

taken from the extremes of the binodal data, which seemed to be more accurate than the data obtained by the analytical method as used previously.

Eastman's best grade of isopropanol was used after it was refluxed and distilled with anhydrous calcium oxide and anhydrous potassium fluoride. It then had d_{20}^{20} 0.7894. However, the small amount of water originally present did not seem to have an important influence on the experimental results, judging from the results obtained by using the isopropanol both before and after dehydration. The authors feel that the error in binodal data does not exceed 1.0% in any case and is usually less than 0.5%.

Summary

Tabular data are given for the ternary systems of water and isopropanol with ten inorganic salts at 25°. Isopropanol is compared with the other water-miscible, saturated aliphatic alcohols. Potassium carbonate and potassium fluoride are the most effective of the ten salts investigated. The rate of decrease of the weight per cent. of isopropanol with respect to the weight per cent. of salt in a liquid phase seems to be a direct function of the weight per cent. of the isopropanol. Values for the numerical constants in the empirical equation are given for ten different systems.

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EQUILIBRIUM IN BINARY SYSTEMS UNDER PRESSURE. I. AN EXPERIMENTAL AND THERMODYNAMIC INVESTIGATION OF THE SYSTEM, NaCl-H₂O, AT 25°

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RECEIVED JULY 13, 1931

PUBLISHED OCTOBER 5, 1931

Introduction

Nature of the Problem.—Very little is known concerning the effect of high pressure on systems containing more than a single component. Despite the scant attention this subject has received, it does not lack interest or importance, for, in a complete investigation of the stability of the various phases in a system, pressure is a factor coordinate with temperature, and its consideration over an extended range is equally desirable. Doubtless the scarcity of data in this field is due to the relative slowness in the development of the necessary technique. Materials under pressure, being difficult to observe directly, require special devices for the study of their behavior; moreover, there are certain complications connected with the production and measurement of very high pressures.

It has now been found possible to study a binary system under high pres-

sure and to work out in detail the conditions of equilibrium between the various phases at pressures considerably above 10,000 bars (metric atmospheres). The system chosen was NaCl-H₂O, because it was important to know accurately some of the properties of the components and of the solutions at atmospheric pressure, and for this system the necessary data were already available.

In attacking a new type of problem it is advisable to simplify it as much as possible. Accordingly the present investigation will be confined to a single temperature, 25°, and the specific problem will be the determination of the changes in the state of the system for variations in pressure (P) and concentration (x) at a fixed temperature (t). In a two-component system under pressure¹ there may exist one, two or three phases. At constant temperature, therefore, the system will accordingly be divariant, monovariant or invariant. The first case involves the volumes of the phases; the second, the various freezing point-solubility curves; and the third, the congruent and incongruent melting points and pressure eutectics analogous to ordinary eutectics in a (T, x) diagram. In a comprehensive study of a system consideration should be given to each of these types of equilibrium. This may seem obvious when temperature is one of the variables, but for systems under pressure the particular spots on which to focus our attention are not self-evident, because we are unfamiliar with even the qualitative aspects of the equilibrium relations.

Available Methods of Attack.—For the investigation of the conditions of equilibrium between phases in systems under pressure, there are two principal classes of methods, the direct and the indirect. In the methods of the first and more familiar class a freezing point or other transformation is observed by measuring some change that is associated with the transformation. Hence there are a number of possible procedures, each with its counterpart in the determination of the effect of temperature upon phase relations. For example, equilibrium may be allowed to take place at a particular pressure, and a sample of one phase (*e. g.*, solution) drawn off and analyzed;² or, for solutions of electrolytes, the solubility may be determined by measuring (*in situ*) the electrical conductivity of the saturated solution.³ Perhaps the simplest method in this category consists in noting the volume-change during the change of phase, as has been done by Bridgman⁴ and others for one-component systems. When there is more

¹ We are here neglecting the case of very low pressure and considering the system under a pressure always greater than the vapor pressure of any phase (so-called condensed system).

² This method was used by Cohen and Sinnige [*Z. physik. Chem.*, **67**, 432 (1909)] and by Sill [THIS JOURNAL, **38**, 2632 (1916)] for measuring the solubility of salts in water at pressures up to about 1000 bars.

³ Adams and Hall, *J. Wash. Acad. Sci.*, **21**, 183-194 (1931).

⁴ See, for example, Bridgman, *Proc. Am. Acad. Arts Sci.*, **47**, 415 (1911).

than one component this procedure is less advantageous, but it has been used for a few measurements on the two-component system now under consideration.

Indirect methods are available for the determination of freezing pressures as well as freezing temperatures. It is well known that the temperature of a transformation may be determined without causing the transformation actually to take place; if the phases that are concerned in the transformation have been identified, it is possible to calculate freezing point or solubility curves from calorimetric measurements. Such calculations involve the entropy of the various phases, the third law of thermodynamics enabling us to assign an absolute value to the entropy. Similarly, for a system under pressure, the solubility and freezing point curves may be determined from known values of the volumes of the phases when under pressure. The *thermal* indirect method, although a powerful tool, is often not especially advantageous, because the transformation temperature usually can be measured directly with satisfactory accuracy. On the other hand, for the study of systems *under pressure*, the indirect method is probably more generally useful than any other. Volumes and volume changes can be measured with a high degree of precision, and from a knowledge of the volumes the equilibrium curves can be calculated with greater ease and higher accuracy than they can be determined directly. In the present work both the direct and the indirect methods have been employed, but much more use has been made of the indirect, or thermodynamic, method.

NOMENCLATURE

- t , Centigrade temperature
- T , absolute temperature
- P , pressure in general
- p , vapor pressure
- m , molality (moles per 1000 g. of solvent)
- m_1 , mass of component 1 (water)
- M_1 , formula weight of component 1
- N_1 , number of moles of component 1, m_1/M_1
- x_1 , weight fraction of component 1
- X_1 , mole fraction of component 1
- x_0 , weight fraction of anhydrous salt in a salt hydrate
- X_0 , mole fraction of anhydrous salt in a salt hydrate
- $\phi \equiv (x_0 - x_2)/(1 - x_2)$ (for a salt hydrate, x_2 denoting the concentration of the saturated solution)
- V , total volume
- v , specific volume (volume per gram)
- \bar{v}_1 , fictive, or partial, volume of component 1, $(\partial V/\partial m_1)_{t, P, m}$
- k , compression, relative volume decrease under pressure, $(V_0 - V)/V_0$
- β , compressibility (*i. e.*, relative compressibility, $\partial k/\partial P$)
- β' , specific compressibility, $-\partial v/\partial P$
- $\bar{\beta}'_1$, fictive compressibility, $-\partial \bar{v}_1/\partial P$, of component 1

F , free energy (Gibbs' ζ)

\bar{F}_1 , partial molal free energy of component 1, $\partial F/\partial N_1$

μ_1 , chemical potential of component 1, $\partial F/\partial m_1 (= \bar{F}_1/M_1)$

H , enthalpy (heat content)

\bar{H}_1 , fictive enthalpy (partial heat content) of component 1, $\partial H/\partial m_1$

Subscript zero refers to atmospheric pressure.

Subscript i refers to the pressure at which $\text{NaCl}\cdot 2\text{H}_2\text{O}$ inverts to NaCl and solution.

Subscripts w, s, d, g, m, l, Fe , refer, respectively, to H_2O , NaCl , $\text{NaCl}\cdot 2\text{H}_2\text{O}$, glass, Hg, pressure fluid and iron.

Superscript prime refers to the "initial" pressure in the high-pressure measurements (usually 2000 bars), except in equation (44) where the primes and double primes refer to two different phases in equilibrium.

$\Delta_x \bar{v}_1 \equiv \bar{v}_1 - (\bar{v}_1)_w$ (constant pressure)

$\Delta_P \bar{v}_1 \equiv \bar{v}_1 - (\bar{v}_1)_0$ (constant concentration)

$\Delta_x \mu_1 \equiv \mu_1 - (\mu_1)_w$

$\Delta_x \mu_2 \equiv \mu_2 - (\mu_2)_s$

Subscript x or P may be omitted when there is no danger of ambiguity.

Principle of the Thermodynamic Method.—In a one-component system the best criterion of equilibrium involves the free energy, F , which is defined by the equation, $F = E + PV - TS$, the symbols, in order, denoting the energy, pressure, volume, temperature and entropy. Moreover, in a multi-component system the stability of the various phases depends upon the closely related chemical potential,⁵ which for component n is denoted by the symbol μ_n and is equal to $(\partial F/\partial m_n)_{P, T, m}$, m_n being the mass of component n , and the subscript m indicating that the masses of all the other components are held constant. At a fixed temperature and pressure the necessary and sufficient condition for equilibrium is that for any actual component its μ shall have the same value in all of the phases.

The change of F under pressure, at constant temperature (and for any homogeneous material of constant composition), depends solely on the volume. Thus

$$\left(\frac{\partial F}{\partial P}\right)_{t, m} = V \quad (1)$$

In general, that is, for systems of more than one component, it is necessary to deal with μ rather than F . We must then write

$$\left(\frac{\partial \mu_n}{\partial P}\right)_{t, m} = \bar{v}_n \quad (2)$$

The change of μ_n under pressure thus depends on \bar{v}_n , which is called the partial or fictive volume of component n and is defined by the equation, $\bar{v}_n = (\partial V/\partial m_n)_{P, t, m}$. Since (1) the fictive volumes in any phase can be readily calculated from the densities (or from the specific volumes) over

⁵ (a) Gibbs, "Scientific Papers," New York, 1906, Vol. I, pp. 65, 87. If the unit of mass is the mole, then μ is the partial molal free energy (see (b) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," New York, 1923, p. 203).

a range of concentration, and since (2) the \bar{v} 's determine the μ 's, and (3) the μ 's, the conditions under which the various phases are stable, it is evident that a knowledge of the volumes under pressure is sufficient to enable us to construct an equilibrium diagram for a system subjected to a specified pressure—provided that the identity of the phases concerned in the equilibrium, and their stability relations at atmospheric pressure or some other pressure, are already known.⁶ Equation 2, together with the principle of the equality of the μ 's at equilibrium, forms the basis of the indirect method; the equilibrium in a system under pressure is determined by measuring only the volume change, under pressure, of each of the phases involved, and thence calculating the variations in the several potentials.

The "Compression."—Attention is directed to the fact that it is the total change in volume under pressure, and not the compressibility, that is the starting point in the application of the thermodynamic method. Moreover, volume changes are directly measured but compressibility is a derived quantity. In practice the relative volume change, a quantity proportional to the total change, is more frequently used. This is the total volume change divided by the initial volume, and is of sufficient importance to justify receiving a shorter name. It will here be called the *compression*. It is denoted by the letter k and is defined as follows

$$k = -\frac{\Delta V}{V_0} = \frac{V_0 - V}{V_0} \quad (3)$$

V_0 being the total volume of a given amount of material at atmospheric pressure and V the total volume at any other pressure. The term compression, or bulk compression, has been used heretofore⁷ with the same significance, but does not seem to be very well known. It is not uncommon to speak of the compressibility (*e. g.*, of liquids) when it is the compression that is meant; and there is a considerable advantage in having a word for each of these ideas. The use of "compression" in the specific sense will probably not seriously conflict with its more general meaning (the act of compressing).

The Change of Volume of Sodium Chloride Solutions under Pressure

Low-Pressure Experiments.—The method used for measuring the volume change at high pressures does not give good results at pressures below 1000 bars. It was necessary, therefore, to make a separate series of measurements for all of the solutions at low pressures. This was done with a piezometer illustrated in Fig. 1. It consists of a bulb of Pyrex glass, which has at the top a ground-glass stopper surrounded by a mercury seal, and at the bottom a re-entrant capillary tube drawn down at the upper end

⁶ In this connection, see R. W. Goranson, "Thermodynamic Relations in Multi-component Systems," Carnegie Inst. Wash., Publ. No. 408, 153-161 (1930).

⁷ Parsons and Cook, *Proc. Roy. Soc. (London)*, 85, 332-348 (1911).

to a tip, which is bent at right angles to the main part of the tube. The bulb is inserted in a thin-walled cylindrical capsule of stainless steel, containing 1 to 3 cc. of mercury. Before being used, the Pyrex bulb was carefully annealed by heating to 550° in an electric furnace, holding at that temperature for fifteen minutes and then dropping the temperature at the rate of about 1° per minute for the first twenty minutes and then as rapidly as the furnace would cool.

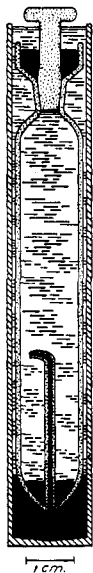


Fig. 1.—Piezometer used for measuring the volume change of the solutions at low pressures. The compression of the solution is determined by the amount of mercury trapped in the glass bulb. The piezometer may also be used at high pressures.

The piezometer was subjected to pressure in an apparatus in which pressure was measured with an accuracy of 1 bar. Temperature was maintained constant to about 0.1° . Under pressure the liquid within the bulb contracts, whereupon mercury flows up the central tube and drops off the tip, collecting at the bottom. When the pressure is released, the solution increases in volume, and flows out through the tube, leaving the mercury trapped in the bottom. The weight of mercury is then a measure of the amount of the compression (relative volume change) of the solution at the highest pressure to which it was subjected. Correction must be made for the volume change of the Pyrex glass and of the mercury, under pressure, and also for the volume of the capillary stem, because the mercury which it holds at the maximum pressure is subsequently forced out by the solution and does not remain in the bulb. The "back-lash" provided by the central tube is an advantage rather than a disadvantage. Without this feature the piezometer would measure the volume change corresponding to the sum of all the arithmetical *increases* of pressure, so that if the pressure drops momentarily (owing to equalization of temperature or for any other reason) and then is raised again an incorrect result would be obtained. In the present piezometer a temporary drop in pressure does no harm unless the drop is more than sufficient to drive out all the mercury that was in the central tube. For the piezometer shown in Fig. 1 this permissible fall in pressure is of the order of 100 bars for aqueous solutions at low pressures.

It may also be noted that it is not necessary that the bulb be filled with solution at the temperature of the thermostat. If the solution, when introduced, is at any temperature below that of the thermostat, then when the piezometer is placed in the pressure apparatus the solution expands as the temperature approaches equilibrium, and the surplus amount remains in the steel capsule (since the liquid for transmitting pressure is lighter than any of the solutions).

The procedure for measuring the compression of the solutions at low pressures was as follows. Solutions of 5, 10, 15, 20 and 25% by weight were made up from sodium chloride that had been recrystallized once from aqueous solution by precipitation with hydrochloric acid. The bulb was filled with one of the solutions, special care being taken that the central stem was completely filled and that there were no air bubbles anywhere in the bulb. It was wiped dry on the outside, the stopper lightly greased with stopcock grease and inserted in the top, and the cup around the stopper filled with mercury. The bulb was then placed in the capsule, and the capsule in the pressure apparatus. About fifteen minutes was allowed for the equalization of temperature, and pressure was applied slowly until it was within 20 bars of the desired pressure. After an interval of ten minutes for dissipating the heat produced in compressing the liquid the pressure was increased to the maximum desired, released slowly and the bulb taken out, after which the mercury was removed from the bulb, dried and weighed. The volume change of the solution was calculated by the formula

$$k = \frac{(V_m)_0(1 - k_m) + (V_t)_0(1 - k_g)}{V_0} + k_g \quad (4)$$

where k denotes the compression, or fractional volume change of the solution at the given pressure, k_m and k_g denote, respectively, the values of the compression for mercury and glass at the same pressure, V_0 , $(V_m)_0$, and $(V_t)_0$ denote, respectively, the volume of the liquid (that is, the total inside volume of bulb and stem), the volume of the mercury remaining in the bulb, and the inside volume of the central stem, the subscript zero referring to atmospheric pressure. This equation follows directly from a mathematical expression of the fact that at any pressure the total volume is equal to the sum of the various parts. (The necessary values of k_m and k_g will be found in Table II.)

