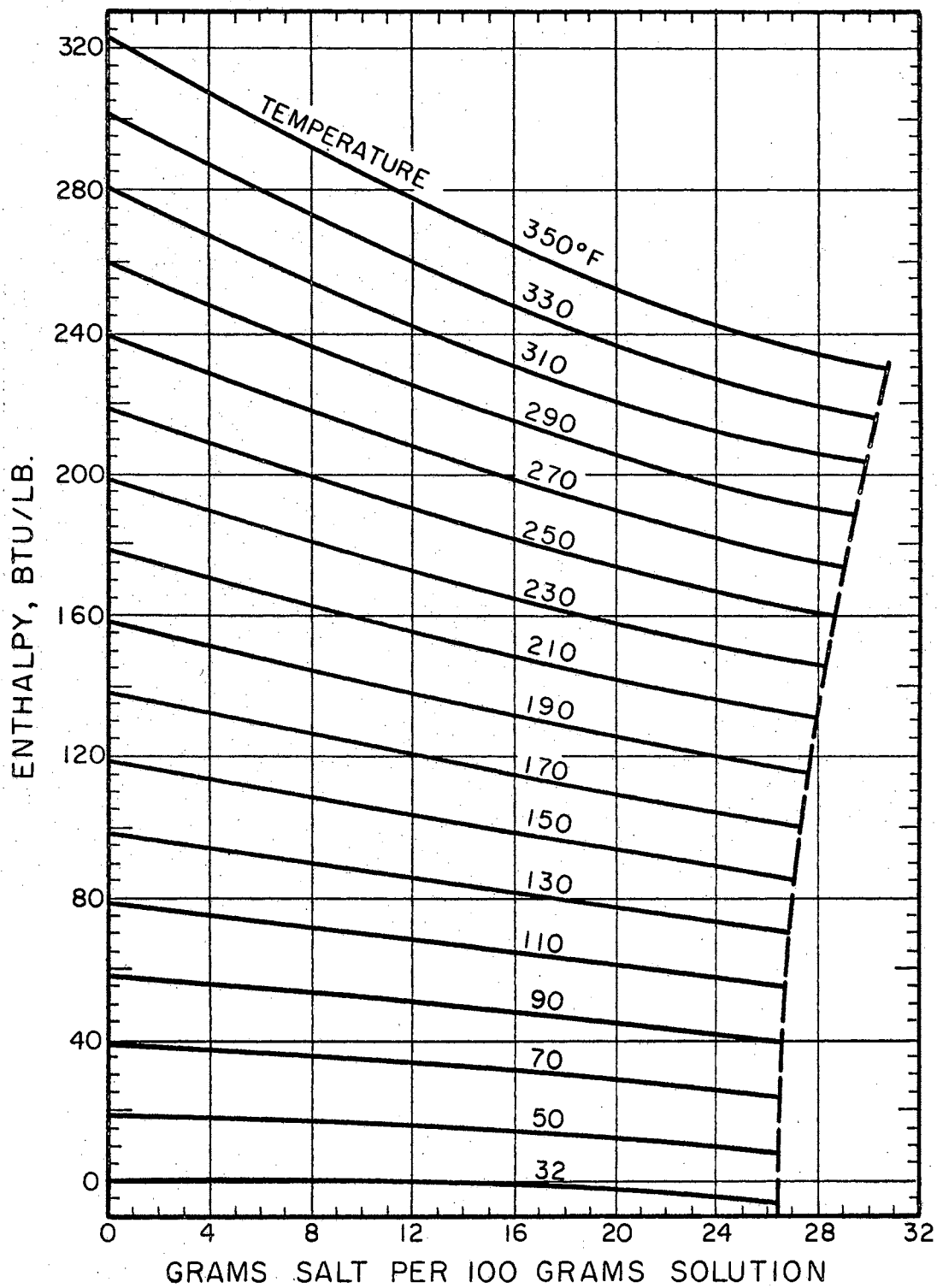


Figure 13. Enthalpy at 10 Atmospheres

atmosphere, but unfortunately the 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 (38). The values of enthalpy in Table XXI differ from Kusunoki's values less than 1 calorie per gram approximately if the datum values are properly adjusted. 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.

Entropy at 25°C and 1 Atmosphere

The partial entropy \bar{s}_i of component i in a mixture is related to activity by the definition

$$\bar{g}_i - \bar{g}_i^{\circ} = \bar{h}_i - T\bar{s}_i - (\bar{h}_i^{\circ} - T\bar{s}_i^{\circ}) = RT \ln a_i.$$

Rearranging the terms gives the partial molal entropies for solvent and solute of a binary solution as

$$\bar{s}_1 = \bar{s}_1^{\circ} - R \ln a_1 + \frac{\bar{h}_1 - \bar{h}_1^{\circ}}{T} \quad (5-7)$$

and

$$\bar{s}_2 = \bar{s}_2^{\circ} - R \ln a_2 + \frac{\bar{h}_2 - \bar{h}_2^{\circ}}{T} \quad (5-8)$$

The entropy s of the solution consisting of n_1 moles of water and n_2 moles of salt may be found by summing the products of the moles of each

component times its partial molal entropy. Substitution of Equation (5-1) for q_d leads to

$$s = n_1 \bar{s}_1^{\circ} + n_2 \bar{s}_2^{\circ} - \frac{n_2 q_d}{T} - R(n_1 \ln a_{\pm} + 2n_2 \ln a_{\pm}) \quad (5-9)$$

where a_{\pm} denotes the mean activity. Based on the ionic activity coefficients determined by Robinson (36), the heats of formation compiled by Rossini (38) and the $\ln a_{\pm}$ from Equation (2-3), the values of entropy at 25°C and 1 atmosphere have been calculated and tabulated in Table XXII. In this calculation, the entropy of saturated water at 0°C and the entropy of salt in the infinitely dilute solution at 25°C and 1 atmosphere are taken to be zero. For the ease of later computations, the results were fitted into an interpolation formula as follows:

$$s = 0.0876 + 0.067594387x - 1.2767431x^2 + 1.7277596x^3 \quad (5-10)$$

where s is in BTU per degree Rankine per pound and x is in grams salt per 100 grams of solution.

