[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

THE MELTING CURVE OF SODIUM CHLORIDE DIHYDRATE. AN EXPERIMENTAL STUDY OF AN INCONGRUENT MELTING AT PRESSURES UP TO TWELVE THOUSAND ATMOSPHERES

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RECEIVED JULY 28, 1930 PUBLISHED NOVEMBER 5, 1930

Under atmospheric pressure sodium chloride dihydrate melts incongruently at 0.1°, forming solid sodium chloride and a saturated solution of that salt. Below this temperature the dihydrate is the stable solid phase in contact with a saturated solution of sodium chloride, although it exhibits such reluctance to appear that special methods are necessary to bring about its formation. A study of the system $NaCl-H_2O$, at 25° and under high pressure, which is being undertaken by one of us, required an answer to the question—at what pressures, if any, is $NaCl\cdot 2H_2O$ the stable phase at 25°, a question which could best be answered by a determination of the influence of pressure on the melting point of the dihydrate.

A detailed study of this problem was also of interest as an example of the course of the melting curves of substances melting with decomposition. Although such substances are numerous, only a few such as $Na_2SO_4\cdot 10H_2O$,[1] $Cd(NO_3)_2\cdot 4H_2O$,[2] $Ca(NO_3)_2\cdot 4H_2O$,[2] $CaCl_2\cdot 6H_2O$[3] have been examined under pressure and none under pressures greater than 3 kilobars.[4] In the case of $Na_2SO_4\cdot 10H_2O$ there is a maximum on the melting curve in the neighborhood of 500 bars, but in other cases no maxima were realized experimentally.

In this paper we shall give an account of the experimental determination of the following data about the transition point of sodium chloride dihydrate: the volume change at atmospheric pressure; the temperature of the transition point up to pressures of about 12 kilobars; and the volume changes which accompany the inversion at these pressures. We shall also calculate the heat of transition both from the melting curve under pressure and from the solubility curves at atmospheric pressure.

Experimental

Sodium chloride dihydrate, as has been mentioned, exhibits great reluctance to crystallize from solution, but, following a suggestion of Meyer-

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[1] G. Tammann, *Z. physik. Chem.*, **46**, 818 (1903); E. A. Block, *ibid.*, **82**, 429 (1913).

[2] Puschin, *J. Russ. Phys.-Chem. Soc.*, **37**, 382 (1905); M. Hasselblatt, *Z. anorg. allgem. Chem.*, **119**, 320 (1922).

[3] Tammann, "Kristallisieren und Schmelzen," Leipzig, **1903**.

[4] 1 bar = 10^6 dynes per sq. cm.; 1 kilobar = 10^3 bars (approx. 1000 atmospheres). See Adams and Gibson, *J. Wash. Acad. Sci.*, **20**, 213 (1930).

hoffer and Saunders,[5] we found that it was possible to prepare the pure hydrate easily and in any desired quantity by cooling a solution of sodium chloride, saturated at room temperature, to below $-5°$ and throwing on the surface of the solution a small amount of carbon dioxide snow. Immediately a cloud of fine crystals of the dihydrate appeared in solution. Below $-5°$ the solubility of sodium chloride is much greater than that of $NaCl{\cdot}2H_2O$, so that introduction of solid sodium chloride into the cold bath of dihydrate crystals results in immediate solution of anhydrous salt and precipitation of more dihydrate.

The mother liquor was removed from the crystals by decantation and suction through a chilled filter.

Change in Volume Accompanying the Melting of $NaCl{\cdot}2H_2O$ at One Atmosphere.—It was difficult to dry the dihydrate completely; hence the dilatometer (a glass one of the usual kind) was filled with the moist salt. Any air was carefully pumped out and xylene introduced as index liquid. During all these operations the temperature of the salt was kept below 0°. When filled and sealed up the dilatometer was immersed in a cold bath and the heights of the meniscus of the xylene in the capillary at different temperatures were read. The changes in height of the meniscus, corrected for temperature of the capillary and irregularities in the bore, were converted to volume changes and plotted against temperature. From the curve was read the increase in volume accompanying the decomposition at 0.1°, which is the mean of the inversion temperatures as given in the literature (0.15°) and as determined by us (0.05°).

After each experiment the amounts of anhydrous sodium chloride and water contained in the dilatometer were determined, and hence with the knowledge of the solubility of sodium chloride at the inversion point we could calculate the actual amount of solid $NaCl{\cdot}2H_2O$ whose volume change on melting was measured.

If A is the weight of salt and water and B the weight of salt in the dilatometer, x_2 and x_0 the weight fractions of sodium chloride in the saturated solution and the solid dihydrate, respectively, at 0°, and m_2 the unknown weight of solid dihydrate before inversion, we find that

$$m_2 = \frac{B - Ax_2}{x_0 - x_2}$$

x_2 was taken from the data of Berkeley[6] as 0.2633 and x_0 is 0.6187. Two experiments were performed, m_2 being 9.628 g. in the first and 8.846 in the second.