The volume of the bulb was about 8.5 cc., and the diameter of the hole at the tip of the central tube was about 0.5 mm. Hence the volume of the individual drops of mercury that fell off the tip was approximately 0.1 cu. mm. This corresponds to an error of 0.00001 in the compression or about 1 part in 3000 of the compression of the solutions at 1000 bars. On the other hand, the accuracy of the pressure measurement was 1 part in 1000 at 1000 bars. Discrepancies, however, amounting to several parts in 1000, were occasionally observed, probably because at first not enough attention was paid to the necessity of filling the bulb with solution at or below the temperature of the thermostat.

In Table I are shown the results at 500 and 1000 bars. For each of the five solutions, and also for water, the table gives the value of k , that is, the fractional decrease in volume ($-\Delta V/V_0$) for the given solution at the

given pressure. Each result is the mean of several measurements which showed an average discrepancy of 3 or 4 units in the fifth place after the decimal point. The table also shows: (1) the values of $(\partial k/\partial x_2)_P$, that is, the change of k with respect to concentration, x_2 , expressed in weight fraction of sodium chloride; and (2) other data, which will be explained in a later section.

TABLE I

RESULTS AT LOW PRESSURES FOR VOLUME CHANGE OF SODIUM CHLORIDE SOLUTIONS. TEMPERATURE, 25°

The compression, $(V_0 - V)/V_0$, is denoted by k ; the weight fraction of NaCl by x_2 ; and the "partial" or "fictive" volumes of H₂O and of NaCl by \bar{v}_1 and \bar{v}_2 , respectively. The subscript zero refers to atmospheric pressure.

$P = 500$ bars

x_2	0	0.05	0.10	0.15	0.20	0.25
k	0.0212 ₀	0.0192 ₂	0.0175 ₈	0.0161 ₀	0.0146 ₇	0.0132 ₇
$-\partial k/\partial x_2$.0424	.0354	.0314	.0293	.0282	.0277
$\bar{v}_1 - (\bar{v}_1)_0$	-.0213	-.0210	-.0205	-.0201	-.0195	-.0190
$\bar{v}_2 - (\bar{v}_2)_0$.0364	.0263	.0202	.0165	.0140	.0122

$P = 1000$ bars

x_2	0	0.05	0.10	0.15	0.20	0.25
k	0.0393 ₀	0.0361 ₃	0.0331 ₄	0.0303 ₆	0.0277 ₂	0.0251 ₄
$-\partial k/\partial x_2$.0654	.0614	.0579	.0549	.0528	.0510
$\bar{v}_1 - (\bar{v}_1)_0$	-.0394	-.0391	-.0385	-.0378	-.0370	-.0360
$\bar{v}_2 - (\bar{v}_2)_0$.0549	.0439	.0358	.0305	.0267	.0235

High-Pressure Experiments (a) Apparatus and Method.—At pressures above 1000 bars the measurements on the volume change of the solutions were made by the now well-known piston-displacement method. This method has been employed extensively by Bridgman⁸ mainly for obtaining the compressibilities of liquids. At this Laboratory it has been used in determining the cubic compressibility of a large number of solids and has proved to be convenient for this purpose, as well as capable of high precision. The piston-displacement method apparently was first used over twenty years ago, by Cowper and Tammann.⁹ In an improved form it was employed by Parsons and Cook,⁷ who measured the compression of several liquids at pressures up to 6000 bars, and introduced the now common procedure of eliminating the correction for extraneous volume changes by making a second series of measurements in which a block of steel replaced part of the liquid. The piezometer described above may also be used at high pressures, but it was found that the piston-displacement method, while yielding results of about the same accuracy as the piezometer, was much more rapid, since a series of measurements at ten or twelve different pres-

⁸ Bridgman, *Proc. Am. Acad. Arts Sci.*, **49**, 1-114 (1913).

⁹ Cowper and Tammann, *Z. physik. Chem.*, **68**, 281-288 (1909).

tures could be made within a period of time no more than twice that required for a single measurement with the piezometer.

For some reason not yet explained it does not seem possible to obtain with solutions quite as much accuracy as the previous experience with the comparatively incompressible solids would have led one to expect. This may be due to the fact that in the case of solutions much larger piston-displacements are involved, and that there will consequently be much more opportunity for irregularities of various kinds. The accuracy obtained was, however, satisfactory for the present purpose—the irregularities in the volume changes of the solutions at a pressure of 10,000 bars are not greater than 1 part in 1000, and the *variation* of this volume change with concentration is now known with an accuracy corresponding to an uncertainty considerably less than 1 part in 1000 of the volume change of any single solution at 10,000 bars.

The apparatus in the form used for solutions is illustrated in Fig. 2. A thick-walled cylinder, or "bomb," of vanadium steel is filled with *n*-butyl ether, in which hydrostatic pressure is developed by means of a piston and special packing, which is forced into the bomb by means of a hydraulic press. The whole pressure apparatus is enclosed in a simple air thermostat, the temperature in which is held constant to within a few hundredths of a degree. Immersed in the liquid is a thin-walled capsule of "stainless steel," which is made a loose fit for the hole in the bomb. A cylindrical bulb of Pyrex glass contains the solution under investigation. The bulb is drawn down at one end so that the opening is about 2 mm. in diameter and this end dips into mercury contained in the bottom of the capsule, in order to prevent the solution from coming in contact with the pressure medium. From the amount of movement of the piston the volume change of the material may be determined. The total motion may be 35 mm., or more, over the pressure range 1–12,000 bars, but only a part of it (one-half or less) is due to the compression of the sample. The remainder is caused by the compression of the pressure fluid and other materials within the bomb and by the increase in internal volume of the bomb under pressure. In order to eliminate these latter effects, it is necessary to make a separate series of measure-

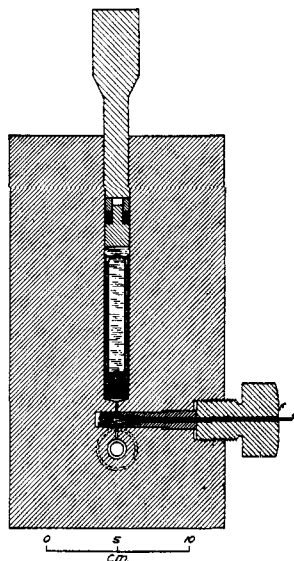


Fig. 2.—Apparatus for determining the volume change under high pressures by the piston-displacement method. The liquid under investigation is prevented from coming in contact with the pressure fluid by being placed in a glass bulb the open end of which dips into mercury.

ments in which the material under investigation is replaced by an equal volume of a substance of known compressibility.¹⁰

Pressure was measured with a resistance gage consisting of a small coil of Therlo wire, 100 ohms in resistance, immersed in the pressure fluid and connected to an arrangement for measuring the resistance, through a pressure-tight electrically insulated fitting shown in detail in Fig. 3. The present arrangement of the insulating material is considerably better than the one used previously; a single packing-plug has successfully withstood over 200 applications of high pressure and is still in good working order. The change in resistance (about 2 ohms at 10,000 bars) was measured with an accuracy such that 1 division on the scale corresponded to about 1 bar, which was ample accuracy, since the movement of the piston, as determined by a dial micrometer, was read to 1 micron, and the pressure change caused by a piston-displacement of 1 micron was, for measurements with solutions, of the order of 1 bar except at low pressures.

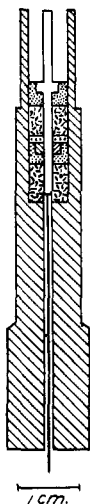


Fig. 3.—Detailed arrangement of packing of insulated lead for the electrical pressure gage shown in Fig. 2. The insulated material around the central steel stem consists of (starting at the bottom): limestone, 6 mm.; talc, 3 mm.; rubber, 1 mm.; limestone, 5 mm.; and talc, 3 mm.

In order to fix the scale of the electrical pressure gage it was (1) compared at 1500 bars with an absolute gage of the free-piston type, and (2) calibrated at one or more higher pressures by observing the freezing pressures of suitable materials. At first mercury (freezing at 11,370 bars at 20° according to Bridgman)¹¹ was used, but later water, being somewhat more convenient to work with, was used for the calibration point. About 10 cc. of distilled water was placed in a glass bulb similar to that shown in Fig. 2, and pressure applied until freezing began—usually about 1500 bars in excess of the equilibrium freezing pressure is required to start the freezing—after which the pressure was lowered to the approximate expected freezing pressure. Upon being allowed to stand undisturbed for about one-half hour, the pressure attained the equilibrium value, which could be duplicated to within 2 or 3 bars. On the assumption that the freezing pressure of mercury at 20° is 11,370 bars, the freezing pressure of water at 25° had been found by a separate series of measurements to be 9630 bars, which is about 25 bars higher than the value obtained by

¹⁰ For further details see Bridgman, *Proc. Am. Acad. Arts Sci.*, **48**, 324 (1912); Adams, Williamson, and Johnston, *THIS JOURNAL*, **41**, 1 (1919); Adams and Gibson, *Proc. Nat. Acad. Sci.*, **12**, 275 (1926); **15**, 713 (1929).

¹¹ Bridgman, *Proc. Am. Acad. Arts Sci.*, **47**, 432 (1912).

Bridgman¹² for the pressure under which water at 25° solidifies to ice_{V_I}; but it may be noted that his results at about this temperature show individual variations considerably greater than the above-mentioned difference.

For Therlo wire the relation between resistance and pressure appears to be not quite linear, but the pressure scale is fixed almost entirely by the high pressure point. If subsequently the freezing pressure of water at 25° should be found to differ appreciably from 9630 bars, the results obtained in the present investigation at pressures above 1500 bars could then be corrected accordingly.

A complete set of readings (in the high-pressure experiments) for a given solution consisted of (1) a series of readings of pressure and of piston displacement at the even 1000's of bars from the highest pressure down to 1000 bars and an additional reading at 1500 bars, and (2) a similar series of measurements with the reference substance in place of the solution. Before the first (highest pressure) reading the pressure was raised 500 bars above the desired pressure and then lowered. It was very important that in the two series the *maximum pressure be exactly the same*, for otherwise large errors due to the hysteresis in the non-uniformly stressed bomb will arise. In the early part of this investigation a great many useless measurements were made before the full importance of this was appreciated.

Readings usually were taken on a definite time schedule; the time between readings at the even 1000's of bars was eight minutes, of which three minutes was required for lowering the pressure and adjusting it to the desired value, four minutes for the completion (to a sufficient degree) of thermal equilibrium within the bomb, and one minute for taking the readings.

On account of the freezing of the water, measurements with it were not made at pressures higher than 10,000 bars; even here it is super-pressed by about 400 bars, and before the first reading was taken it withstood always an additional 500 bars pressure. Although in the measurements of its volume change water has been taken this 800 bars above its freezing pressure some twenty times, only once did it freeze under this amount of super-pressing. With the 5, 10 and 15% sodium chloride solutions measurements were made up to 11,000 bars and with the 20 and 25% solutions at 12,000 bars.

The volume changes at the various pressures were calculated by means of the equation

$$k - k' = \frac{S}{V_0} \left[\Delta L(1 + \alpha P) + \Delta l'_0 \alpha (P - P') + (\Delta l'_0 + \Delta \lambda') \frac{k_i - k'_i}{1 - k'_i} \right] + (k_r - k') \frac{(V_r)_0}{V_0} \quad (5)$$

¹² Bridgman, *Proc. Am. Acad. Arts Sci.*, **47**, 518, 521 (1912).

in which k denotes the compression ($-\Delta V/V_0$) at the pressure P ; V , the volume of the sample; S , the cross-sectional area of the hole in the bomb; ΔL , the difference, at the pressure P , reckoned from the initial pressure P' , in the travel of the piston in the two series of measurements; $\Delta l'$, the difference at P' in the absolute position of the piston in the two series; α , the change per bar in the cross-section of the hole (here taken as 1.2×10^{-6}); k_l and k'_l , respectively, the values at P and P' of k of the liquid used for transmitting pressure; k_r , the compression of the reference material at the pressure P , and in which $\Delta \lambda'$ equals $(V' - V'_r)/S$, V' and V'_r denoting, respectively, the volumes of the material under investigation and of the reference substance at P' . The subscript zeros refer to atmospheric pressure and the primes to the "initial" pressure (usually 2000 bars).

For convenience and future reference there are collected in Table II the values of k for several substances, which either are used repeatedly in the determination of the volume change of the solutions at high or low pressures, or are to be referred to in a later section of this paper. The results for water were obtained in the course of the present investigation; those for sodium chloride,¹³ Bessemer steel,¹⁴ Pyrex glass,¹⁵ mercury,¹¹ and *n*-butyl ether,¹⁵ came from the sources indicated.

TABLE II

THE COMPRESSION, k , AT 25°, FOR VARIOUS MATERIALS USED IN CONNECTION WITH THE PRESENT SERIES OF MEASUREMENTS (SEE TEXT FOR REFERENCES)

Pressure in bars	Fractional decrease in volume, k ($= -\Delta V/V_0$)					
	Water	Sodium chloride	Bessemer steel	Pyrex glass	Mercury	<i>n</i> -Butyl ether
1	0.0000	0.00000	0.00000	0.00000	0.00000	0.0000
500	.0212	.00205	.00030	.00151	.00201	.0439
1000	.0393	.00409	.00060	.00303	.00399	.0747
1500	.0555	.00611	.00090	.00456	.00594	.0964
2000	.0699	.00812	.00119	.00608	.00786	.1156
3000	.0945	.01208	.00178	.00915	.01157	.1441
4000	.1152	.01598	.00236	.01224	.01518	.1665
5000	.1330	.01982	.00294	.01534	.01861	.1843
6000	.1485	.02360	.00352	.01846	.02191	.1998
7000	.1622	.02731	.00409	.02159	.02507	.2132
8000	.1746	.03095	.00465	.02475	.02807	.2246
9000	.1858	.03454	.00521	.02792	.03090	.2353
10000	.1964	.03806	.00579	.03111	.03360	.2448
11000	(.2059)	.04151	.00632	.03432	.03615	.2532
12000	(.2147)	.04492	.00687	.03754	.03856	.2608

(b) **Results for $k - k'$.**—In the determination of the compression of aqueous solutions at high pressures it was more convenient and satisfactory to measure first the compression of water using soft steel as the comparison

¹³ Adams, Williamson and Johnston, *op. cit.*, p. 39.

¹⁴ Bridgman, *Proc. Am. Acad. Arts Sci.*, **58**, 174 (1923).

¹⁵ Adams and Gibson, *J. Wash. Acad. Sci.*, **21**, 381 (1931).

material, and then to determine the compression of the various solutions with reference to water. This procedure provides a direct measurement of the *difference* in compression between the solution and pure water, and it is this difference in compression, or, more precisely, the compression-concentration gradient which is of most direct use in the thermodynamic treatment of solutions under pressure. Moreover, for reasons which will appear below, it is desirable to deal separately with the high- and low-pressure results.

In Table III are presented the values of $k - k'$ for sodium chloride solutions of six different concentrations (including the end member, pure water) at pressures from 1000 to 12,000 bars, except in the case of water and the moderately concentrated solutions, for which the maximum pressure was limited on account of the possibility of freezing.