Entropy Table

By holding the composition of the solution constant, the entropy at any temperature T and pressure P may be related to the entropy in a given state (T_0, P_0) as follows:

$$s = s_0 + \int_{T_0}^T \frac{c_p}{T} dT - \int_{P_0}^P \left(\frac{\partial v}{\partial T} \right)_P dP. \quad (5-11)$$

The values of entropy at the concentrations of 0, 5, 10, 15, 20 and 25

TABLE XXII
ENTROPY AT 25 °C AND 1. ATMOSPHERE

Molality	Heat of Dilution cal/gm Salt	Ln a_{\pm}	Entropy, Btu/lb °R	
			Eq. (5-9)	Eq. (5-10)
0.1	-1.4487	-2.5531	0.0885	0.0880
0.2	-1.5587	-1.9178	0.0889	0.0882
0.3	-1.4737	-1.5468	0.0891	0.0884
0.4	-1.2994	-1.2833	0.0891	0.0885
0.5	-1.0759	-1.0772	0.0891	0.0885
0.6	-0.8232	-0.9073	0.0890	0.0885
0.7	-0.5528	-0.7619	0.0888	0.0884
0.8	-0.2719	-0.6351	0.0885	0.0882
0.9	0.0146	-0.5221	0.0882	0.0880
1.0	0.3034	-0.4202	0.0878	0.0877
1.2	0.8789	-0.2418	0.0869	0.0870
1.4	1.4422	-0.0874	0.0859	0.0862
1.6	1.9862	0.0505	0.0848	0.0851
1.8	2.5071	0.1752	0.0836	0.0840
2.0	3.0027	0.3305	0.0820	0.0827
2.2	3.4719	0.3949	0.0809	0.0813
2.4	3.9145	0.4942	0.0795	0.0798
2.6	4.3305	0.5876	0.0780	0.0783
2.8	4.7203	0.6764	0.0765	0.0767
3.0	5.0846	0.7613	0.0749	0.0750
3.2	5.4240	0.8426	0.0733	0.0733
3.4	5.7393	0.9208	0.0716	0.0716
3.6	6.0314	0.9968	0.0700	0.0698
3.8	6.3012	1.0707	0.0683	0.0681
4.0	6.5496	1.1420	0.0666	0.0663
4.2	6.7773	1.2115	0.0648	0.0646
4.4	6.9854	1.2794	0.0631	0.0628
4.6	7.1745	1.3460	0.0613	0.0610
4.8	7.3457	1.4109	0.0596	0.0593
5.0	7.4995	1.4747	0.0578	0.0576
5.2	7.6369	1.5374	0.0560	0.0559
5.4	7.7585	1.5989	0.0542	0.0542
5.6	7.8651	1.6597	0.0524	0.0525
5.8	7.9573	1.7194	0.0506	0.0509
6.0	8.0359	1.7779	0.0489	0.0493

grams salt per 100 grams of solution have been determined by letting $T_0 = 25^\circ\text{C}$ and $P_0 = 1$ atmosphere in order to use Equation (5-10) for s_0 . The results of calculations are shown in Table XXIII and Figure 14.

Heat of Vaporization

A molecule which leaves the surface of a liquid must overcome the forces of attraction of the other molecules in the liquid. The intermolecular forces of attraction are relatively large because the molecules are much closer together in the liquid state than in the vapor state. In order to overcome these attractive forces, energy must be supplied to the liquid in the form of heat. The heat required to vaporize a substance may be accurately computed from the slope of vapor pressure curve and the corresponding specific volumes of the liquid and vapor phases. This relation was first discovered by the French engineer Clapeyron before the formal formulation of the first law of thermodynamics (1834), but its deduction from the modern point of view was due to Clausius.

The Clausius-Clapeyron relation applies only to a single component system in equilibrium. For a binary solution, there is no such unique relation between changes in pressure and temperature. In the case of an aqueous solution of nonvolatile salt, the vapor pressure has a definite value only when the temperature and the concentration are held constant, and a modified version of the Clausius-Clapeyron relation is derived by Denbigh (5) as follows:

$$\left(\frac{\partial p}{\partial T}\right)_x = \frac{\bar{h}_g - \bar{h}_l}{T(\bar{v}_g - \bar{v}_l)}$$

TABLE XXIII

ENTROPY IN BTU PER POUND PER DEGREE RANKINE

Temp., °F	Salt Weight, gm/100 gm Solution					
	0	5	10	15	20	25
(At Vapor Pressure)						
32	0.0000	0.0051	0.0047	0.0001	-0.0077	-0.0175
35	0.0061	0.0109	0.0102	0.0053	-0.0027	-0.0127
40	0.0162	0.0204	0.0192	0.0139	0.0055	-0.0048
45	0.0262	0.0299	0.0282	0.0224	0.0136	0.0031
50	0.0361	0.0392	0.0370	0.0308	0.0217	0.0109
55	0.0458	0.0484	0.0458	0.0391	0.0297	0.0186
60	0.0555	0.0576	0.0545	0.0474	0.0376	0.0263
65	0.0650	0.0666	0.0631	0.0556	0.0454	0.0339
70	0.0745	0.0756	0.0716	0.0637	0.0532	0.0413
75	0.0839	0.0845	0.0800	0.0717	0.0608	0.0488
80	0.0932	0.0933	0.0883	0.0796	0.0684	0.0561
85	0.1024	0.1020	0.0966	0.0875	0.0759	0.0634
90	0.1115	0.1106	0.1048	0.0952	0.0834	0.0706
95	0.1205	0.1192	0.1129	0.1029	0.0908	0.0777
100	0.1294	0.1276	0.1209	0.1106	0.0981	0.0848
105	0.1383	0.1360	0.1288	0.1181	0.1053	0.0918
110	0.1471	0.1443	0.1367	0.1256	0.1125	0.0987
115	0.1558	0.1526	0.1445	0.1331	0.1196	0.1056
120	0.1644	0.1607	0.1523	0.1404	0.1266	0.1124
125	0.1730	0.1688	0.1599	0.1477	0.1336	0.1191
130	0.1815	0.1769	0.1675	0.1549	0.1405	0.1258
135	0.1899	0.1848	0.1751	0.1621	0.1473	0.1324
140	0.1982	0.1927	0.1825	0.1692	0.1541	0.1389
145	0.2065	0.2005	0.1900	0.1762	0.1609	0.1454
150	0.2147	0.2083	0.1973	0.1832	0.1675	0.1518
155	0.2229	0.2160	0.2046	0.1901	0.1741	0.1582
160	0.2310	0.2237	0.2118	0.1970	0.1807	0.1645
165	0.2390	0.2312	0.2190	0.2038	0.1872	0.1708
170	0.2470	0.2388	0.2261	0.2105	0.1936	0.1770
175	0.2549	0.2462	0.2332	0.2172	0.2000	0.1831
180	0.2628	0.2537	0.2402	0.2238	0.2063	0.1892
185	0.2706	0.2610	0.2471	0.2304	0.2126	0.1952
190	0.2783	0.2683	0.2540	0.2370	0.2188	0.2012
195	0.2860	0.2756	0.2609	0.2434	0.2249	0.2071
200	0.2936	0.2828	0.2677	0.2499	0.2311	0.2130
205	0.3012	0.2899	0.2744	0.2562	0.2371	0.2188
210	0.3088	0.2970	0.2811	0.2626	0.2431	0.2246
212	0.3118	0.2999	0.2838	0.2651	0.2455	0.2269
215	0.3162	0.3041	0.2877	0.2688	0.2491	0.2303
220	0.3237	0.3111	0.2943	0.2751	0.2550	0.2360
225	0.3311	0.3180	0.3009	0.2812	0.2609	0.2416
230	0.3384	0.3250	0.3074	0.2874	0.2667	0.2472