TABLE III

RESULTS AT HIGH PRESSURES FOR VOLUME CHANGE OF SODIUM CHLORIDE SOLUTIONS.
TEMPERATURE, 25°

The difference between the compression of the solution and that of pure water is Δk . The primes refer to the values at the "initial" pressure, 2000 bars

Pressure in bars	$-10^4(\Delta k - \Delta k')$ $k - k'$		$-10^4(\Delta k - \Delta k')$ $k - k'$		$-10^4(\Delta k - \Delta k')$ $k - k'$	
	$x_2 = 0$		$x_2 = 0.05$		$x_2 = 0.10$	
1000	0	-0.0306	-202	-0.0286	-404	-0.0266
1500	0	-.0144	-104	-.0134	-191	-.0125
2000	0	.0000	0	.0000	0	.0000
3000	0	.0246	130	.0233	262	.0220
4000	0	.0453	243	.0429	498	.0403
5000	0	.0631	299	.0601	623	.0569
6000	0	.0786	363	.0750	712	.0715
7000	0	.0923	396	.0883	780	.0845
8000	0	.1047	472	.1000	887	.0958
9000	0	.1159	469	.1112	938	.1065
10000	0	.1265	516	.1213	998	.1165
11000	0	(.1360)	540	.1306	1038	.1256
12000	0	(.1448)
	$x_2 = 0.15$		$x_2 = 0.20$		$x_2 = 0.25$	
1000	-585	-0.0247	-762	-0.0230	-954	-0.0211
1500	-259	-.0118	-330	-.0111	-429	-.0101
2000	0	.0000	0	.0000	0	.0000
3000	408	.0205	542	.0192	644	.0182
4000	712	.0382	963	.0357	1155	.0337
5000	931	.0538	1229	.0508	1521	.0479
6000	1092	.0671	1460	.0640	1776	.0608
7000	1212	.0802	1627	.0760	2018	.0721
8000	1356	.0911	1785	.0868	2198	.0827
9000	1431	.1016	1872	.0972	2334	.0926
10000	1481	.1117	1978	.1067	2459	.1019
11000	1537	.1206	2061	.1154	2584	.1102
12000	2146	.1233	2667	.1181

At each concentration several series of measurements were made, the results here shown being the mean of the several series, in which the average discrepancy was about 0.00007 in k or Δk . The data at 11,000 and 12,000 were obtained by using soft steel as the standard—at these pressures and at 25°, water is too far above its freezing pressure to be of use as a reference material. The table shows, first, $\Delta k - \Delta k'$, that is, the directly determined difference between k , the compression of the solution, and k_w , that of water, reckoned from the pressure P' , Δk being equal to $k - k_w$, from which follows the identity

$$\Delta k - \Delta k' \equiv (k - k_w) - (k' - k'_w) \equiv (k - k') - (k_w - k'_w) \quad (6)$$

From the first and third terms it is evident that $k - k'$ may be obtained from $\Delta k - \Delta k'$ by adding $k_w - k'_w$, which, for the various pressures, is the $k - k'$ given in the table under the heading, $x_2 = 0$.

The results for the *differences* between k in the solution and in pure water are given to 0.00001. The error of reading the piston displacement corresponds to only about 0.00002; the last digit therefore has some significance, and is useful in the determination of the important compression-concentration gradient (see below). On the other hand, the values of $k - k'$ (and of k) have been rounded off to the nearest 0.0001, because various factors (*e. g.*, uncertainty in the pressure scale itself) prevent the absolute values of k from being known at present with any greater accuracy.

(c) **Final Results for the Compression, k .**—By combining the results for $k - k'$ with the low-pressure results given in Table I, we obtain the values of k for the various concentrations and pressures. This is accomplished by first obtaining k' at each concentration by subtracting the $k - k'$ at 1000 bars from the corresponding k at 1000 bars (given in Table I) and then adding the k' thus obtained to the values of $k - k'$ at the same concentration. Table IV shows the results for k and also for Δk . The latter may be obtained by subtracting k_w (*i. e.*, k at $x_2 = 0$) at any pressure from k for the given solution at the same pressure, or, as is evident from the first and second terms of equation (6), by finding the value of $k' - k'_w$ (*i. e.*, Δk at $P = 2000$) for a given concentration and adding this value to the values of $\Delta k - \Delta k'$ at the same concentration as given in Table III.

The effect of concentration on the volume change of sodium chloride solutions under pressure is shown graphically in Fig. 4. At a given pressure the compression decreases considerably with increasing concentration, but the relative change is less at high than at low pressures. Thus at 10,000 bars the compression of a 25% solution is 0.76 of that of water, while at 1000 bars the ratio is 0.64.

(d) **The Compressibility.**—The compressibility, β (sometimes called the relative compressibility), is defined by the relation

$$\beta = -\frac{1}{V_0} \frac{dV}{dP} = \frac{dk}{dP} \quad (7)$$

TABLE IV
THE COMPRESSION, k , FOR SODIUM CHLORIDE SOLUTIONS AT 25°

Δk is the difference between the value of k for the solution and that for pure water

Pressure in bars	$x_2 = 0$		$x_2 = 0.05$		$x_2 = 0.10$	
	k	$-10^4 \Delta k$	k	$-10^4 \Delta k$	k	$-10^4 \Delta k$
1	0.0000	0	0.0000	0	0.0000	0
500	.0212	0	.0192	20	.0176	36
1000	.0393	0	.0361	32	.0331	62
1500	.0555	0	.0513	42	.0472	83
2000	.0699	0	.0647	52	.0597	102
3000	.0945	0	.0880	65	.0817	128
4000	.1152	0	.1076	76	.1000	152
5000	.1330	0	.1248	82	.1166	164
6000	.1485	0	.1397	88	.1312	173
7000	.1622	0	.1530	92	.1442	180
8000	.1746	0	.1647	99	.1555	191
9000	.1858	0	.1759	99	.1662	196
10000	.1964	0	.1860	104	.1762	202
11000	(.2059)	0	.1953	106	.1853	206
12000	(.2147)	0
	$x_2 = 0.15$		$x_2 = 0.20$		$x_2 = 0.25$	
1	0.0000	0	0.0000	0	0.0000	0
500	.0161	51	.0147	65	.0133	79
1000	.0304	89	.0277	116	.0251	142
1500	.0433	122	.0396	159	.0361	194
2000	.0551	148	.0507	192	.0462	237
3000	.0756	189	.0699	246	.0644	301
4000	.0933	219	.0864	288	.0799	353
5000	.1089	241	.1015	315	.0941	389
6000	.1228	257	.1147	338	.1070	415
7000	.1353	269	.1267	355	.1183	439
8000	.1462	284	.1375	371	.1289	457
9000	.1567	291	.1479	379	.1388	470
10000	.1668	296	.1574	390	.1481	483
11000	.1757	302	.1661	398	.1564	495
120001740	407	.1643	504

and the specific compressibility, β' , by the relation

$$\beta' = -\frac{dv}{dP} = v_0 \frac{dk}{dP} = v_0 \beta \tag{8}$$

since $v/v_0 = V/V_0$. Here V is the total volume, and v the specific volume, *i. e.*, the volume of 1 g. of material, the subscript zero referring to atmospheric pressure. The compressibility, β , is the one more commonly used but the specific compressibility, β' , is more closely related to thermodynamic quantities. Neither, however, is of much use in the thermodynamic study of systems under pressure; it is the compression that is directly applicable to such investigations. Nevertheless, it is of general interest to note the compressibility, β , of the different solutions. This may

best be determined by representing k as a function of P and differentiating the equation. Although many types of equations were tried, the only one that was satisfactory for the whole pressure range was

$$k = BP + CP^2 + D(1 - e^{-EP}) \quad (9)$$

in which B , C , D and E are constants (at a fixed concentration); but in the limited range from 1 to 1000 bars a simple quadratic appears to fit very

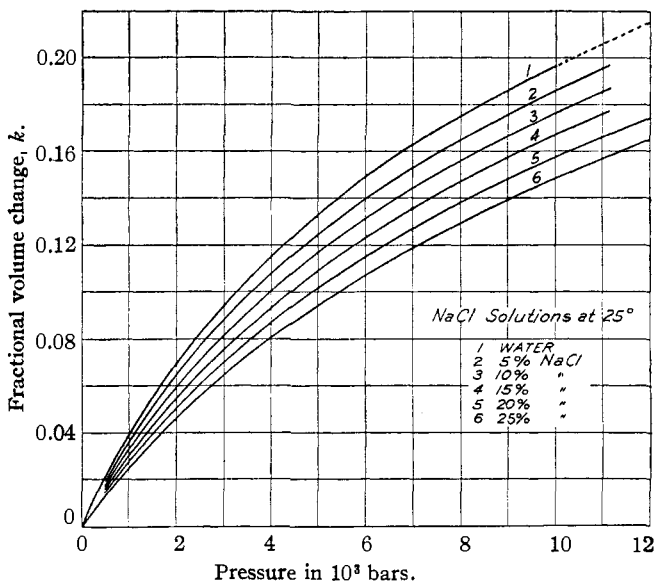


Fig. 4.—The compression (*i. e.*, the relative volume change) of sodium chloride solutions at various pressures.

well. For water the values of the constants in equation (9) were, $B = 16.362 \times 10^{-6}$, $C = -3.42 \times 10^{-10}$, $D = 0.06800$ and $E = 0.00042$, and were determined by noting that

$$\log \frac{d^3 k}{dP^3} = \log DE^3 - 0.4343 EP \quad (10)$$

plotting the third tabular differences of k against P on "semi-log" coordinate paper, passing the best straight line through the points, estimating D and E from the slope and intercept of the straight line, subtracting $D(1 - e^{-EP})$ from k at each pressure and solving for B and C by the method of least squares. How well equation (9) fits the data for water may be judged from the differences between the observed and calculated values of k , which at the even 1000's of bars beginning at 1 and ending at 10,000 were, respectively, 1, 0, 0, -1, -1, 1, 1, 1, 0, -1 and 0 units in the fourth place after the decimal point. Equation (9) was used to extrapolate k for water from 10,000 to 12,000 bars; the values of k shown in parentheses in Tables II and

IV are the results of this extrapolation. The equation was also fitted to the results for the 25% sodium chloride solution. The constants, $B = 15.7 \times 10^{-6}$, $C = -3.7 \times 10^{-10}$, $D = 0.02800$ and $E = 0.00042$ gave a satisfactory representation, although not so good as in the case of water.

By differentiation of equation (9) there is obtained for the compressibility

$$\beta = B + 2CP + DE e^{-EP} \quad (11)$$

From this expression, with the known values of the constants, the compressibility of water and of a 25% sodium chloride solution was calculated, and the results were plotted in Fig. 5. At $P = 1$ the solution has a much

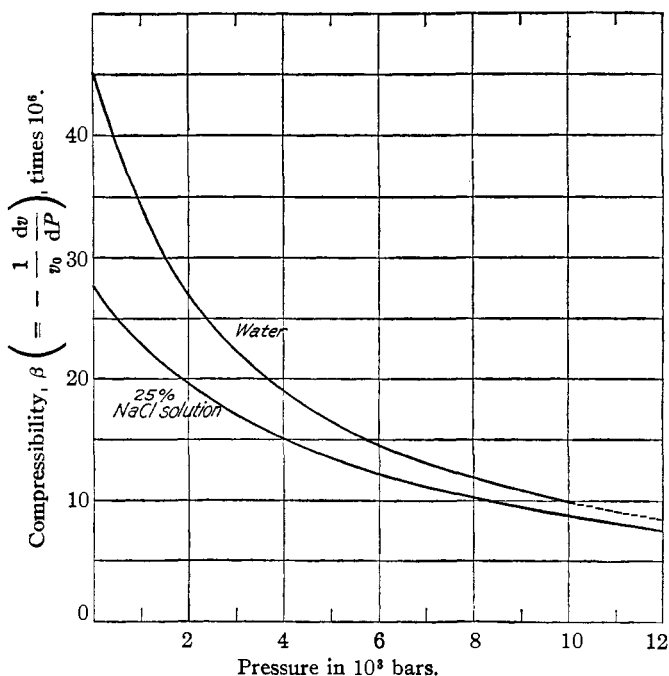


Fig. 5.—The compressibility of water and of a 25% sodium chloride solution. At high pressures the compressibilities are nearly the same.

lower compressibility than water (27.4 against 44.9) but at high pressures the difference is not so great, the corresponding values of $10^6 \beta$ at $P = 10,000$ being 8.3 and 9.4, respectively. The initial compressibility, β_0 , calculated from the measurements over the whole pressure range, may be in error by several tenths of one per cent.; indeed, some additional measurements at very low pressures indicated that for water β_0 is 45.2×10^{-6} at 25° .

Comparison with Results of Other Investigators.—No previous measurements of the compression of solutions at high pressures have been

made, but Gilbaut¹⁶ determined at 300 atm. the compression of sodium chloride solutions. His results agree very well with those interpolated at 300 atm. from the present measurements. More recently Hubbard and Loomis¹⁷ and Pooler¹⁸ determined the compressibility of sodium chloride solutions by measuring the velocity of sound waves in the liquid, the former at very high and the latter at low ("audio-") frequencies. A calculation of the isothermal compressibility, $10^6\beta_0$, at 25° from their results yields for water and a 25% sodium chloride solution, respectively, 45.16 and 28.04 (H. and L.), and 45.90 and 28.61 (P.). The results of Hubbard and Loomis agree better with the present determinations of β_0 than do those of Pooler, but it may be noted that the difference in β_0 between water and the 25% solution, 17.1 (H. and L.) and 17.3 (P.) in neither case is very far from the difference, 17.5, as now determined. There are also other earlier measurements on β for sodium chloride solutions at atmospheric pressure, but they are of doubtful value.

For the compression of *water* at high pressures we have the measurements by Bridgman¹⁹ on the volume change of water at various temperatures and pressures including data at 25°, up to 10,000 kg./sq. cm. By conversion of these results, which are given in terms of Δv , to values of k at pressures in bars, it may be seen that Bridgman's results are in each instance lower than the present ones, the differences in 10^4k at the even 1000's of bars from 1000 to 10,000 inclusive being, respectively, 5, 8, 12, 1, 11, 7, 4, 2, 1 and 5.

The "Fictive" or "Partial" Volumes under Pressure.—The principal object in measuring the effect of pressure on the volume of the solutions was to determine at various pressures and for each component the thermodynamic quantity called the fictive or partial volume. The fictive volume, v_2 , of sodium chloride in a solution of a given concentration is defined by the relation

$$\bar{v}_2 = \left(\frac{\partial V}{\partial m_2} \right)_{m_1} \quad (12)$$

and similarly for \bar{v}_1 , the fictive volume of the water, by changing subscripts 1 to 2 and 2 to 1 (pressure and temperature are constant). Here V is the total volume of the solution, and m_1 and m_2 are, respectively, the total weights of the water and sodium chloride. The unit of weight may be either the gram or the mole. The latter is perhaps the more commonly used, but for purposes which do not involve actual chemical reactions (in the usual sense) it is more convenient to deal with fictive quantities that are based on the gram as the unit. In the above equation we shall let V

¹⁶ Gilbaut, *Z. physik. Chem.*, **24**, 385 (1897).

¹⁷ Hubbard and Loomis, *Phil. Mag.*, **5**, 1177-1190 (1928).

¹⁸ Pooler, *Phys. Rev.*, **35**, 832-847 (1930).

¹⁹ Bridgman, *Proc. Am. Acad. Arts Sci.*, **48**, 338 (1912).

be expressed in cc., and \mathbf{m}_1 and \mathbf{m}_2 in grams; whence \bar{v}_2 will be in cc. per g., analogous to ordinary specific volume. The values of \bar{v}_2 at various concentrations may be conveniently calculated from data on densities or specific volumes of solutions by means of the expression, equivalent to (12)

$$\bar{v}_2 = v + x_1 \left(\frac{\partial v}{\partial x_2} \right)_{P,t} \quad (13)$$

Similarly for \bar{v}_1

$$\begin{aligned} \bar{v}_1 &= v + x_2 \left(\frac{\partial v}{\partial x_1} \right)_{P,t} \\ &= v - x_2 \left(\frac{\partial v}{\partial x_2} \right)_{P,t} \end{aligned} \quad (14)$$

In these two equations v denotes the specific volume of the solution, x_1 , the weight fraction of water, and x_2 , that of sodium chloride.

The values of \bar{v}_1 and \bar{v}_2 at *atmospheric pressure* and at various concentrations are shown in Tables VI and VII opposite the numeral 1 in the column labeled "Pressure." They were calculated by equations (14) and (13) from the very accurate measurements by Hall²⁰ on the densities of sodium chloride solutions at 25°, a cubic equation and auxiliary deviation curve being used to evaluate $\partial v / \partial x_2$. The same method might have been employed in order to obtain \bar{v}_1 and \bar{v}_2 at high pressure from the known compression of the solutions; the specific volume at each pressure for various concentrations could have been calculated from the data for k as given in Table IV, by the obvious relation

$$v = v_0(1 - k) \quad (15)$$

(v denoting the specific volume at any pressure, and v_0 that at $P = 1$), and the same procedure then followed as at atmospheric pressure. But it is more accurate as well as less laborious to calculate the *change* in \bar{v}_1 or \bar{v}_2 under pressure directly from the *volume change* of the solutions. Since equation (13) holds at all pressures, it follows that

$$\Delta_P \bar{v}_2 \equiv \bar{v}_2 - (\bar{v}_2)_0 = \Delta v + x_1 \left(\frac{\partial \Delta v}{\partial x_2} \right)_{P,t} \quad (16)$$

and

$$\Delta_P \bar{v}_1 \equiv \bar{v}_1 - (\bar{v}_1)_0 = \Delta v - x_2 \left(\frac{\partial \Delta v}{\partial x_2} \right)_{P,t} \quad (17)$$

$(\bar{v}_1)_0$ and $(\bar{v}_2)_0$ denoting the values of \bar{v}_1 and \bar{v}_2 at atmospheric pressure, and Δv (which in this instance might be written $\Delta_P v$) the increase²¹ in

²⁰ Hall, *J. Wash. Acad. Sci.*, **14**, 167-173 (1924).

²¹ The subscript P after the Δ signifies that the change in the quantity under consideration pertains to two different pressures at the same concentration. Similarly, $\Delta_x \bar{v}_2$ denotes the difference between the values of \bar{v}_2 at two different concentrations at the same pressure. This convention is in accord with the usual mathematical symbolism when there are two or more independent variables [*cf.* Osgood, "Advanced Calculus," 1925, p. 112. When there is little or no danger of ambiguity, the subscript will be omitted, as for example in the Δv of equation (19)].

specific volume under pressure. At each pressure and concentration Δv is readily obtained from k by means of the expression, equivalent to (15)

$$\Delta v = -v_0 k \quad (18)$$

From this point on, one of two methods may be followed: (I) Δv (or k) may be represented as a function of pressure at constant composition, or (II) as a function of concentration at constant pressure.

(Ia).—Let Δv be represented by the power series

$$(x_2, \text{constant}) \quad \Delta v = BP + CP^2 + DP^3 + \dots \quad (19)$$

in which B , C , D and so on, are constants (at any given concentration). Then from (16) it follows immediately that

$$\Delta_P \bar{v}_2 \equiv \bar{v}_2 - (\bar{v}_2)_0 = \left(B + x_1 \frac{\partial B}{\partial x_2} \right) P + \left(C + x_1 \frac{\partial C}{\partial x_2} \right) P^2 + \left(D + x_1 \frac{\partial D}{\partial x_2} \right) P^3 + \dots \quad (20)$$

(Ib).—It may be more convenient to deal directly with k . If

$$(x_2, \text{constant}) \quad k = BP + CP^2 + \dots \quad (21)$$

then, from (18) and (16)

$$\begin{aligned} \Delta_P \bar{v}_2 \equiv \bar{v}_2 - (\bar{v}_2)_0 &= -k v_0 - k x_1 \frac{\partial v_0}{\partial x_2} - x_1 v_0 \left(P \frac{\partial B}{\partial x_2} + P^2 \frac{\partial C}{\partial x_2} + \dots \right) \\ &= -k(\bar{v}_2)_0 - x_1 v_0 \left(P \frac{\partial B}{\partial x_2} + P^2 \frac{\partial C}{\partial x_2} + \dots \right) \end{aligned} \quad (22)$$

(Ic).—Probably the best way known at present for representing k as a function of P over a *large* range of pressures is by equation (9) above. In this case, we find

$$\Delta_P \bar{v}_2 \equiv \bar{v}_2 - (\bar{v}_2)_0 = -k(\bar{v}_2)_0 - x_1 v_0 \left[P \frac{\partial B}{\partial x_2} + P^2 \frac{\partial C}{\partial x_2} + (1 - e^{-EP}) \frac{\partial D}{\partial x_2} + DP e^{-EP} \frac{\partial E}{\partial x_2} \right] \quad (23)$$

(IIa).—Considering now $\Delta_P v$ (the change in specific volume,²² due to the pressure increase) as a function of x_2 at a specified pressure, let us suppose that the data are represented by the equation

$$(P, \text{constant}) \quad -\Delta_P v = a + bx_2 + cx_2^2 + dx_2^3 + \dots \quad (24)$$

in which a , b , c , d and so on, are constants (at any given pressure). Then, from (16) it follows that

$$\Delta_P \bar{v}_2 \equiv \bar{v}_2 - (\bar{v}_2)_0 = -a - b - cx_2(2 - x_2) - dx_2^2(3 - 2x_2) - \dots \quad (25)$$

(IIb).—In order to treat separately the results at high pressures for the compression of the solutions, we express $k - k'$ as a function of x_2 . Let

$$(P, \text{constant}) \quad k - k' = a + bx_2 + cx_2^2 \quad (26)$$

Then, from (18) and (16) we have

$$\bar{v}_2 - \bar{v}'_2 = -v_0(k - k') - x_1 v_0 \frac{\partial(k - k')}{\partial x_2} - (k - k') x_1 \frac{\partial v_0}{\partial x_2}$$

²² It should be noted that in this instance it is much less confusing to use the notation, $\Delta_P v$, rather than Δv .

Hence, from (13) and (26) it follows that

$$\begin{aligned}\bar{v}_2 - \bar{v}'_2 &= -(\bar{v}_2)_0 (k - k') - x_1 v_0 \frac{\partial(k - k')}{\partial x_2} \\ &= -(\bar{v}_2)_0 (k - k') - x_1 v_0 (b + 2c x_2)\end{aligned}\quad (27)$$

This important equation allows us to calculate the change in \bar{v}_2 from pressure P' to pressure P directly from $k - k'$. If P' is 1, then $k' = 0$ and $\bar{v}'_2 = (\bar{v}_2)_0$, and the above equation becomes

$$\Delta_P \bar{v}_2 \equiv \bar{v}_2 - (\bar{v}_2)_0 = -(\bar{v}_2)_0 k - x_1 v_0 \frac{\partial k}{\partial x_2} \quad (28)$$

Equations similar to (20), (22), (23), (25), (27) and (28), but giving \bar{v}_1 instead of \bar{v}_2 may be obtained in each instance by changing all subscripts 1 to subscripts 2 and 2 to 1. For convenience, we may also make use of the obvious relation, $dx_2/dx_1 = -1$; thus, in analogy with (28), we may write

$$\Delta_P \bar{v}_1 \equiv \bar{v}_1 - (\bar{v}_1)_0 = -(\bar{v}_1)_0 k + x_2 v_0 \frac{\partial k}{\partial x_2} \quad (29)$$

All of the above equations, as well as the similar ones that might have been written for \bar{v}_1 , are important and in convenient form for calculation of fictive volumes from compression measurements.²³ The choice of the particular method or of the form of equation will depend upon the pressure range, the general character of the results for k or Δv and the ease with which they can be represented by one of the empirical relations between k or Δv and P or x_2 . In the present instance it was found, unexpectedly, that, within the error of experiment, the high pressure results, that is, $k - k'$, could be represented by a simple linear function of the concentration x_2 (the same is not true of Δv as a function of x_2). Therefore it was advantageous to use equation (27) for calculating $\bar{v}_2 - \bar{v}'_2$, and the homolog of (27) for calculating $\bar{v}_1 - \bar{v}'_1$. The first step was to determine for each pressure the compression-concentration gradient, $\partial(k - k')/\partial x_2$, that is, the constant b in equation (26), the constant c being zero. This was done by the method of least squares. The results of the calculation of b are shown in Table V. These values were smoothed by means of the equation

$$-10^5 b \equiv -10^5 \left(\frac{\partial(k - k')}{\partial x_2} \right)_P = B(P - P') + D(1 - e^{-E(P - P')}) \quad (30)$$

in which $B = 0.246$, $D = 8410$ and $E = 0.00034$. The equation fits the results for b very well, except at $P = 1000$, as may be seen by an inspection of the table. The values of $\bar{v}_2 - \bar{v}'_2$ and of $\bar{v}_1 - \bar{v}'_1$ for each concentration and for the various pressures from 1000 to 12,000 bars, were then com-

²³ By the substitution of thermal expansion for diminution in volume under pressure, the equations may also be used for the calculation of fictive volumes at various temperatures. An equation analogous to the one given in Method Ia was used by Gibson [*J. Phys. Chem.*, 31, 496-510 (1927)] in determining the effect of temperature on the fictive volumes in sodium sulfate solutions.

puted, by means of equation (27) and its homolog. In this computation, the *smoothed* values of $\partial(k - k')/\partial x_2$ were used except at 1000 bars. Next, by means of equations (28) and (29), the low-pressure data for k were used to determine \bar{v}_2 and \bar{v}_1 at 500 and 1000 bars with the results shown in Table I. At these low pressures k (reckoned from atmospheric pressure) does not bear a simple linear relation to x_2 ; with increasing concentration the compression first decreases rapidly and then more slowly. A cubic or exponential equation might possibly represent the data with sufficient accuracy, but the procedure here followed, which was satisfactory and less laborious, consisted in taking the tabular differences of k (x_2 being the argument) and then determining $\partial k/\partial x_2$, by well-known mathematical devices, from these tabular differences.

TABLE V
THE COMPRESSION-CONCENTRATION GRADIENT FOR THE HIGH-PRESSURE RESULTS

Pressure in bars	$-\frac{\partial(k - k')}{\partial x_2}$	$-\frac{\partial(k - k')}{\partial x_2}$	Difference times 10^4
		(calcd. from Equation 30)	
1000	-0.0379	-0.0366	-13
1500	-.0165	-.0169	4
2000	.0000	.0000	0
3000	.0263	.0266	-3
4000	.0466	.0463	3
5000	.0612	.0610	2
6000	.0717	.0723	-6
7000	.0812	.0809	3
8000	.0880	.0878	2
9000	.0936	.0934	2
10000	.0979	.0981	-2
110001022	..
120001058	..

Finally the high- and low-pressure results were combined to give the values of \bar{v}_1 and \bar{v}_2 . It is important to note that either \bar{v}_1 or \bar{v}_2 may be computed directly from the known values of the other. We have the relation

$$x_1 \left(\frac{\partial \bar{v}_1}{\partial x_2} \right)_P = -x_2 \left(\frac{\partial \bar{v}_2}{\partial x_2} \right)_P \quad (31)$$

from which it follows that at any given pressure

$$\bar{v}_1 = v_w - \int_{(\bar{v}_2)_w}^{\bar{v}_2} \frac{x_2}{x_1} d\bar{v}_2 = v_w - \int_0^{x_2} \frac{x_2}{x_1} \frac{\partial \bar{v}_2}{\partial x_2} dx_2 \quad (32)$$

since $(\bar{v}_1)_w = v_w$. A more convenient form of the equation, since it allows us to deal with smaller numbers, is

$$\bar{v}_1 = (\bar{v}_1)_0 + \Delta v_w - \int_{(\Delta P \bar{v}_2)_w}^{\Delta P \bar{v}_2} \frac{x_2}{x_1} d\Delta P \bar{v}_2 \quad (33)$$

in which Δv_w denotes the increase in v_w between atmospheric pressure and the given pressure. As a check on the original calculation of \bar{v}_1 , all of the values were computed again, using equation (33) and numerical integration. It appears to be more convenient to calculate both \bar{v}_1 and \bar{v}_2 directly from k .

The final results for \bar{v}_1 and \bar{v}_2 are listed in Tables VI and VII. The former also shows, first, $\Delta_p \bar{v}_1$, which equals $\bar{v}_1 - (\bar{v}_1)_0$, the change of \bar{v}_1 under pressure at the specified concentration, and, second, $\Delta_x \bar{v}_1$, which is $\bar{v}_1 - (\bar{v}_1)_w$, the difference (at a given pressure) between \bar{v}_1 in the solution of stated

TABLE VI
 "FICTIVE," OR "PARTIAL," VOLUME OF WATER IN SODIUM CHLORIDE SOLUTIONS UNDER PRESSURE

The subscript zero refers to atmospheric pressure, and $\Delta_x \bar{v}_1$ is the difference between the value of \bar{v}_1 in the solution and that in pure H₂O (at a given pressure)

Pressure in bars	$\bar{v}_1 - (\bar{v}_1)_0$ ($= \Delta_p \bar{v}_1$)	$x_2 = 0$		$\bar{v}_1 - (\bar{v}_1)_0$ ($= \Delta_x \bar{v}_1$)	$x_2 = 0.05$	
		\bar{v}_1	$10^4(\Delta_x \bar{v}_1)$		\bar{v}_1	$10^4 \Delta_x \bar{v}_1$
1	0.0000	1.0029	0	0.0000	1.0021	- 8
500	- .0213	0.9816	0	- .0210	0.9811	- 5
1000	- .0394	.9635	0	- .0391	.9630	- 5
1500	- .0556	.9473	0	- .0554	.9467	- 6
2000	- .0701	.9328	0	- .0696	.9325	- 3
3000	- .0948	.9081	0	- .0942	.9079	- 2
4000	- .1155	.8874	0	- .1148	.8873	- 1
5000	- .1334	.8695	0	- .1328	.8693	- 2
6000	- .1489	.8540	0	- .1483	.8538	- 2
7000	- .1627	.8402	0	- .1620	.8401	- 1
8000	- .1751	.8278	0	- .1740	.8281	3
9000	- .1863	.8166	0	- .1855	.8166	0
10000	- .1970	.8059	0	- .1959	.8062	3
11000	(- .2064)	(.7964)	0	- .2054	.7967	3
12000	(- .2153)	(.7876)	0
		$x_2 = 0.10$			$x_2 = 0.15$	
1	0.0000	1.0002	-27	0.0000	0.9976	-53
500	- .0205	0.9797	-19	- .0201	.9775	-41
1000	- .0385	.9617	-18	- .0378	.9598	-37
1500	- .0545	.9457	-16	- .0535	.9441	-32
2000	- .0685	.9317	-11	- .0675	.9301	-27
3000	- .0930	.9072	- 9	- .0916	.9060	-21
4000	- .1131	.8871	- 3	- .1119	.8857	-17
5000	- .1311	.8691	- 4	- .1295	.8681	-14
6000	- .1468	.8534	- 6	- .1448	.8528	-12
7000	- .1606	.8396	- 6	- .1585	.8391	-11
8000	- .1725	.8277	- 1	- .1703	.8273	- 5
9000	- .1837	.8165	- 1	- .1816	.8160	- 6
10000	- .1942	.8060	1	- .1924	.8052	- 7
11000	- .2035	.7967	3	- .2017	.7959	- 5
12000

TABLE VI (Concluded)

Pressure in bars	$\bar{v}_1 - (\bar{v}_1)_0$ ($= \Delta_P \bar{v}_1$)	\bar{v}_1	$10^4(\Delta_x \bar{v}_1)$	$\bar{v}_1 - (\bar{v}_1)_0$ ($= \Delta_P \bar{v}_1$)	\bar{v}_1	$10^4 \Delta_x \bar{v}_1$
	$x_2 = 0.20$			$x_2 = 0.25$		
1	0.0000	0.9945	-84	0.0000	0.9911	-118
500	-.0195	.9750	-66	-.0190	.9721	-95
1000	-.0370	.9575	-60	-.0360	.9551	-84
1500	-.0526	.9419	-54	-.0513	.9398	-75
2000	-.0665	.9280	-48	-.0648	.9263	-65
3000	-.0902	.9043	-38	-.0884	.9027	-54
4000	-.1101	.8844	-30	-.1080	.8831	-43
5000	-.1277	.8668	-27	-.1252	.8659	-36
6000	-.1427	.8518	-22	-.1403	.8508	-32
7000	-.1562	.8383	-19	-.1534	.8377	-25
8000	-.1681	.8264	-14	-.1653	.8258	-20
9000	-.1795	.8150	-16	-.1763	.8148	-18
10000	-.1897	.8048	-11	-.1865	.8046	-13
11000	-.1991	.7954	-10	-.1955	.7956	-8
12000	-.2076	.7869	-7	-.2041	.7870	-6

composition and its value, $(\bar{v}_1)_w$, in pure water; the latter table shows the values of $\Delta_P \bar{v}_2$, and of $\Delta_x \bar{v}_2$, which are similarly defined. The effect of pressure on \bar{v}_1 and \bar{v}_2 is shown graphically in Figs. 6 and 7, in which $\Delta_x \bar{v}_1$ and $\Delta_x \bar{v}_2$ are plotted against concentration for several pressures, and in Fig. 8, which illustrates the course of \bar{v}_2 as a function of pressure at constant x_2 .