TABLE XXIII - Continued

Temp., °F	Salt Weight, gm/100 gm Solution					
	0	5	10	15	20	25
(At Vapor Pressure)						
235	0.3457	0.3318	0.3138	0.2935	0.2725	0.2527
240	0.3530	0.3387	0.3203	0.2995	0.2782	0.2582
245	0.3602	0.3454	0.3266	0.3055	0.2839	0.2636
250	0.3674	0.3522	0.3330	0.3115	0.2895	0.2690
255	0.3745	0.3589	0.3392	0.3174	0.2951	0.2743
260	0.3816	0.3655	0.3455	0.3232	0.3006	0.2796
265	0.3887	0.3721	0.3517	0.3291	0.3061	0.2848
270	0.3957	0.3787	0.3579	0.3349	0.3116	0.2900
275	0.4027	0.3853	0.3640	0.3406	0.3170	0.2952
280	0.4096	0.3918	0.3701	0.3463	0.3224	0.3003
285	0.4165	0.3982	0.3761	0.3520	0.3277	0.3053
290	0.4234	0.4047	0.3821	0.3576	0.3330	0.3104
295	0.4303	0.4110	0.3881	0.3632	0.3382	0.3153
300	0.4371	0.4174	0.3940	0.3687	0.3434	0.3203
305	0.4438	0.4237	0.3999	0.3742	0.3486	0.3252
310	0.4506	0.4300	0.4058	0.3797	0.3537	0.3300
315	0.4573	0.4363	0.4116	0.3851	0.3588	0.3348
320	0.4640	0.4425	0.4174	0.3905	0.3639	0.3396
325	0.4706	0.4487	0.4232	0.3959	0.3689	0.3443
330	0.4772	0.4549	0.4289	0.4012	0.3739	0.3490
335	0.4838	0.4610	0.4346	0.4065	0.3788	0.3536
340	0.4904	0.4671	0.4403	0.4118	0.3837	0.3582
345	0.4969	0.4731	0.4459	0.4170	0.3886	0.3628
350	0.5034	0.4792	0.4515	0.4222	0.3934	0.3673
(Pressure = 1,000 PSIA)						
50	0.0359	0.0389	0.0367	0.0304	0.0212	0.0104
100	0.1288	0.1270	0.1202	0.1099	0.0974	0.0841
150	0.2138	0.2074	0.1964	0.1824	0.1667	0.1511
200	0.2924	0.2817	0.2667	0.2489	0.2302	0.2123
250	0.3659	0.3509	0.3318	0.3105	0.2886	0.2682
300	0.4354	0.4159	0.3928	0.3676	0.3425	0.3194
350	0.5015	0.4776	0.4501	0.4210	0.3924	0.3664
(Pressure = 2,000 PSIA)						
50	0.0357	0.0387	0.0363	0.0300	0.0208	0.0099
100	0.1282	0.1263	0.1195	0.1092	0.0967	0.0834
150	0.2129	0.2065	0.1956	0.1816	0.1659	0.1504
200	0.2912	0.2806	0.2657	0.2480	0.2294	0.2115
250	0.3645	0.3496	0.3307	0.3094	0.2877	0.2674
300	0.4336	0.4144	0.3914	0.3665	0.3415	0.3186
350	0.4994	0.4758	0.4486	0.4197	0.3913	0.3655

TABLE XXIII - Continued

Temp., °F	Salt Weight, gm/100 gm					
	0	5	10	15	20	25
(Pressure = 3,000 PSIA)						
50	0.0355	0.0384	0.0359	0.0295	0.0203	0.0094
100	0.1276	0.1257	0.1189	0.1085	0.0960	0.0827
150	0.2120	0.2056	0.1947	0.1807	0.1652	0.1496
200	0.2901	0.2795	0.2647	0.2471	0.2286	0.2107
250	0.3630	0.3483	0.3295	0.3084	0.2868	0.2666
300	0.4319	0.4129	0.3901	0.3654	0.3405	0.3177
350	0.4974	0.4740	0.4470	0.4184	0.3902	0.3646
(Pressure = 4,000 PSIA)						
50	0.0353	0.0380	0.0356	0.0291	0.0198	0.0089
100	0.1270	0.1250	0.1182	0.1078	0.0953	0.0820
150	0.2111	0.2048	0.1939	0.1799	0.1644	0.1489
200	0.2889	0.2785	0.2637	0.2462	0.2277	0.2100
250	0.3616	0.3470	0.3284	0.3075	0.2859	0.2658
300	0.4302	0.4114	0.3888	0.3642	0.3396	0.3169
350	0.4954	0.4723	0.4456	0.4172	0.3891	0.3637
(Pressure = 5,000 PSIA)						
50	0.0351	0.0377	0.0352	0.0286	0.0193	0.0084
100	0.1264	0.1244	0.1175	0.1071	0.0946	0.0814
150	0.2102	0.2039	0.1931	0.1791	0.1636	0.1482
200	0.2878	0.2774	0.2627	0.2453	0.2269	0.2092
250	0.3603	0.3458	0.3273	0.3065	0.2851	0.2651
300	0.4285	0.4100	0.3876	0.3632	0.3386	0.3161
350	0.4934	0.4706	0.4441	0.4159	0.3881	0.3628

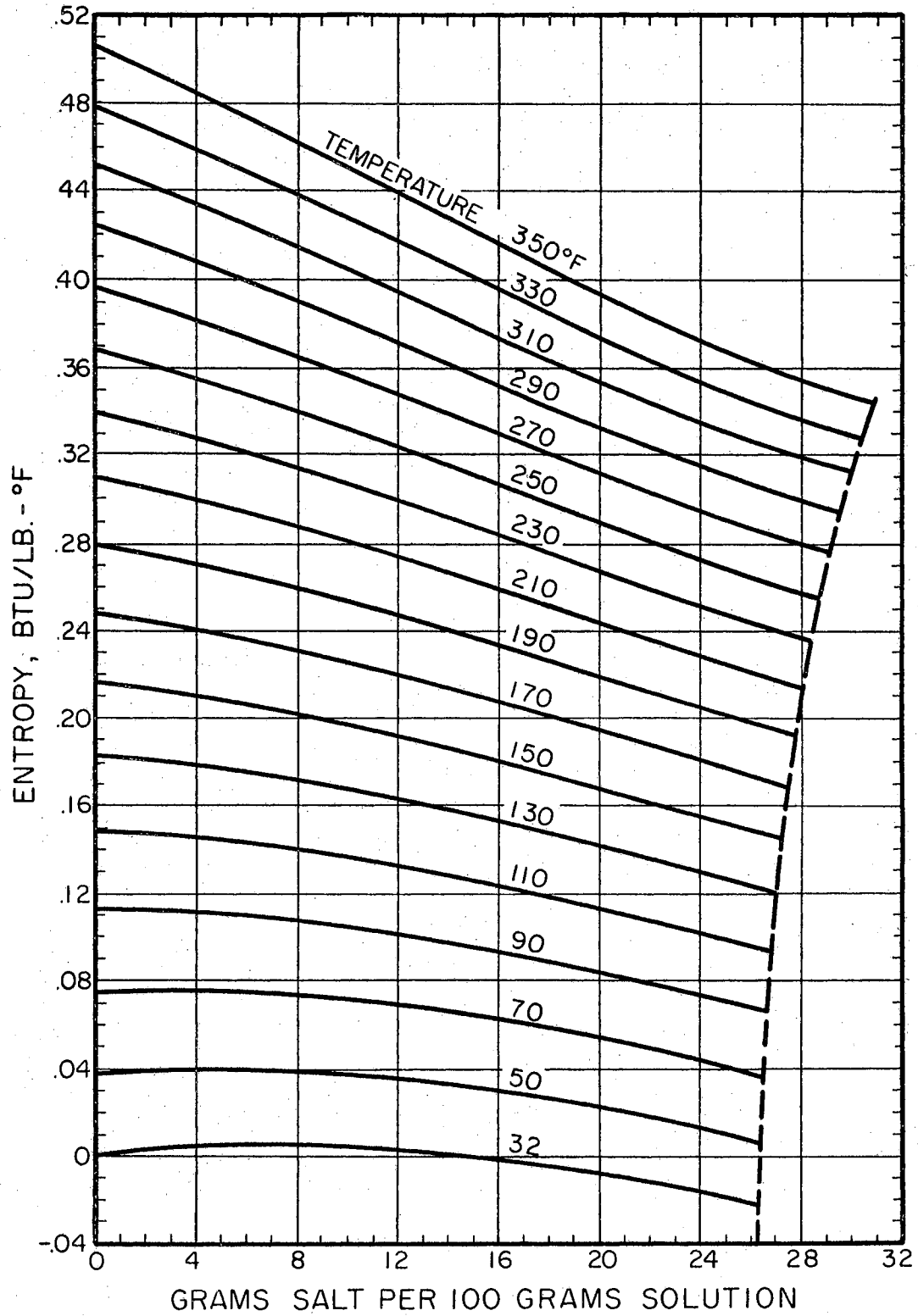


Figure 14. Entropy at 10 Atmospheres

where the partial molal volume and partial molal enthalpy of water in solution are denoted by the respective quantities with a subscript 1, and the molal volume and molal enthalpy in the vapor phase with a subscript g. The difference between \bar{h}_g and \bar{h}_1 is the heat being supplied from the surroundings to evaporate one mole of water from solution at constant concentration. Obviously this is not the same as the heat of vaporization of pure water.

By adding \bar{h}_g to both sides of Equation (3-5) and rearranging terms, the heat of vaporization of water for a given solution may be given in terms of that for an infinitely dilute solution and the activity by the equation

$$\bar{h}_g - \bar{h}_1 = \bar{h}_g^\circ - \bar{h}_1^\circ + RT^2 \left(\frac{\partial \ln a_1}{\partial T} \right)_{P,x} \quad (5-12)$$

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. In accordance with the data established by the Third International Conference on Steam Tables (48), 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:

$$\begin{aligned} \bar{h}_g - \bar{h}_1^\circ = & 1093.3254 - 0.57909483t + 0.228937 \times 10^{-5}t^2 \\ & - 0.11130559 \times 10^{-5}t^3 \end{aligned} \quad (5-13)$$

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 T and x at constant pressure is given by Equation (2-3). The general expression for $\ln a_1$, as discussed in Chapter II, is

$$\ln a_1 = \ln a_{1(P_0)} + \frac{1}{RT} \int_{P_0}^P (\bar{v}_1 - \bar{v}_1^0) dP \quad (5-14)$$

where $\ln a_{1(P_0)}$ is a function of T and x at the fixed pressure P_0 ; \bar{v}_1 and \bar{v}_1^0 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 volume of solution by the relation