A study of the results for the fictive volumes of sodium chloride and water in the solutions under pressure reveals many interesting things, of which only two will be noticed at the present time.

TABLE VII

"FICTIVE," OR "PARTIAL," VOLUME OF SODIUM CHLORIDE IN AQUEOUS SOLUTIONS UNDER PRESSURE. $\Delta_x \bar{v}_2 = \bar{v}_2 - (\bar{v}_2)_w$

Pressure in bars	$\bar{v}_2 - (\bar{v}_2)_0$ ($= \Delta_P \bar{v}_2$)	\bar{v}_2	$10^4(\Delta_x \bar{v}_2)$	$\bar{v}_2 - (\bar{v}_2)_0$ ($= \Delta_P \bar{v}_2$)	\bar{v}_2	$10^4 \Delta_x \bar{v}_2$
	$x_2 = 0$			$x_2 = 0.05$		
1	0.0000	0.2914	0	0.0000	0.3304	390
500	.0364	.3278	0	.0263	.3567	289
1000	.0549	.3463	0	.0439	.3743	280
1500	.0717	.3631	0	.0586	.3890	259
2000	.0840	.3754	0	.0694	.3998	244
3000	.1035	.3949	0	.0862	.4166	217
4000	.1172	.4086	0	.0978	.4282	196
5000	.1268	.4182	0	.1056	.4360	178
6000	.1336	.4250	0	.1111	.4415	165
7000	.1382	.4296	0	.1146	.4450	154
8000	.1416	.4330	0	.1172	.4476	146
9000	.1439	.4353	0	.1186	.4492	139
10000	.1455	.4369	0	.1196	.4500	131
110001203	.4507	..

TABLE VII (Concluded)

Pressure in bars	$\bar{v}_2 - (\bar{v}_2)_0$ ($= \Delta P \bar{v}_2$)	$x_2 = 0.10$			$x_2 = 0.15$		
		\bar{v}_2	$10^4(\Delta_P \bar{v}_2)$	$\bar{v}_2 - (\bar{v}_2)_0$ ($= \Delta P \bar{v}_2$)	\bar{v}_2	$10^4 \Delta_P \bar{v}_2$	
1	0.0000	0.3539	625	0.0000	0.3725	811	
500	.0202	.3741	463	.0165	.3890	612	
1000	.0358	.3897	434	.0305	.4030	567	
1500	.0488	.4027	396	.0421	.4146	515	
2000	.0583	.4122	368	.0504	.4229	475	
3000	.0729	.4268	319	.0632	.4357	408	
4000	.0830	.4369	283	.0718	.4443	357	
5000	.0896	.4435	253	.0773	.4498	316	
6000	.0939	.4478	228	.0807	.4532	282	
7000	.0965	.4504	208	.0827	.4552	256	
8000	.0983	.4522	192	.0840	.4565	235	
9000	.0992	.4531	178	.0844	.4569	216	
10000	.0997	.4536	167	.0842	.4567	198	
11000	.0999	.4538	..	.0840	.4565	..	
		$x_2 = 0.20$			$x_2 = 0.25$		
1	0.0000	0.3873	959	0.0000	0.3991	1077	
500	.0140	.4013	735	.0122	.4113	835	
1000	.0267	.4140	677	.0235	.4226	763	
1500	.0371	.4244	613	.0327	.4318	687	
2000	.0443	.4316	562	.0391	.4382	628	
3000	.0555	.4428	479	.0486	.4477	528	
4000	.0628	.4501	415	.0550	.4541	455	
5000	.0672	.4545	363	.0586	.4577	395	
6000	.0700	.4573	323	.0605	.4596	346	
7000	.0714	.4587	291	.0615	.4606	310	
8000	.0720	.4593	263	.0616	.4607	277	
9000	.0719	.4592	239	.0612	.4603	250	
10000	.0715	.4588	219	.0604	.4595	226	
11000	.0710	.4583	..	.0597	.4586	..	
12000	.0704	.4577	..	.0589	.4580	..	

(1) As the pressure is increased, \bar{v}_1 in solutions of any concentration decreases by an amount not very different from the decrease in the specific volume of water at the same pressure. This will be the behavior of the fictive volumes of all components in a solution which is nearly ideal in the usual sense.²⁴ Turning our attention now to \bar{v}_2 , the fictive volume of sodium chloride in solutions under pressure, we note the astonishing fact that \bar{v}_2 increases with increasing pressure, except at the highest pressures in the most concentrated solutions. The increase is especially striking in the dilute solutions. Thus, for example, in a 5% solution \bar{v}_2 increases from

²⁴ In a solution that at all pressures is ideal in accordance with the well-known thermodynamic definition, it can easily be shown that the (liquid) components mix without change of volume; in an ideal solution, therefore, each fictive volume at any pressure is equal to the specific volume (at that pressure) of the corresponding pure (liquid) component.

0.3304 to 0.4500 when the pressure is raised from 1 to 10,000 bars, while in a 25% solution \bar{v}_2 , initially 0.3991, increases to a maximum of 0.4603 at 8000 bars. Above this pressure it decreases, and thus at high pressures behaves as would be expected at all pressures in more normal, and certainly in ideal solutions. The physical meaning of the increase may perhaps be better understood when more data on various solutions are accumulated but it must be remembered that the fictive volume itself has only a vague

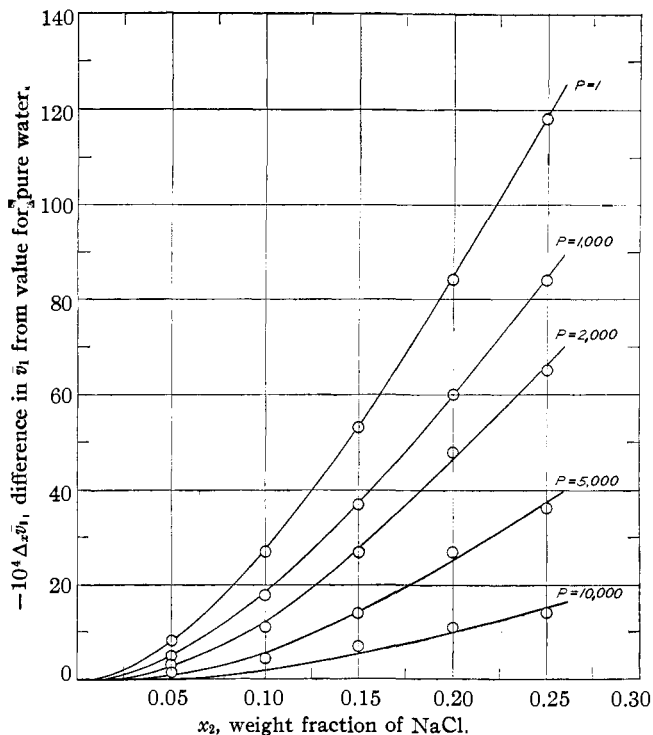


Fig. 6.—The change of the fictive, or partial, volume, \bar{v}_1 of water in sodium chloride solutions as the concentration is increased. At high pressures the variation with concentration is relatively small.

connection with the internal constitution of the solution.²⁵ Primarily it is a quantity, arbitrarily defined in terms of other and directly measurable quantities, and of practical importance in thermodynamic calculations. It is the magnitude of \bar{v}_1 and of \bar{v}_2 , rather than their physical interpretation, that is of immediate interest.

²⁵ On the other hand, we have the well-known relation $V = m_1\bar{v}_1 + m_2\bar{v}_2 + \dots$, which means that the total volume of a solution is equal to the sum of the products of the weights of each component and the corresponding fictive volumes, and from which it might be argued that the fictive volume is the volume actually occupied by 1 g. of the material in solution.

(2) By reference to Fig. 6 and Table VI it may be noted that at high pressure \bar{v}_1 is much less affected by changes of concentration than at low pressure. For example, at atmospheric pressure \bar{v}_1 is 0.0118 less in a 25% solution of sodium chloride than at zero concentration, while at 10,000 bars the difference is only 0.0013. A similar situation exists for \bar{v}_2 , as may be seen by inspection of Fig. 7 and Table VII, and also by noting the way in which the curves for \bar{v}_2 in Fig. 8 are crowded together at the higher pressures. This means that under very high pressures the relations between

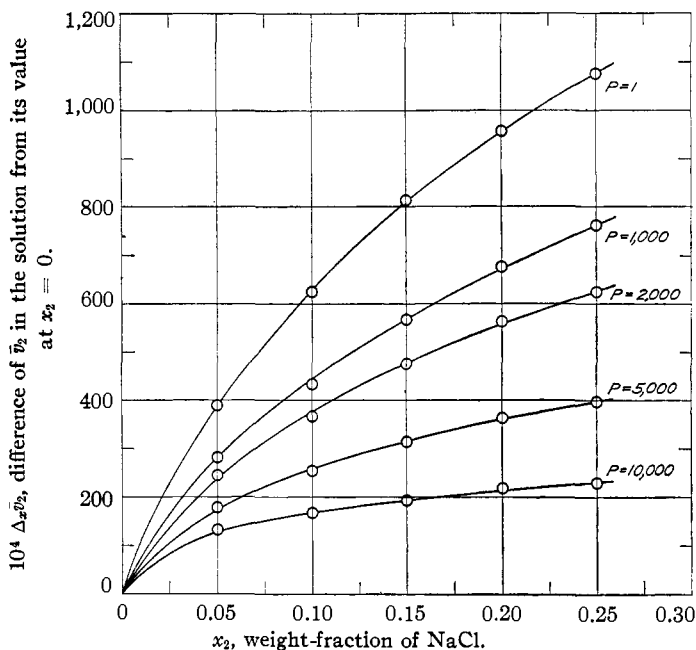


Fig. 7.—The change (at various pressures) of the fictive, or partial, volume of sodium chloride in sodium chloride solutions as the concentration is increased.

pressure, concentration and fictive volumes are much simpler than at atmospheric pressure—which is a conclusion of the utmost importance in connection with the study of equilibrium in systems under pressure. Among other consequences, it permits us to extrapolate safely certain quantities over a considerable range of pressure (see below).

The Fictive Compressibility.—From the present measurements there can be calculated also the interesting factor called the fictive or partial compressibility. For the water or sodium chloride, respectively, it is denoted by the symbol $\bar{\beta}'_1$, or $\bar{\beta}'_2$, and (*e. g.*, for the sodium chloride is defined by the relation (at constant temperature)

$$\bar{\beta}'_2 = - \left(\frac{\partial \bar{v}_2}{\partial P} \right)_x \quad (34)$$

It bears a close relation to β' , the *specific compressibility* of the solution, which differs from β and is defined by equation (8). From equations (8), (13) and (34) it follows that

$$\bar{\beta}'_2 = \beta' + x_1 \left(\frac{\partial \beta'}{\partial x_2} \right)_P \quad (35)$$

This expression might have been used for the definition²⁶ of $\bar{\beta}'_2$.

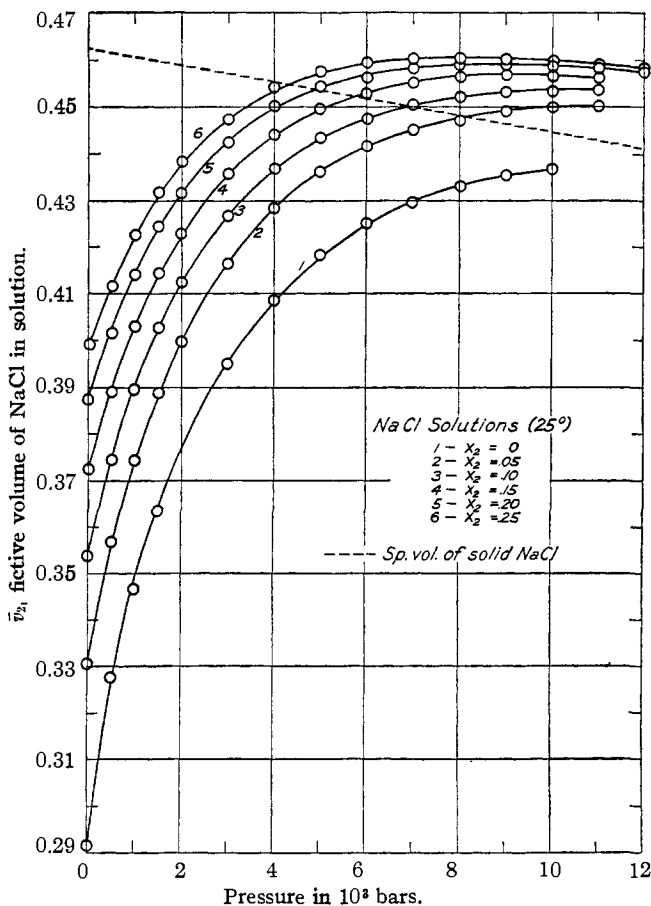


Fig. 8.—The fictive volume of sodium chloride plotted as a function of pressure for various concentrations. The dotted line shows the specific volume of solid sodium chloride under pressure.

It is evident, from equation (34), that $\bar{\beta}'_2$ may be determined by differentiating any of the above equations used for calculating \bar{v}_2 from Δv or

²⁶ A third way of defining $\bar{\beta}'_2$ is suggested by the fact that if we substitute (12) in (34), reverse the order of partial differentiation, and make use of the equality $V = mv$, we obtain $\bar{\beta}'_2 = \partial(m\beta')/\partial m_2$, in close analogy with the definition of \bar{v}_2 , according to which $\bar{v}_2 = \partial V/\partial m_2 = \partial(mv)/\partial m_2$.

k (Nos. 20, 22, 23, 25, 27 or 28). With sufficient accuracy for some purposes it may also be obtained from the tabular differences of \bar{v}_2 . This method was used in order to plot the curves shown in Fig. 9—except at low pressures, for which $\bar{\beta}'_2$ was calculated by differentiating equation (23). The increase in \bar{v}_2 under pressure, mentioned above, obviously means that $\bar{\beta}'_2$ is negative. In dilute solutions it has a large negative value comparable in magnitude with the compressibility of water, but of opposite sign; only in concentrated solutions at pressures near the upper end of the experimental range does it change sign and acquire a slowly changing positive value.

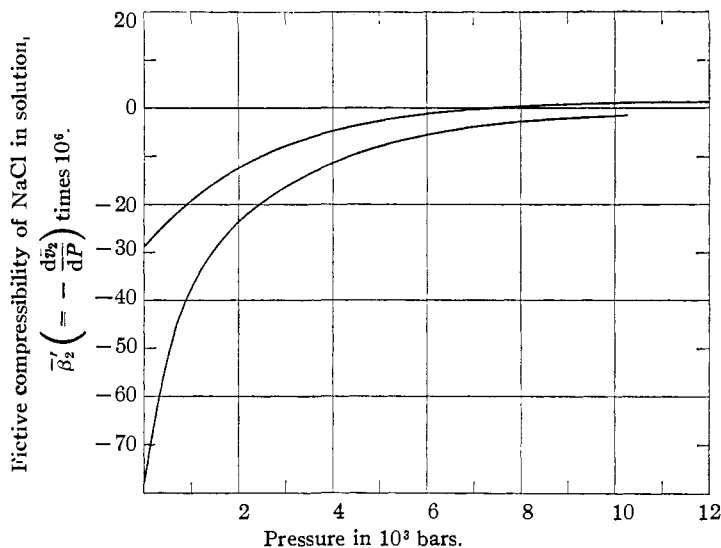


Fig. 9.—The fictive compressibility of sodium chloride in solution. Except at very high pressures this is *negative*; that is, v_2 is increased by pressure. The lower curve is for $x_2 = 0.25$, and the upper for $x_2 = 0$.

The fictive compressibility, $\bar{\beta}'_1$, of the water in solution may be computed from equations similar to (34) or (35) but with opposite subscripts. In sodium chloride solutions at 25° $\bar{\beta}'_1$ does not differ notably from the compressibility of pure water; moreover, $\bar{\beta}'_1$ is always greater than β' for the solution and less than β' for pure water, at the same pressure.

Determination of Equilibrium by the Thermodynamic Method

Calculation of μ_1 and μ_2 .—As explained in the introduction the equilibrium between the various phases in a system depends upon the values of the chemical potential, μ , for each component in each phase,²⁷ and the μ 's

²⁷ Instead of the potential, μ , we might have used the activity, a , which is related to μ as follows: $d\mu_n = (RT/M_n)d \ln a_n$, R being the gas constant, M_n the (arbi-

at any pressure can be calculated directly from the fictive volumes. By integration of equation (2) we obtain

$$(x, \text{constant}) \quad \mu_1 = (\mu_1)_0 + \int_1^P \bar{v}_1 dP \quad (36)$$

from which μ_1 can readily be determined. If we use the equation in this form, however, it will be found that we must deal with large numbers; four or five significant figures are required to express the data with the necessary accuracy. It is much more convenient to deal with the *differences* of μ_1 . Since equation (36) holds for any concentration of sodium chloride, including zero, it follows that

$$(x, \text{constant}) \quad \Delta_x \mu_1 \equiv \mu_1 - (\mu_1)_w = \Delta_x (\mu_1)_0 + \int_1^P \Delta_x \bar{v}_1 dP \quad (37)$$

Here, as before, the subscript zero refers to atmospheric pressure, and $\Delta_x \bar{v}_1$ denotes the difference, $\bar{v}_1 - (\bar{v}_1)_w$ at any pressure, between \bar{v}_1 for the specified concentration and its value in pure water at the same pressure. By means of this equation we may calculate $\Delta_x \mu_1$ directly from the values of $\Delta_x \bar{v}_1$ as given in Table VI, and it is important to note that in this case it is not necessary to deal with large numbers; in only one instance ($P = 1$, $x_2 = 0.25$) are more than two digits required for representing the data for $\Delta_x \bar{v}_1$. The integration can be carried out analytically if \bar{v}_1 can be expressed as an integrable function of P ; or, if this is not convenient, we can resort to graphical or numerical integration. If \bar{v}_1 is expressed in cc. and P in bars, μ_1 or $\Delta \mu_1$ in equations (36) or (37) will be in decijoules per gram. Satisfactory results for the values of the definite integral in (37) were obtained by numerical integration, the well-known "one-third rule" being used except at high pressures, for which the simpler "trapezoidal rule" was sufficiently accurate.

In Table VIII are shown the results for μ_1 , the chemical potential of water, in sodium chloride solutions under pressure. The table gives first the values of $\Delta_x \mu_1 - \Delta(\mu_1)_0$ as calculated directly from (37), and second the results for $\Delta_x \mu_1$, which were obtained by adding $\Delta(\mu_1)_0$ at the same concentration. Data on μ_1 at atmospheric pressure, that is $(\mu_1)_0$, may be secured from several sources, such as the freezing points or vapor pressures of the solutions, or the e. m. f. of cells containing the solutions. From (a) trary) formula weight of the component in question, and T the absolute temperature. The activity is more clearly advantageous in those instances in which the concentration of the component in question is very small. But along the freezing point-solubility curves in the system, NaCl-H₂O, the concentration (in the solution) of the component corresponding to the solid phase in equilibrium with the solution is always fairly large. Moreover, the numerical calculation of a involves the choice of an arbitrary constant, and the choice of this constant would affect the way in which the activity would be utilized in the determination of equilibrium under pressure. It seems preferable for the present to use the more fundamental μ and to reserve the discussion of activity under pressure for a future occasion.

TABLE VIII

CHEMICAL POTENTIAL, μ_1 , OF WATER IN SODIUM CHLORIDE SOLUTIONS UNDER PRESSURE

$\Delta_x \mu_1$ is the difference (in joules) between the value of μ_1 for the particular concentration and the value for pure water at the same pressure. $\Delta_x(\mu_1)_0$ is the difference at $P = 1$

Pressure in bars	$(\Delta_x \mu_1)_0 - \Delta_x \mu_1$	$(\mu_1)_w - \mu_1$ ($= -\Delta_x \mu_1$)	$(\Delta_x \mu_1)_0 - \Delta_x \mu_1$	$(\mu_1)_w - \mu_1$ ($= -\Delta_x \mu_1$)	$(\Delta_x \mu_1)_0 - \Delta_x \mu_1$	$(\mu_1)_w - \mu_1$ ($= -\Delta_x \mu_1$)
	$x_2 = 0$		$x_2 = 0.05$		$x_2 = 0.10$	
1	0	0	0.00	4.23	0.00	9.04
1000	0	0	.06	4.3	.22	9.3
2000	0	0	.11	4.3	.37	9.4
3000	0	0	.15	4.4	.47	9.5
4000	0	0	.18	4.4	.53	9.6
5000	0	0	.20	4.4	.57	9.6
6000	0	0	.22	4.4	.62	9.7
7000	0	0	.24	4.4	.68	9.7
8000	0	0	.25	4.5	.72	9.8
9000	0	0	.25	4.5	.73	9.8
10000	0	0	.25	4.5	.73	9.8
11000	0	0	.25	4.5	.73	9.8
	$x_2 = 0.15$		$x_2 = 0.20$		$x_2 = 0.25$	
1	0.00	15.65	0.00	23.95	0.00	34.90
1000	.45	16.1	.72	24.7	1.01	35.9
2000	.77	16.4	1.26	25.2	1.76	36.7
3000	1.01	16.7	1.67	25.6	2.35	37.3
4000	1.20	16.9	1.99	25.9	2.84	37.7
5000	1.36	17.0	2.28	26.2	3.24	38.1
6000	1.49	17.1	2.52	26.5	3.59	38.5
7000	1.60	17.3	2.73	26.7	3.88	38.8
8000	1.68	17.3	2.89	26.8	4.10	39.0
9000	1.74	17.4	3.04	27.0	4.29	39.2
10000	1.78	17.4	3.18	27.1	4.42	39.3
11000	1.82	17.5	3.28	27.2	4.49	39.4
12000			3.36	27.3	4.55	39.5

the principle of the equality of the μ 's in the different phases, (b) equation (2), and (c) an assumption that the ideal gas law holds for the vapor, it follows that

$$\mu_1 - (\mu_1)_w = \Delta(\mu_1)_0 = \frac{RT}{M_1} \ln \frac{p}{p_0} \tag{38}$$

By means of this equation and the results of Bousfield and Bousfield²⁸ for the vapor pressures at 18° of sodium chloride solutions $\Delta(\mu_1)_0$ was calculated, and then corrected to 25° by the formula

$$(\Delta\mu_1)_{T-T_0} = \frac{T_0}{T} (\Delta\mu_1)_T - \left(\frac{T_0}{T} - 1\right) (\Delta\bar{h}_1)_{T-T_0} + \left(\frac{T_0}{T} - 1 - \ln \frac{T_0}{T}\right) T_0 \Delta(\bar{c}_P)_1 \tag{39}$$

²⁸ Bousfield and Bousfield, *Proc. Roy. Soc. (London)*, **A103**, 429-443 (1923). That these results are quite reliable is indicated by some unpublished measurements by Dr. R. E. Gibson of this Laboratory.

which is a convenient form of the well-known equation for expressing free energy as a function of temperature. Here T_0 is a fixed absolute temperature (in this instance 298.1°), T is the temperature at which $\Delta\mu_1$ is first determined, $\Delta\bar{h}_1$ is the difference in fictive enthalpy (or partial heat content) of the water, and $\Delta(\bar{c}_P)_1$ is the difference in fictive, or partial, heat capacity, the differences being taken in the same sense as with $\Delta\mu_1$.

For comparison, $\Delta\mu_1$ was also calculated from the known freezing points of sodium chloride solutions by the formula

$$(\Delta\mu_1)_T = -1.223(-\Delta t) + 3.82 \times 10^{-3}(-\Delta t)^2 + 4.6 \times 10^{-6}(-\Delta t)^3 \quad (40)$$

This is a modified form of the equation given by Lewis and Randall (Ref. 5b, footnote 1, page 283), for calculating free energies from the freezing point lowering, $-\Delta t$, in aqueous solutions, and gives $\Delta\mu_1$ at the freezing temperature, T , of the particular solution. The $\Delta\mu_1$'s were then corrected to 25° by (39). The values of $\Delta\mu_1$ obtained by the two methods agreed quite satisfactorily.²⁹ Their average is shown for each concentration, opposite the entry, $P = 1$, in Table VIII.

The procedure for calculating μ_2 under pressure is the same as for μ_1 , except that μ_2 being negatively infinite at $x_2 = 0$, we choose the saturated solution for reference, and by analogy with (37) we write

$$\Delta_x\mu_2 \equiv \mu_2 - (\mu_2)_s = \Delta(\mu_2)_0 + \int_1^P (\bar{v}_2 - (\bar{v}_2)_s) dP \quad (41)$$

in which the subscript s refers to the concentration of the solution saturated at atmospheric pressure ($x_2 = 0.2642$). The necessary data for $\bar{v}_2 - (\bar{v}_2)_s$ are readily obtained from Table VI, by a slight extrapolation to the reference concentration. As in the calculation of μ_1 , numerical integration was employed. The results for $\Delta_x\mu_2 - \Delta(\mu_2)_0$ are given in Table IX. By adding $\Delta(\mu_2)_0$ we could obtain the values of $\Delta_x\mu_2$, but since they are not essential in connection with the present investigation, they will not be tabulated here. Attention is directed to the fact that although, as x_2 approaches zero, $\Delta_x\mu_2$ and μ_2 become negatively infinite, a finite value can be assigned to their increase under pressure, and can be computed by means of equation (41).

The Freezing Pressure Curve of Ice_{V1}.—After the somewhat lengthy preparatory computation we pass now to the determination of the freezing pressure and solubility curves—which is relatively simple. At 25° water freezes to ice_{V1} at a pressure of 9630 bars. Addition of a solute to the water will raise the freezing pressure, just as at atmospheric pressure it

²⁹ In many instances it would be advantageous to calculate μ_1 from μ_2 , which in turn may be calculated from available tables for γ , the activity coefficient of the solute. For a di-ionic electrolyte $a_2 = m^2\gamma^2$, m being the molality; the relation between a_2 and μ_2 is given in footnote 27; and μ_1 may be determined from μ_2 by the expression

$$\mu_1 = - \int_{x_1}^{x_2} \frac{d\mu_2}{x_1}$$

TABLE IX

CHANGE OF CHEMICAL POTENTIAL, μ_2 , OF SODIUM CHLORIDE IN AQUEOUS SODIUM CHLORIDE SOLUTIONS UNDER PRESSURE (JOULES) $\Delta_x \mu_2$ is written for $\mu_2 - (\mu_2)_0$ and is the difference between the value of μ_2 in the given concentration (and at any pressure) and its value in a 26.42% solution at the same pressure. The subscript zero refers to atmospheric pressure

Pressure in bars	$(\Delta_x \mu_2)_0 - \Delta_x \mu_2$ in joules						
	$x_2 = 0$	$x_2 = 0.05$	$x_2 = 0.10$	$x_2 = 0.15$	$x_2 = 0.20$	$x_2 = 0.25$	$x_2 = 0.2642$
1	0.0	0.0	0.0	0.0	0.0	0.0	0
1000	9.5	6.1	4.2	2.6	1.3	.2	0
2000	16.6	10.6	7.3	4.5	2.2	.4	0
3000	22.5	14.2	9.8	6.0	2.9	.6	0
4000	27.5	17.2	11.8	7.2	3.5	.7	0
5000	31.9	19.6	13.4	8.2	3.9	.7	0
6000	35.6	21.7	14.8	8.9	4.3	.8	0
7000	38.9	23.4	15.9	9.6	4.5	.8	0
8000	41.9	24.9	16.9	10.1	4.7	.9	0
9000	44.6	26.1	17.7	10.5	4.8	.9	0
10000	47.0	27.2	18.3	10.8	4.9	.9	0
11000	..	28.0	18.9	11.1	5.0	.9	0
12000	5.0	.9	0

will lower the freezing temperature. In either case the equilibrium is determined by the principle of the equality of the μ 's. More specifically, a solution of a given concentration will be in stable equilibrium with ice_{VI} at that pressure for which $\mu_{VI} = \mu_1$. In actual practice it is more convenient to deal with the difference between μ of the solid or of the water in the solution and the μ of pure water at the same pressure. Thus

$$\mu_{VI} - (\mu_1)_w = \mu_1 - (\mu_1)_w \equiv \Delta_x \mu_1 \quad (42)$$

is the criterion of equilibrium, in the form actually used. Results for $\Delta_x \mu_1$ at various pressures and for various concentrations have been given in Table VIII; and $\mu_{VI} - (\mu_1)_w$ can be calculated readily from the specific volume of water and of ice_{VI}. For this purpose equation (36) or (37) takes the form

$$\mu_{VI} - \mu_w = \int_{P_0}^P (v_{VI} - v_w) dP \quad (43)$$

P_0 being the freezing pressure of pure water (at the given temperature). The specific volume of ice_{VI} at P_0 (9630 bars) was determined from the change of volume upon melting, by the piston-displacement method. The change in volume for 1 g., which is $v_w - v_{VI}$ at P_0 , was found to be 0.0714 cc. This is in fair agreement with Bridgman's³⁰ value, 0.0707, at the same pressure, and we shall take the average, 0.0710, as the volume difference. Subtracting this value from v_w at 9630 bars gives 0.7388 for v_{VI} at P_0 . From the compressibility³¹ of ice_{VI}, we obtain Δv_{VI} , the change in v_{VI}

³⁰ Bridgman, *Proc. Am. Acad. Arts Sci.*, **47**, 537 (1912).

³¹ For ice_{VI} β' has been found by Bridgman [*Proc. Am. Acad. Arts Sci.*, **48**, 362 (1912)] to be 0.46×10^{-6} per bar, and not to change very much over the pressure range 4000 to 10,000 bars.

with pressure, and then v_{VI} at the various pressures, as shown in Table X. The table also shows the values of $\mu_{VI} - \mu_w$ obtained from $v_{VI} - v_w$ by use of equation (43), with numerical integration. The results for 13,000 and for 14,000 bars were obtained by extrapolation.

TABLE X
DIFFERENCE BETWEEN μ FOR WATER AND FOR ICE_{VI} AT VARIOUS PRESSURES
The subscripts w and VI refer to the pure liquid and solid, respectively

Pressure in bars	v_w g./sq. cm.	Δv_{VI} g./sq. cm.	v_{VI} g./sq. cm.	$v_{VI} - v_w$ g./sq. cm.	$\mu_{VI} - \mu_w$ joules
7000	0.8402	0.0121	0.7509	-0.0893	20.9
8000	.8278	.0075	.7463	- .0815	12.4
9000	.8166	.0029	.7417	- .0749	4.6
9630	.8098	.0000	.7388	[- .0710]	0.0
10000	.8059	- .0017	.7371	- .0688	- 2.6
11000	.7964	- .0063	.7325	- .0639	- 9.2
12000	.7876	- .0109	.7279	- .0597	-15.4
13000				(- .0558)	-21.2
14000				(- .0524)	-26.6

The freezing pressure for each concentration was determined by finding the pressure at which $\Delta_x \mu_1$ equals $\mu_{VI} - \mu_w$, which was done graphically by plotting $\Delta_x \mu_1$ against P for each x_2 and finding the intersection with the curve for $\mu_{VI} - \mu_w$, as illustrated in Fig. 10. The same result could have been obtained by making a table of $\mu_1 - \mu_{VI}$ and finding, by interpolation, the pressure at which this quantity becomes zero, but the method used probably shows more clearly the relations involved. The curves of Fig. 10 also give a graphical illustration of the important fact that when the pressure is very high $\Delta_x \mu_1$ hardly changes at all with increasing pressure. This fortunate circumstance allows us to extrapolate $\Delta_x \mu_1$ with safety and, since the extrapolation of $\mu_{VI} - \mu_w$ is also easy, to obtain reliable results for the freezing pressure curve at pressures considerably beyond the usual experimental range.