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

Because the partial quantities are derived from an extensive property by simple differentiation, it is permissible to choose either mass or mole as unit of quantity. With the same notations as in Equation (5-6) for the coefficients, the difference between the two partial volumes may be written as

$$\begin{aligned} \bar{v}_1 - \bar{v}_1^0 = & -x(D_{v1} + D_{v2}T + D_{v3}T^2) - 2x^2(E_{v1} + E_{v2}T + E_{v3}T^2) \\ & + Px(F_{v1} + F_{v2}T + F_{v3}T^2) + 2Px^2(G_{v1} + G_{v2}T + G_{v3}T^2) \\ & + 0.5P^2x(H_{v1} + H_{v2}T + H_{v3}T^2). \end{aligned}$$

Consequently,

$$\begin{aligned} \frac{1}{RT} \int_{P_0}^P (\bar{v}_1 - \bar{v}_1^0) dP = & \frac{1}{6RT^2} \left\{ [6x(D_{v1} - D_{v3}T^2) + 12x^2(E_{v1} - E_{v3}T^2)](P - P_0) \right. \\ & + [3x(-F_{v1} + F_{v3}T^2) + 6x^2(-G_{v1} + G_{v3}T^2)](P^2 - P_0^2) \\ & \left. + x(-H_{v1} + H_{v3}T^2)(P^3 - P_0^3) \right\}. \end{aligned}$$

Thus, $\ln a_1$ at any vapor pressure may be determined. The numerical value of the last term in Equation (5-14) is very small in comparison with the value of $\ln a_1$ at 10 atmospheres. Table XXIV shows the calculated differences between $(\bar{h}_g - \bar{h}_1)$ and $(\bar{h}_g - \bar{h}_1^0)$ from 0 to 350°F. 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 (5-13), is the heat required for the phase transition of water in solution from liquid to vapor at constant temperature and composition.

TABLE XXIV

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	-1.63	-3.10	-4.52	-5.63
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

TABLE XXIV - Continued

Temp., °F	Salt Weight, gm/100 gm Solution					
	1	5	10	15	20	25
240	0.14	0.51	1.34	3.12	6.30	11.40
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	5.36	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	19.18
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

CHAPTER VI

SUMMARY AND CONCLUSION

An effort has been made to gather information on the thermodynamic properties of aqueous sodium chloride solution. It is hoped that this information may supplement the basic data for the desalination processes. Fortunately a sufficient amount of experimental data was found in the literature to support this study.

In Chapter II interpolation formulae for vapor pressure and for logarithm of activity of water were developed from osmotic coefficients. The activity of water may be derived from either vapor pressure or osmotic coefficient; however, the data on osmotic coefficient appear to be more precise than vapor pressure, particularly in the region of low salt concentration. In the early stage of this study, the data on vapor pressure were used to compute the activity. Consequently, the calculated values of specific heat did not agree very well with the experimental data. Some time ago Gastaldo (11) tried to calculate the relative partial molal enthalpy of sea water with the activities which were based on the vapor pressures by ordinary measurements. The results of his calculations also were very poor. Undoubtedly the vapor pressures reported in literature are generally not precise enough for the accurate determination of partial thermal properties. The data on osmotic coefficient, used in Chapter II, come from very precise measurements of boiling point, vapor pressure, or electromotive force (10, 14, 45, 46). Based

on the osmotic coefficients, the logarithms of activity of water have been calculated and fitted into an equation of nine constants, Equation (2-3). The variation of logarithms of activity with pressure was proved to be negligible for a pressure change of 10 atmospheres or less. Equation (2-7) is an interpolation formula for vapor pressures determined from osmotic coefficients. Of the many different equations for vapor pressure, the most popular one is perhaps the Antoine equation. This equation does not represent the vapor pressures of water as accurately as the Nernst equation, but it can be expressed explicitly in terms of temperature. Equation (2-11), from which the boiling temperature of solution can be readily calculated, is an adaptation of the Antoine equation that fits the vapor pressure of pure water.

The experimental data on specific heat are not only scarce but also slightly inconsistent, as shown in Figure 7. Therefore, in Chapter III the specific heat was determined from activity of water, solubility, specific heat of pure water and specific heat of solid salt by following the established rules of partial molal quantities. To make it easy for the calculation of enthalpy and entropy, the results were fitted by a simpler empirical formula, Equation (3-27), which gives the functional relation among the specific heat, temperature and concentration at 10 atmospheres. The pressure dependency of specific heat is discussed in Chapter IX.

In the middle portion of this study, an experimental program was initiated to determine an equation that accurately represents the pressure-volume-temperature-concentration data. For pure water, the data adopted by the Third International Conference on Steam Tables (48) cover the specific volumes of compressed water to 400 kg per sq cm; but for

the solution, the coverage of available data on density does not extend to the high pressure region (7, 51). Under this situation a decision was made to measure the pressure effect on the specific volume of solution in order to have sufficient data for the equation of state, and the experiment was carried out as described in Chapter IV. By means of a calibrated positive-displacement pump, the change of volume with the change of pressure at a fixed temperature was measured for solutions under pressures up to 5,000 psia in the range of 70 to 350°F and 0 to 25 grams salt per 100 grams solution. From the experimental data so obtained, the values of partial derivative of v with respect to P have been determined with probable error of about $\pm 4.5\%$ of the true value. Since the thermal properties of liquid are insensitive to the pressure change, the error of this magnitude will not cause serious consequences to the values of specific volume, enthalpy and entropy. The test results indicate that the larger the amount of salt added, the greater the lowering of the value of this derivative. To fit the experimental data regarding the specific volumes, Equation (4-13) was arbitrarily chosen as a general expression for the explicit representation of v . In this equation, the temperature functions $A(T)$, $B(T)$, $C(T)$, $D(T)$ and $E(T)$ were determined with the data from literature, and the remaining three temperature functions were obtained by curve-fitting the partial derivative of v with respect to P .