In Table XI are shown the freezing pressures for the solutions of various concentrations, as determined from the intersections of the curves in Fig. 10. By inspection of the table it may be seen that with increasing concentration (at constant temperature) the freezing pressure is raised at a

TABLE XI
FREEZING PRESSURE OF ICE_{VI} IN CONTACT WITH SODIUM CHLORIDE SOLUTIONS AT 25°

wt. fraction of NaCl	P in bars	$P - P_0$ (ice _{VI})	$t_0 - t$ (ice _I)	$\frac{t_0 - t}{P - P_0} 10^3$
0.00	9630	0	0.00	...
.05	10270	640	3.03	0.47
.10	11070	1440	6.54	.45
.15	12320	2690	10.89	.41
.20	14130	4500	16.47	.37
.25	16570	6940	23.96	.35

rapidly increasing rate. This is analogous to the usual course of freezing point curves (at variable temperature and constant pressure), but it is evident from the tabulated values of the ratio of the freezing temperature lowering to the freezing pressure elevation for the same concentration that the curve of the latter will show the greater increase in slope.

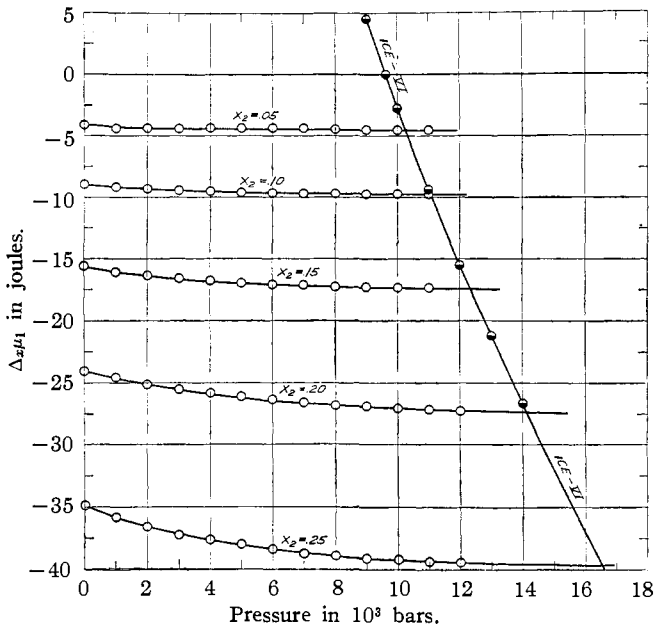


Fig. 10.—The chemical potential, μ_1 , of water in sodium chloride solutions at 25° (referred to the μ of pure water at the same pressure). The intersections with the curve for the μ of ice_{v1} give the freezing pressures of the various solutions.

The Solubility Curve. (a) Sodium Chloride.—The determination of the equilibrium curve with sodium chloride as the solid phase could be carried out in the same manner that was used for the freezing pressure curve, and, in many instances this would be the best procedure. But, as will be seen later, the change in solubility of sodium chloride under pressure is so small that in this case another procedure is more convenient. It will be sufficient to evaluate the derivative expressing the change of solubility with pressure. For two-phase equilibrium in a two-component system we can write the general equation³²

$$\frac{\bar{h}_2'' - \bar{h}_2'}{T} dT - (\bar{v}_2'' - \bar{v}_2') dP = \frac{\partial \mu_2''}{\partial x_2} dx_2'' - \frac{\partial \mu_2'}{\partial x_2} dx_2' \quad (44)$$

³² In a slightly different form this equation is given by Adams, *J. Wash. Acad. Sci.*, 16, 274 (1926). See also Williamson and Morey, *THIS JOURNAL*, 40, 54 (1918).

if component 2 occurs in both phases—and a similar equation for component 1 if it is actually present in each phase. The prime superscripts refer to one phase and the double primes to the other phase. By \bar{h}_2 is meant the fictive, or partial, enthalpy of component 2. This equation follows directly from (a) the principle of the equality of the μ 's and (b) the fact that in any phase μ is a function of T , P and x . From equation (44) there can be written immediately any of the "solution laws," such as for freezing point lowering, boiling point elevation, vapor pressure lowering, osmotic pressure, and so on, as well as the one here sought. If the primes refer to the solid sodium chloride, we have from (44), since T and x_2' are constant, the desired relation for the effect of pressure on solubility,

$$\frac{dx_2}{dP} = \frac{v_s - \bar{v}_2}{\partial\mu_2/\partial x_2} \quad (45)$$

Here v_s ($\equiv \bar{v}_2'$) is the specific volume of solid sodium chloride, and the superscripts, being no longer necessary, are omitted. In this equation, if P is in bars, and v in cc., $\partial\mu_2/\partial x_2$ must be expressed in decijoules.

Of the quantities necessary for use in (45), \bar{v}_2 has been given in Table VII, v_s is easily obtained from k for sodium chloride (see Table II) together with the specific volume at atmospheric pressure, and $\partial\mu_2/\partial x_2$ may be determined from the data used to calculate μ_1 , or from μ_1 itself. It is considerably more difficult to obtain a reliable value for the slope of μ_2 than for the quantity itself. This is largely because there are very few suitable measurements in strong solutions. The calculation of $\partial\mu_2/\partial x_2$ was made in a number of different ways, of which the best five were as follows. (A) The values of γ as given by Lewis and Randall³³ were represented as a quadratic function of \sqrt{m} , m being the molality, and $\partial\mu_2/\partial x_2$ calculated from $\partial\gamma/\partial m$ by the equation

$$\frac{\partial\mu_2}{\partial x_2} = \frac{2RT}{M_2} \frac{(1000 + mM_2)^2}{1000 M_2} \left(\frac{1}{m} - \frac{1}{\gamma} \frac{\partial\gamma}{\partial m} \right) \quad (46)$$

in which M_2 is the formula weight of sodium chloride. (B) These values of γ were represented also by an equation giving $\log \gamma$ as a quadratic function of $\log m$, and (46) then applied. (C) From the e. m. f. data of Allmand and Polack³⁴ γ was recalculated and fitted by a quadratic function of \sqrt{m} . (D) The measurements on vapor pressure lowering,²⁸ already referred to, were applied to the equation

$$\frac{\partial\mu_2}{\partial x_2} = - \frac{x_1 RT}{x_2 M_1 p} \frac{dp}{dx_2} \quad (47)$$

obtained by differentiating (38) with respect to x_2 and multiplying by $-x_1/x_2$, the value of dp/dx_2 being calculated from tabular differences. (E) Use was made of the change of solubility with temperature together with the following relation, which may be derived from (44)

³³ Lewis and Randall, Ref. 5b, p. 351.

³⁴ Allmand and Polack, *J. Chem. Soc.*, **115**, 1020-1039 (1919).

$$\text{(At saturation)} \quad \frac{\partial \mu_2}{\partial x_2} = \frac{\Delta \bar{h}_2}{T} \frac{dx_2}{dT} \quad (48)$$

dx_2/dT being taken as 0.00011. The results obtained for $\partial \mu_2/\partial x_2$, at $P = 1$ and $x_2 = 0.2642$, by these five methods were, respectively, 755, 750, 710, 744 and 691 joules; the average, 730, will be taken as the most probable value. Other methods, such as representing γ , or the e. m. f. \mathbf{E} , as a quadratic function of m gave results for $\partial \mu_2/\partial x_2$ that were widely different and probably not so trustworthy.

Before proceeding to the calculation of the solubility under pressure, we must take account of the fact that under pressure (and at constant concentration) $\partial \mu_2/\partial x_2$ will not be the same as at atmospheric pressure. We have

$$\frac{\partial}{\partial P} \left(\frac{\partial \mu_2}{\partial x_2} \right) = \frac{\partial}{\partial x_2} \left(\frac{\partial \mu_2}{\partial P} \right) = \left(\frac{\partial \bar{v}_2}{\partial x_2} \right)_P \quad (49)$$

At any pressure and concentration $\partial \bar{v}_2/\partial x_2$ can be calculated from the known values of $\Delta_P v$, the change (with pressure) of the specific volume of the solution. Thus from (16) it follows that

$$(P, \text{ constant}) \quad \frac{\partial \bar{v}_2}{\partial x_2} = \frac{\partial^2 v_0}{\partial x_2^2} + x_1 \frac{\partial^2 \Delta v}{\partial x_2^2} \quad (50)$$

But in the present instance it is sufficiently accurate to determine $\partial \bar{v}_2/\partial x_2$ directly from the tabular differences of \bar{v}_2 (see Table VII), and thence to calculate the change of $\partial \mu_2/\partial x_2$ under pressure by integration of equation (49).

The known values of v_s , \bar{v}_2 and $\partial \mu_2/\partial x_2$ at various pressures are then inserted in the integrated form of (45)

$$x_2 = (x_2)_0 + \int_1^P \frac{v_s - \bar{v}_2}{\partial \mu_2/\partial x_2} dP \quad (51)$$

and x_2 calculated by numerical integration. The essential steps and the results for x_2 , the solubility of sodium chloride under pressure, are shown in Table XII. The values of \bar{v}_2 and $\partial \mu_2/\partial x_2$ under the sign of integration were taken at $x_2 = 0.2642$, which is the solubility³⁵ of sodium chloride at 25° and atmospheric pressure.

For greater accuracy the results thus obtained for x_2 at each pressure should be regarded as first approximations, and new values of \bar{v}_2 and of $\partial \mu_2/\partial x_2$ calculated at the approximated x_2 's, and the integration repeated; but the change of solubility of sodium chloride under pressure is so small that this is hardly necessary. It may be noted that the solubility change at pressures above 12,000 bars is obtained from the easily extrapolated values of $\partial \mu_2/\partial x_2$ and of $v_s - \bar{v}_2$.

(b) $\text{NaCl} \cdot 2\text{H}_2\text{O}$.—Within a certain range of temperature and pressure the stable solid phase in contact with the solution is not NaCl but NaCl·

³⁵ Adams and Hall, *J. Wash. Acad. Sci.*, **21**, 191 (1931).

TABLE XII
SOLUBILITY OF SODIUM CHLORIDE IN WATER AT VARIOUS PRESSURES. TEMPERATURE, 25°

Pressure in bars	v_3	\bar{v}_3 at $x_2 = 0.264$	$v_3 - (\bar{v}_3)_{\text{saln.}}$ $\times 10^4$	$\frac{\partial \bar{v}_3}{\partial x_2}$ at $x_2 = 0.264$	$\frac{\partial \mu_3}{\partial x_2}$ joules	$10^2 \Delta x_2$ increase of solubility	x_2
1	0.4625	0.4019	606	0.188	730	0.00	0.2642
500	.4615	.4137	478	.164	739	.37	.2779
1000	.4606	.4247	359	.140	746	.65	.2707
1500	.4596	.4336	260	.120	753	.86	.2728
2000	.4587	.4398	189	.106	759	1.01	.2743
3000	.4569	.4488	81	.074	768	1.18	.2760
4000	.4551	.4550	1	.054	774	1.23	.2765
5000	.4533	.4584	-51	.044	779	1.20	.2762
6000	.4516	.4601	-85	.030	783	1.11	.2753
7000	.4499	.4610	-111	.022	785	.99	.2741
8000	.4482	.4609	-127	.012	787	.84	.2726
9000	.4465	.4605	-140	.010	788	.67	.2709 ^a
10000	.4449	.4596	-147	.004	789	.49	.2691 ^a
11000	.4433	.4586	-153	.000	789	.30	.2672 ^a
12000	.4417	.4580	-163	.000	789	.09	.2651
13000			(-169)		(789)	-.13	.2629
14000			(-175)		(789)	-.34	.2608
15000			(-181)		(789)	-.57	.2587
16000			(-187)		(789)	-.80	.2562

^a Metastable solubility. NaCl·2H₂O is the stable solid phase at the corresponding pressures.

2H₂O. It was found by Adams and Gibson³⁶ that the incongruent melting point of NaCl·2H₂O is raised by pressure, reaches a maximum temperature at about 10,000 bars, and then decreases. For a clear understanding of how this affects the present problem it is necessary to refer to the (P, t) diagram of the inversion, as given by Fig. 11. The two arrows mark the points at which the 25° line cuts the (P, t) curve and show that along the solubility (P, x) curve at 25° NaCl·2H₂O is the stable phase at all pressures between 8000 and 11,800 bars. Therefore in the last column of Table XII the results for this pressure range represent the *metastable* solubility of sodium chloride. Incidentally, it may be noted that if the present investigation had been made at a temperature 1° higher, NaCl·2H₂O would not have entered the system.

In order to determine the solubility curve of the dihydrate we could choose as the components for the solution, NaCl·2H₂O and excess of H₂O, and proceed exactly as above, first obtaining v_d , the specific volume of solid NaCl·2H₂O, \bar{v}_3 the fictive volume of NaCl·2H₂O in solution, and $\partial \mu_3 / \partial x_2$, and then using the equation, similar to (51)

$$x_2 = (x_2)_i + \int_{P_i}^P \frac{v_d - \bar{v}_3}{\partial \mu_3 / \partial x_2} dP \quad (52)$$

³⁶ Adams and Gibson, THIS JOURNAL, 52, 4252-4264 (1930).

in which the subscript i refers to the lower of the two pressures at which both NaCl and NaCl·2H₂O are stable in contact with solution. The same end can be accomplished, with less labor, by proceeding directly from the already available values of \bar{v}_2 and $\partial\mu_2/\partial x_2$ and the known change in volume when NaCl·2H₂O decomposes to sodium chloride plus saturated solution.

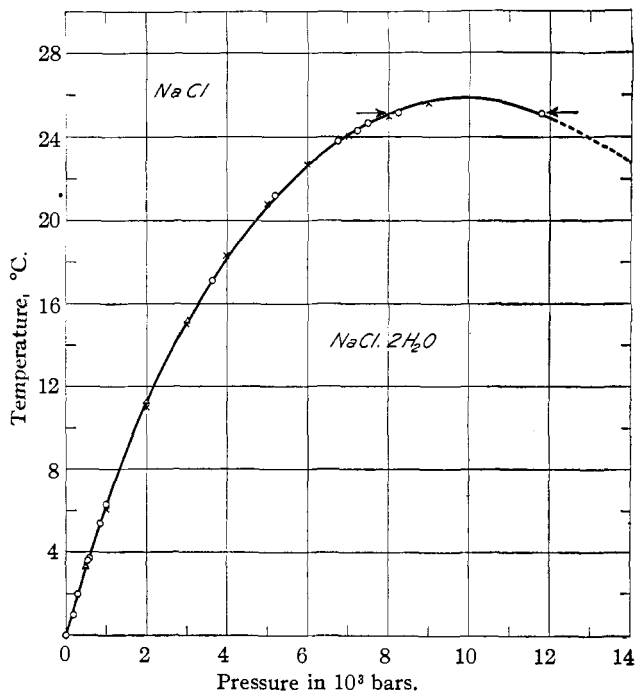


Fig. 11.—The (P, t) curve for the incongruent melting of NaCl·2H₂O (after Adams and Gibson). The two points where the line for 25° crosses the curve are indicated by arrows, and correspond to the pressures between which, along the solubility curve in the (P, x) diagram, the dihydrate is the stable phase (see Fig. 12).