The enthalpy and entropy at 25°C and 1 atmosphere were calculated by taking the saturated water at 0°C and the salt in infinitely dilute solution at 25°C as the reference states for water and salt respectively. In these calculations the heat of dilution was based on the heat of formation by Rossini (38). Subsequently, the computations of enthalpy

and entropy were extended to other temperatures and pressures by taking advantage of the interpolation formulae, which have already been developed, for specific heat and specific volume. Finally, the heat of vaporization was computed, and the difference of this between solution and pure water is shown in Table XXIV.

In conclusion, this study has yielded practical equations for computing the thermal properties of aqueous sodium chloride solution in the 32 to 350°F temperature range, based on the data in hand. The method of determining the specific heat and the development of the P-v-T-x relation are noticeably unconventional.

If the pressure is not over 10 atmospheres, the pressure dependencies of specific volume, enthalpy and entropy may be neglected so that the computations become simple. A short list of Fortran arithmetic functions which may be called for the computations of vapor pressure, heat of vaporization, specific volume, enthalpy and entropy at a moderate pressure is shown in Appendix B. By adding a few terms to the arithmetic function, the pressure dependency of specific volume can be easily included. Simple expressions for the pressure effect on the values of enthalpy and entropy have not been developed; however, the estimate can be made by interpolating the values in Tables XXII and XXIII.

Because of the unknown reliabilities of the data in the literature and the complex nature of calculations, rigorous estimates of probable error have not been made for each property presented; nevertheless, an effort was made to compare the experimental data and the derived values from the various sources. Although the agreement between the specific heats calculated with the method in this study and the heat capacities

measured by calorimeters at temperatures below 80°C is gratifying, the degree of accuracy of the calculated values at higher temperatures is unknown due to the possible propagation of errors resulting from the mathematical manipulation of the empirical formulae. The recommendations of future work include the error analysis for each property and the direct measurements of specific heats in the high temperature region.

BIBLIOGRAPHY

- (1) Adams, L. H., and R. E. Hall. "Solubility of Sodium Chloride." Journal of the Washington Academy of Sciences, Vol. 21 (1931), p. 193.
- (2) Amagat, M. E. H. "Memoires sur l'elasticite et la dilatation des fluides." Annales de Chimie et de Physique (France), 6 series, Vol. 29 (1893), p. 545.
- (3) Badger, W. L., and E. M. Baker. "Studies in Evaporator Design." Transactions of American Institute of Chemical Engineers, Vol. 13 (1929), p. 151.
- (4) Baker, E. M., and V. H. Waite. "Boiling Point of Salt Solution Under Varying Pressures." Chemical and Metallurgical Engineering, Vol. 25 (1921), p. 1139.
- (5) Denbigh, K. The Principle of Chemical Equilibrium. London: Cambridge University Press, 1955, p. 218.
- (6) Dorsey, N. E. Properties of Ordinary Water-Substance. New York: Reinhold Publishing Corporation, 1940, p. 234.
- (7) Fabuss, B. M. Thermodynamic Properties of Saline Water. Progress Report 136, U. S. Office of Saline Water, 1965, pp. 30, 61.
- (8) Fabuss, B. M., and A. Korosi. "Vapor Pressure of Binary Aqueous Solutions of NaCl, KCl, Na₂SO₄ and MgSO₄ at Concentrations and Temperatures of Interest in Desalination Process." Desalination, Vol. 1 (1966), p. 139.
- (9) Freyer, E. B. "Sonic Studies of the Physical Properties of Liquid - The Velocity of Sound in Solutions of Certain Alkali Halides and Their Compressibilities." Journal of American Chemical Society, Vol. 53 (1931), p. 1313.
- (10) Gardner, E. R., P. J. Jones, and H. J. de Nordwall. "Osmotic Coefficients of Some Aqueous Sodium Chloride Solutions at High Temperature." Transactions of Faraday Society (London), Vol. 59 (1963), p. 1994.
- (11) Gastaldo, C. "Determination of Coefficients for Thermodynamic Equations for Determining the Properties of Sea Water, Particularly Vapor Pressure." University of California in Los Angeles, Report 61-80 (1962), p. 35.

- (12) Gucker, F. T., and T. R. Rubin. "The Apparent Molal Isochoric Heat Capacity of Electrolytes." Journal of American Chemical Society, Vol. 57 (1935), p. 78.
- (13) Guggenheim, E. Q. Thermodynamics: An Advanced Treatment for Chemists and Physicists. Amsterdam: North-Holland Publishing Company, 1957, p. 393.
- (14) Harned, H. S., and L. F. Nims. "The Thermodynamic Properties of Aqueous Sodium Chloride Solutions from 0 to 40°." Journal of American Chemical Society, Vol. 54 (1932), p. 423.
- (15) Hess, C. B., and B. E. Gramkee. "The Specific Heats of Some Aqueous Sodium and Potassium Chloride Solutions at Several Temperatures." Journal of Physical Chemistry, Vol. 44 (1940), p. 483.
- (16) Hirschler, A. E. "Vapor Pressures of Saturated Solutions." Journal of American Chemical Society, Vol. 38 (1946), p. 1.
- (17) Hubbard, J. C., and A. L. Loomis. "Velocity of Sound in Liquids by the Sonic Interferometer." Philosophical Magazine and Journal of Science (London), 7th Series, Vol. 5 (1928), p. 1177.
- (18) Jessup, R. S. "The Heat Content of Frozen Sodium and Calcium Brines." Refrigerating Engineering, Vol. 22 (1931), p. 166.
- (19) Kaufmann, D. W. Sodium Chloride. New York: Reinhold Publishing Corporation, 1960, p. 603.
- (20) Keenan, J. H., and F. G. Keyes. Thermodynamic Properties of Steam. New York: John Wiley and Sons Company, 1936, pp. 28-75.
- (21) Keevil, N. B. "Vapor Pressure of Aqueous Solutions at High Temperature." Journal of American Chemical Society, Vol. 64 (1942), p. 845.
- (22) Kell, G. S. "Precise Representation of Volume Properties of Water at One Atmosphere." Journal of Chemical and Engineering Data, Vol. 21 (1967), p. 66.
- (23) Kell, G. S., and E. Whalley. "The PVT Properties of Water I. Liquid Water in the Temperature Range 0 to 150°C and at Pressure up to 1 kb." Philosophical Transactions of the Royal Society (London), Series A, Vol. 258 (1965), p. 565.
- (24) Kelly, K. K. "Contributions to the Data on Theoretical Metallurgy." Bulletin 476, U. S. Bureau of Mines, 1949. p. 166.