When 1 g. of dihydrate goes into solution, the increase of volume obviously is $-(v_d - \bar{v}_3)$. An identical volume change will occur if the dihydrate first inverts, forming ϕ grams of anhydrous salt, which then dissolves. It may be readily shown that $\phi = (x_0 - x_2)/(1 - x_2)$, x_2 being the concentration of the saturated solution and x_0 the ratio of the formula weight of NaCl to that of NaCl·2H₂O. Hence the total change of volume is $\Delta V + \phi(\bar{v}_2 - v_s)$, ΔV being the increase in volume accompanying the incongruent melting of 1 g. of NaCl·2H₂O, and since this equals $-(v_d - \bar{v}_3)$, we have

$$v_d - \bar{v}_3 = \phi(v_s - \bar{v}_2) - \Delta V \quad (53)$$

Furthermore, it may be easily shown³⁷ that

$$\frac{\partial \mu_3}{\partial x_2} = \phi \frac{\partial \mu_2}{\partial x_2} \quad (54)$$

which is a relation of the greatest importance for dealing with equilibrium curves that involve solid phases not variable in composition and not identical with either of the originally chosen components. By substituting (53) and (54) in (52) we obtain the working equation

$$x_2 = (x_2)_i + \int_{P_i}^P \frac{v_s - \bar{v}_2 - \frac{\Delta V}{\phi}}{\partial \mu_2 / x_2} dP \quad (55)$$

which is in convenient form for determining the solubility curve of the dihydrate from data already in hand. At 25°, ϕ is found to be 0.482, and the values of ΔV at various pressures may be taken from the paper mentioned above.³⁶

TABLE XIII
SOLUBILITY, AT 25°, OF NaCl·2H₂O IN H₂O UNDER PRESSURE

Pressure in bars	$\frac{\Delta V}{\text{NaCl} \cdot 2\text{H}_2\text{O}} \rightarrow \text{NaCl}$	$\Delta V/\phi$	$v_s - \bar{v}_2 - \frac{\Delta V}{\phi}$	$10^2 \Delta x_2$	Wt. fraction (of NaCl)
4000	0.0144	0.0298	-0.0297	2.09	0.2851 ^a
5000	.0106	.0220	-.0271	1.72	.2814 ^a
6000	.0076	.0158	-.0243	1.39	.2781 ^a
7000	.0051	.0106	-.0217	1.10	.2752 ^a
8000	.0029	.0060	-.0187	.84	.2726
9000	.0009	.0019	-.0159	.62	.2704
10000	-.0008	-.0017	-.0130	.43	.2685
11800	-.0022	-.0045	-.0108	.28	.2670
12000	-.0033	-.0068	-.0095	.15	.2657 ^a

^a Metastable solubility. Sodium chloride is the stable solid phase at the corresponding pressures. If the calculation be extended downward to $P = 1$, the value obtained for the metastable solubility of NaCl·2H₂O at atmospheric pressure is 30.2 wt. per cent. (of the anhydrous salt).

The results of the calculation are shown in Table XIII, which gives the solubility of NaCl·2H₂O in terms of x_2 , the weight fraction of anhydrous salt in the saturated solution. By comparison of this table with the pre-

³⁷ The relation can be derived as follows: Let the two components in the solution be NaCl·2H₂O and excess H₂O, instead of, as usual, NaCl and total H₂O. Then for 1 g. of solution the mass, m_3 , of the component NaCl·2H₂O will be x_2/x_0 , and the mass, m_4 , of (excess) H₂O will be $1 - (x_2/x_0)$. According to the well-known equation (97) of Gibbs (*op. cit.*, p. 88), at constant P and t , $m_3 d\mu_3 = m_4 d\mu_4 \equiv m_4 d\mu_1$.

$$\text{Hence} \quad \frac{\partial \mu_3}{\partial x_2} = -\frac{m_4}{m_3} \frac{\partial \mu_1}{\partial x_2} = \frac{x_2}{x_1} \frac{m_4}{m_3} \frac{\partial \mu_2}{\partial x_2} = \frac{x_0 - x_2}{1 - x_2} \frac{\partial \mu_2}{\partial x_2} = \phi \frac{\partial \mu_2}{\partial x_2}$$

Expressed in molal units the equivalent relation is

$$\frac{\partial \bar{F}_3}{\partial X_2} = (N + 1) \frac{X_0 - X_2}{1 - X_2} \frac{\partial \bar{F}_2}{\partial X_2}$$

in which \bar{F} denotes the partial molal free energy, X_2 is the mole fraction of the salt in the solution, X_0 is that in the hydrate and N is the total number of moles of salt and water in one mole of the hydrate.

ceding one it will be observed that in the pressure range for which the dihydrate is the stable form, the dihydrate has the lesser solubility—which, of course, is as it should be. If the calculation be extended downward to $P = 1$, the (metastable) solubility of $\text{NaCl}\cdot 2\text{H}_2\text{O}$ at atmospheric pressure and at 25° is found to be 30.2 weight per cent. This is in good agreement with the result obtained by graphical extrapolation of the ordinary solubility curve (t, x) upward from 0° .

The Equilibrium Diagram

General Characteristics.—The results for the freezing pressure curve of ice-III and for the two solubility curves are plotted in Fig. 12. On the right of the diagram the solubility curves are shown on an enlarged scale.

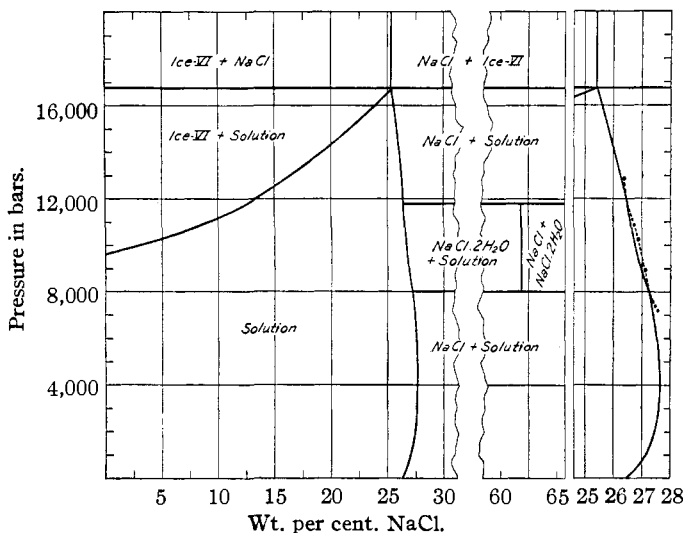


Fig. 12.—Equilibrium diagram for the system, $\text{NaCl-H}_2\text{O}$, under pressure at 25° . The freezing pressure curve and the solubility curve intersect at a pressure eutectic. On the right the solubility curve is shown on an enlarged scale.

The solubility of sodium chloride, which at atmospheric pressure is 26.42%, is increased at first by pressure but the rate of change falls off at higher pressures and a maximum is reached at 4000 bars, the solubility at this point being 27.6%. A further increase of pressure causes the solubility to diminish steadily, but, at pressures between 8000 and 11,800 bars, $\text{NaCl}\cdot 2\text{H}_2\text{O}$ not sodium chloride is the solid phase that is stable in contact with the liquid (see Fig. 11). In other words, increase of pressure causes the system to pass through two transformation points at the pressures indicated. Although for this pressure range the equilibrium line is the solubility curve of the dihydrate, the rate of the reaction in the direction of the formation

of $\text{NaCl}\cdot 2\text{H}_2\text{O}$ is practically *nil*, and it is easy to realize experimentally the unstable portion of the sodium chloride solubility curve, which in the diagram is shown by the dotted line. Above 11,800 bars sodium chloride is again the stable solid phase and its solubility diminishes steadily until at 16,700 bars the curve intersects the freezing pressure curve for ice_{VI} , at which point the solubility has fallen to 25.4%. The freezing pressure line starts on the left at 9630 bars (the freezing pressure of pure water) and for increasing concentration curves upward with rapidly increasing slope. The remaining boundary lines of the various fields in the diagram are drawn in accordance with the usual conventions. At the place where the freezing pressure and the solubility curve meet three phases are present; the intersection is therefore an invariant point (at constant temperature). In all respects it is similar to an ordinary eutectic in a (t, x) diagram, and hence it may be called a pressure eutectic. When any mixture of sodium chloride and water at 25° is compressed, the pressure after reaching 16,700 bars will remain constant until the remaining solution has completely solidified to $\text{NaCl} + \text{Ice}_{\text{VI}}$.

If the mixture contains 27.2%, or more, of sodium chloride, the pressure will remain constant also during the formation and during the decomposition of dihydrate at the transformation pressures already mentioned (provided that equilibrium is always attained). These two invariant points are analogous to incongruent melting points on a temperature-concentration diagram, but in the present instance it should be noted that at both invariant points we have present the same three phases. A similar situation in an ordinary melting diagram (t, x) is not known, but might exist for a mixture that, when heated at constant pressure, first melted incongruently and then at a higher temperature became completely solid again, that is, if the (P, t) curve of the incongruent melting reached a maximum pressure and then bent back toward the t -axis.

If a mixture of water and sodium chloride containing 27.5% of the latter is subjected to increasing pressure, and if the system remains always in equilibrium, its behavior will be as follows. At first the liquid phase will dissolve more salt, because initially the solubility is increased by pressure. At 2300 bars all the solid will have disappeared, and from 2300 to 6250 bars the system will consist solely of homogeneous solution, but at the latter pressure solid sodium chloride will begin to crystallize out. Upon further increase of pressure the solid sodium chloride increases in amount, until at 8000 bars all the solid reacts with water to form $\text{NaCl}\cdot 2\text{H}_2\text{O}$, which at 11,800 bars breaks up to form sodium chloride again. The solubility then continues to decrease, causing more sodium chloride to be deposited, until finally at 16,700 bars the whole mass solidifies to a mixture of ice_{VI} and sodium chloride. The line representing the increase of pressure has crossed v_2 of the eight fields in the diagram, and the changes

that have taken place may be indicated thus: $\text{NaCl} + \text{Soln.} \xrightarrow{2300} \text{Soln.}$
 $\xrightarrow{6250} \text{NaCl} + \text{Soln.} \xrightarrow{8000} \text{NaCl} \cdot 2\text{H}_2\text{O} + \text{Soln.} \xrightarrow{11800} \text{NaCl} + \text{Soln.} \xrightarrow{16700}$
 $\text{Ice}_{\text{VI}} + \text{NaCl}.$

It is instructive to compare a pressure diagram, such as the one shown here, with the more familiar melting diagram, in which temperature is variable and pressure constant. Both consist of freezing point-solubility lines, which meet at eutectics or other invariant points and divide the diagram into fields representing the conditions of stability of the various combinations of phases. Indeed, the two kinds of diagrams are quite similar in appearance except that the pressure diagram seems to be upside down. This is because, in general, *increasing* pressure produces the same kind of effect as *decreasing* temperature. For example, materials freeze when the temperature is lowered, and (as a rule) when the pressure is raised. Furthermore, the addition of another material to a pure substance usually lowers its freezing temperature and raises its freezing pressure. This is equivalent to the statement that solubility normally increases with temperature, but normally decreases with pressure.

Comparison with Direct Measurements.—The freezing pressure and solubility curves of the equilibrium diagram were plotted from the results of the indirect (thermodynamic) method, but it was possible to check part of each curve by direct determinations of equilibrium. The measurements mentioned above^{2,3} on the solubility of sodium chloride at low pressures by three different methods agree fairly well with the results shown in Table XII and Fig. 12; the discrepancies are not greater than the probable error of the direct determinations.

A direct measurement was also made on the freezing pressure of a 5% sodium chloride solution by a modification of the method for observing the freezing pressure of water in the calibration of the pressure gage (see above). The high-pressure bomb illustrated in Fig. 2 was used for this purpose, the solution being placed in a glass bulb similar to that which contained the solutions during the course of the compression measurements. It is much less simple to determine the freezing pressure of a solution than that of a pure liquid. This is because when solid freezes out the concentration of the solution changes, which alters the freezing pressure. The difficulty is similar to that encountered in the measurement of melting temperatures in a binary system by the heating curve method.

The procedure for determining the freezing pressure of the solution was as follows. The pressure in the bomb was raised sufficiently above the freezing pressure for freezing to begin. About 1500 bars super-pressure was required. As soon as freezing began, as shown by a sudden drop in pressure, the pressure was immediately lowered to a point just above the expected freezing pressure, and by trial there was found the position of

the piston for which the pressure would remain stationary. The pressure and piston position were recorded, and, after raising the pressure so that a little more ice_{V_I} would separate out, the equilibrium pressure and piston displacement again noted. In this way three or four pairs of results for equilibrium pressure and piston travel were obtained and plotted on a sheet of graph paper. The intersection of the line passing through the points with the line obtained by plotting a new series of pressures against piston displacements, made after the ice_{V_I} had all been allowed to melt, obviously gave the true freezing pressure of the solution. This was found to be 650 bars higher than the freezing pressure of pure water at the same temperature—which agrees satisfactorily with the indirect determination, 640 bars, shown in the third column of Table XI.

While it is gratifying to find that direct measurements confirm the results of the indirect determinations, it may be doubted whether there is any need—except as a protection against errors in computation—for a verification of the thermodynamic method. In accuracy, convenience and suitability for safe extrapolation this method seems to be the most advantageous one for the study of multi-component systems at very high pressures.

Acknowledgment.—The author wishes to thank Dr. R. E. Gibson, Dr. R. W. Goranson and Dr. George Tunell, who have read the manuscript of this paper and have made many valuable suggestions.

Summary

Measurements of the volume change at pressures up to 12,000 bars (metric atmospheres) have been made for sodium chloride solutions ranging in concentration from 0 to 25 weight per cent.; and from (1) the fractional volume change (here called the *compression*), (2) the known compression for the other phases in the system, NaCl-H₂O and (3) the known conditions of stability at atmospheric pressure, the equilibrium at other pressures has been determined and an equilibrium diagram constructed, showing the stability in the system under high pressure.

At any pressure the compression, k , of the solutions diminishes with increasing concentration; the same is true of the compressibility, β (that is, $\partial k / \partial P$), for which the effect is especially striking at low pressures.

A calculation of \bar{v}_2 and \bar{v}_1 , the fictive, or partial, volumes of the sodium chloride and the water in solution shows that although \bar{v}_1 is decreased by pressure, \bar{v}_2 is *increased* (except at the highest pressures in the most concentrated solutions).

The indirect method for the determination of the freezing pressure and solubility curves is based upon the fundamental principle that equilibrium depends upon the chemical potential, μ , of the various components, and that the μ 's at any pressure may be calculated from the \bar{v} 's. In the appli-

cation of this method the starting point was the difference in compression due to a change in concentration (at the same pressure), and it was necessary to measure this difference with an accuracy corresponding to less than 1 part in 2000 of the total compression at the highest pressure.

In appearance the equilibrium (P, x) diagram resembles the more familiar melting (t, x) diagram. The solubility curve of sodium chloride and the freezing pressure curve of ice_{VI} meet at an invariant point, or pressure eutectic. There are two other invariant points in the system. These are analogous to incongruent melting points and are marked by abrupt changes in slope of the solubility curve.

Direct measurements confirmed the results of the indirect (thermodynamic) method. Attention is directed to the advantages of this method.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITY AND ENTROPY OF SILVER IODATE FROM 16 TO 300° ABSOLUTE. THE ENTROPY OF IODATE ION

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RECEIVED AUGUST 6, 1931

PUBLISHED OCTOBER 5, 1931

This work is a continuation of the program for the evaluation of the entropies of aqueous ions as a means of facilitating the calculation of the thermodynamic properties of solutions. The general theory, together with details of experimental and mathematical method, has been presented in earlier papers by Latimer and co-workers.¹

In this investigation the entropy of iodate ion has been obtained from calorimetric measurements on silver iodate, AgIO₃. The work is entirely similar to that done on barium bromate by Greensfelder and Latimer,^{1e} and the same apparatus was used.

Preparation of Silver Iodate.—Silver iodate was prepared from c. p. silver nitrate and potassium iodate. Upon considering the methods in the literature, in particular that of Hill and Simmons,² a modified procedure was devised, which proved to be simple of execution.

Sufficient quantities of $M/3$ solutions were prepared to yield two moles of silver iodate. On mixing, a finely divided white precipitate was formed. This was suction filtered and slowly washed with six liters of distilled water. The precipitate was then dissolved in c. p. concd. ammonium hydroxide. A very small quantity of a solid black substance remained, possibly an oxynitride of silver. This material was separated by a single filtration.

¹ (a) Latimer and Buffington, *THIS JOURNAL*, **48**, 2297 (1926); (b) Latimer, *ibid.*, **48**, 2868 (1926); (c) Latimer, *J. Phys. Chem.*, **31**, 1267 (1927); (d) Latimer and Greensfelder, *THIS JOURNAL*, **50**, 2202 (1928); (e) Greensfelder and Latimer, *ibid.*, **50**, 3286 (1928); (f) Latimer and Kasper, *ibid.*, **51**, 2293 (1929).

² Hill and Simmons, *ibid.*, **31**, 828 (1909).