- (25) Keyes, F. G. "Methods and Procedures Used in the Massachusetts Institute of Technology Program of Investigation of the Pressures and Volumes of Water to 460°C." Proceedings of American Academy of Arts and Sciences, Vol. 68 (1933), p. 505.
- (26) Keyes, F. G., L. B. Smith, and H. T. Gerry. "The Specific Volume of Steam in the Saturated and Superheated Condition Together with Derived Values of the Enthalpy, Entropy, Heat Capacity and Joule Thomson Coefficients." Proceedings of American Academy of Arts and Sciences, Vol. 70 (1936), p. 329.
- (27) Kusunoki, K. "Construction of Enthalpy-Concentration Diagram for NaCl-H₂O System." Kagaku Kogaku (Japan), V. 21 (1957), p. 775.
- (28) Landolt, H., and R. Börnstein. Physikalisch-Chemische Tabellen. Berlin: Julius Springer, 5 Auflage, 2 Band, 1923, pp. 1383, 1385.
- (29) Lipsett, S. G., F. M. G. Johnson, and O. Maas. "A New Type of Rotating Adiabatic Calorimeter - The Surface Energy and Heat of Solution of Sodium Chloride." Journal of American Chemical Society, Vol. 49 (1941), p. 1927.
- (30) McLean, D. Mechanical Properties of Metals. New York: John Wiley and Sons Company, 1962, p. 8.
- (31) M. W. Kellogg Company. Saline Water Conversion Engineering Data Book. U. S. Government Printing Office, 1965, pp. 12.20, 12.30.
- (32) Nernst, W. The New Heat Theorem. New York: E. P. Dutton and Company, 1917, p. 123.
- (33) Osborne, N. S., and C. H. Meyers. "A Formula and Tables for the Pressure of Saturated Water Vapor in the Range of 0 to 374°C." Journal of Research of the National Bureau of Standards, Vol. 13 (1934), p. 1.
- (34) Othmer, D. F. "Correlating Vapor Pressure and Latent Heat Data." Industrial and Engineering Chemistry, Vol. 32 (1940), p. 848.
- (35) Randall, M., and F. D. Rossini. "Heat Capacities in Aqueous Solution." Journal of American Chemical Society, Vol. 51 (1929), p. 323.
- (36) Robinson, R. A., and R. H. Stokes. Electrolyte Solutions. New York: Academic Press Inc., 1955, pp. 461, 465.
- (37) Robinson, R. A., and H. S. Harned. "Some Aspects of the Thermodynamics of Strong Electrolytes from Electromotive Force and Vapor Pressure Measurements." Chemical Review, Vol. 28 (1941), p. 419.

- (38) Rossini, F. D., et al. "Selected Values of Chemical Thermodynamic Properties." Circular 500, U. S. Bureau of Standards, 1952, p. 450.
- (39) Rutskov, A. P. "Specific Heats of Aqueous Solution of $MgCl_2$, $CaCl_2$, $NaCl$, KCl , KNO_3 , and NH_4NO_3 at 25°, 50°, and 75° C." Journal of Applied Chemistry (USSR), Vol. 21 (1948), p. 820.
- (40) Scatchard, G., W. J. Hamer, and S. E. Wood. "Isotonic Solutions I. The Chemical Potential of Water in Aqueous Solutions of Sodium Chloride, Potassium Chloride, Sulfuric Acid, Sucrose, Urea and Glycerol at 25°." Journal of American Chemical Society, Vol. 60 (1938), p. 3061.
- (41) Schroeder, W. C., A. Gabriel, and E. P. Partridge. "Solubility Equilibria of Sodium Sulfate at Temperature of 150 to 350°." Journal of American Chemical Society, Vol. 57 (1935), p. 1539.
- (42) Seidell, A. Solubilities of Inorganic and Organic Compounds. New York: D. Van Nostrand Company, 1919, p. 640.
- (43) Smith, L. B., and F. G. Keyes. "The Volumes of Unit Mass of Liquid Water and Their Correlation as a Function of Pressure and Temperature." Proceedings of American Academy of Arts and Sciences, Vol. 69 (1934), p. 285.
- (44) Smith, L. B., F. G. Keyes, and H. T. Gerry. "The Vapor Pressure of Water." Proceedings of the American Academy of Arts and Sciences, Vol. 69 (1934), p. 137.
- (45) Smith, R. P. "The Boiling Point Elevation II. Sodium Chloride 0.05 to 1.0M and 60 to 100°." Journal of American Chemical Society, Vol. 61 (1939), p. 500.
- (46) Smith, R. P., and D. S. Hirtle. "The Boiling Point Elevation III. Sodium Chloride 1.0 to 4.0M and 60 to 100°." Journal of American Chemical Society, Vol. 61 (1939), p. 1123.
- (47) Tait, P. G. Properties of Matter. London: Adam and Charles Black Company, 1907, p. 200.
- (48) "The Third International Conference on Steam Tables." Mechanical Engineering, Vol. 57 (1935), p. 710.
- (49) Thomson, G. W. "The Antoine Equation for Vapor-Pressure Data." Chemical Reviews, Vol. 38 (1946), p. 1.
- (50) Washburn, E. W. International Critical Tables of Numerical Data, Physics, Chemistry and Technology. Vol. 2. New York: McGraw-Hill Book Company, 1928, p. 328.

- (51) Washburn, E. W. International Critical Tables of Numerical Data, Physics, Chemistry and Technology. Vol. 3. New York: McGraw-Hill Book Company, 1928, pp. 79, 105, 370.
- (52) Washburn, E. W. International Critical Tables of Numerical Data, Physics, Chemistry and Technology. Vol. 5. New York: McGraw-Hill Book Company, 1928, p. 115.
- (53) Wood, A. B. A Textbook of Sound. New York: Macmillan Company, 1955, pp. 261, 279.

APPENDIX A

LIST OF SYMBOLS

This list does not include symbols used only at a single point. Occasionally, it is necessary to use the same symbol for different quantities. For example, the principal use of G is to represent Gibbs free energy, but it is also used to represent an empirical parameter in some cases. To avoid confusion, all special uses of symbols are described carefully wherever they occur.

A, a, B, b, C, c . . .	Empirical parameters
a	Activity
c	Specific heat, usually with a subscript to indicate conditions
f	Fugacity
G, g	Gibbs free energy
H, h	Enthalpy
k	Compressibility
M	Mass; or molecular weight
m	Molality, moles salt per 1,000 grams solvent
n	Number of moles
P	Total normal pressure
p	Vapor pressure
q	Heat
R	Gas constant

S, s	Entropy
T	Absolute temperature (Kelvin or Rankine scale)
t	Temperature (centigrade or Fahrenheit scale)
V, v	Volume
x	Mole fraction; or weight fraction of salt
Y, y	Any extensive property
ϕ	Osmotic coefficient
-	Placed above a letter to denote partial molal quantity
Subscripts, superscripts	Used to designate conditions, states, or components.

APPENDIX B

FORTRAN ARITHMETIC FUNCTIONS FOR VAPOR PRESSURE, HEAT OF VAPORIZATION, SPECIFIC VOLUME, ENTHALPY AND ENTROPY

Since the liquid solution is only slightly compressible, the difference in thermal properties between a solution at its vapor pressure and a compressed solution at the same temperature is negligible if the pressure is only 100 psi or so higher than the vapor pressure. A correction of this order of magnitude is not warranted by the accuracy of the experimental data. In such a case the following arithmetic functions may be inserted in a Fortran program to compute vapor pressure, heat of vaporization, specific volume, enthalpy and entropy at a given temperature and salt concentration when they are called for.

FORTRAN ARITHMETIC FUNCTIONS

```

C      T=TEMP. IN DEG. K., TF=TEMP. IN DEG. F., XN=MOLE FRACTION, XW=WT.
C      FRACTION, P(T,XW)=VAPOR PRESSURE IN PSIA, HV(TF,XW)=HEAT OF
C      VAPORIZATION IN BTU PER LB., H(T,XW,XN)=ENTHALPY IN BTU PER LB.,
C      S(T,XW,XN)=ENTROPY IN BTU PER LB. PER DEG. F.,V(T,XW)=SPECIFIC
C      VOLUME IN CU. FT. PER LB.
      T=(TF-32.)/1.8+273.16
      XN=XW/(3.244227-2.244227*XW)
      P(T,XN)=14.2233*(EXP(.1E 1-.33204655E-01*XN+.13635246E 0*XN**
11.5)*(.11806432E 2-.38845791E 4/(T-.43107355E 2))+XN*(-.1920361
2E 1+.32750375E 1*XN**0.5-.19866438E 2*XN))
      HV(TF,XW)=.10933254E 4+TF*(-.57909483E 0+TF*(.228937E-03-TF*
1.11130559E-05))+XW*(-.73209467E 0+TF*(.52189427E-01-24795274E-04*
2TF)+XW*(-.24016695E 3+TF*(.73929343E 0+.40422239E-03*TF)+XW*(
3.44575257E 3+TF*(.14413009E 1-.12079358E-02*TF))))
      F1(XN)=.13165380E 1+(-0.88752969E 1+.23071563E 2*XN)*XN
      F2(XN)=-0.20328368E-02+(.36271641E-01-0.62166018E-01*XN)*XN
      F3(XN)=.32218320E-05+(-0.61529387E-04+.10557110E-03*XN)*XN
      H(T,XW,XN)=(25.015*(1.-XW)-30.805561*XW**1.5+161.50632*XW*XW-
179.059598*XW**2.5-114.83149*XW**3+(F1(XN)*(T-298.16)+0.5*F2(XN)*(
2T*T-.88899384E 5)+F3(XN)*(T**3-.26506240E 8)/3.))*1.8
      S(T,XW,XN)=.0876+XW*(.67594387E-01-(.12767431E 1)*XW+.17277596E
11*XW*XW)+F1(XN)*(ALOG(T)-.56976303E 1)+F2(XN)*(T-289.16)+F3(XN)*
2.5*(T*T-.88899384E 5)
      V(T,XW)=(0.59163651E 1+(-0.10357941E-01+0.92700483E-05*T)*T+(
1-.11275221E 4+.10067411E 6/T)/T+XW*(-.25734754E 1+(.11535660E-0
21-.17617526E-04*T)*T+XW*(.31262732E 1+(-.17185204E-01+.25147256E-
304*T)*T))*1.6018490E-01

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VITA

James Chia-San Chou

Candidate for the Degree of

Doctor of Philosophy

Thesis: THERMODYNAMIC PROPERTIES OF AQUEOUS SODIUM CHLORIDE SOLUTIONS
FROM 32 TO 350°F

Major Field: Mechanical Engineering

Biographical:

Personal Data: Born in Kiangsu, China on January 13, 1920, the son of Chen Yi and Yang Tze Chou; married to Lillian Tom on March 3, 1948, father of Gregory K. and Thomas Q. Chou; naturalized on Maui, Hawaii, December 5, 1956.

Education: Graduated from National Institute of Technology (China) in 1941 with a Bachelor of Science degree; received the Master of Science degree in Mechanical Engineering from Georgia Institute of Technology in 1949; completed the requirements for the Doctor of Philosophy degree at Oklahoma State University in July, 1968.

Professional Experience: Employed by Twenty-first Arsenal of National China as an assistant engineer from 1941 to 1943; served in Chinese Air Force as a maintenance engineering officer from 1943 to 1947; employed by Experimental Station of Georgia Institute of Technology as a research assistant in 1950; worked as a design engineer from 1951 to 1959 for Hawaiian Commercial and Sugar Company, Daniel, Mann, Johnson and Mendenhall Company, Honolulu Iron Works Company, Topaides Inc., and Zuckerman and Chou with responsibilities in the design of steam power plant and processing equipment; taught various undergraduate courses in mechanical engineering as a full-time member of the University of Hawaii faculty from 1960 to 1966.

Professional Organizations: Member of American Society of Mechanical Engineers, American Society of Professional Engineers and American Society for Engineering Education.