The results gave 0.0362 and 0.0377, or an average of 0.037 cc./g. of $NaCl{\cdot}2H_2O$ as the *increase* in volume accompanying the transition, $NaCl{\cdot}2H_2O \longrightarrow NaCl + \text{Satd. Soln. at } 0.1°$. By taking Berkeley's value, 1.2090,

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[5] Meyerhoffer and Saunders, *Z. physik. Chem.*, 31, 381 (1899).

[6] Berkeley, *Phil. Trans.*, 203, 189 (1904).

for the density of a saturated salt solution at 0°, and the density of sodium chloride as 2.168,[7] we calculated that the density of $NaCl\cdot 2H_2O$ at 0° is 1.630 g. per ml.

A few qualitative observations on the speed of the reaction may be noted here. The reaction did not proceed at any appreciable rate until the temperature was 1–2° above the inversion point, and even then the rate was slow. It required over an hour for the reaction to go to completion at a temperature of 4°. At constant temperature the reaction accelerated as more and more anhydrous salt was formed, reaching a maximum speed when about half the material had inverted.

The Effect of Pressure on the Transition Point. (a) **Low-Pressure Experiments.**—In order to examine the initial portion of the p–t curve of the melting of $NaCl\cdot 2H_2O$, a sample of the hydrate was enclosed in the bomb of the pressure dilatometer apparatus whose description has already been published in detail.[8]

The bomb was immersed in a low-temperature bath, a suitable pressure generated, and the system, bomb and pressure gage tightly closed. The criterion of the inversion proceeding in any direction was steady change of pressure at constant temperature. At first the temperature of the bath was raised to a point where rise of pressure indicated that the hydrate was decomposing. The temperature was then lowered to a point where falling pressure showed that re-formation of hydrate was taking place. After that the temperature was raised by short intervals, the trend of the pressure change being carefully observed until it was possible to shut the equilibrium temperature within limits of ±0.25°. The results are given in Table I. In this way the points at 180, 270, 550 and 850 bars on the curve in Fig. 2 were obtained. These points established the initial slope of the p–t curve for $NaCl\cdot 2H_2O$ to our satisfaction.

TABLE I

MELTING POINTS OF $NaCl\cdot 2H_2O$ AT LOW PRESSURES

Expt.	Temp., °C.	Pressure, bars	Uncertainty, °C.
DW447	0.05	1	±0.05
DW445	1.0	180	± .1
DW425	2.0	270	± .1
DW439	3.6	535	± .2
DW429	3.7	570	± .25
DW431	5.4	830	± .2
DW435	5.4	855	± .2

(b) **High-Pressure Experiments.**—Determination of points on the melting curve of $NaCl\cdot 2H_2O$ at high pressures required a different experimental technique. The high-pressure apparatus used in this Laboratory

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[7] DeFoe and Compton, *Phys. Rev.*, [2] **25**, 618 (1925).

[8] Kracek and Gibson, *J. Phys. Chem.*, **34**, 190 (1930).

has already been described.[9] It consists essentially of a very heavy-walled steel cylinder or bomb in which the system under investigation is immersed in *n*-butyl ether, a liquid selected because of its high freezing pressure. A special type of leak-proof piston is forced into the open end of the cylinder and hydrostatic pressure generated in the butyl ether. The pressure is measured by an electrical resistance gage.

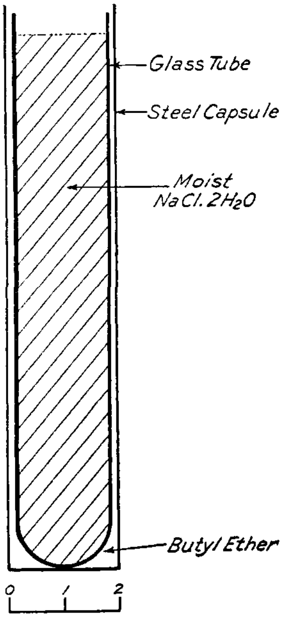

Fig. 1.—Arrangement of the material for the high-pressure experiments.

The apparatus is large and, although protected from minor temperature variations by an insulating housing, is approximately at the temperature of the room. The apparatus could be held constant for a day at temperatures between 17 and 26°, and by following a special procedure it was possible to determine the equilibrium pressures at these temperatures. A glass tube (see Fig. 1) was filled with slightly moist dihydrate, placed in a somewhat larger steel tube filled with butyl ether and kept for half an hour in a eutectic mixture of chloroform and carbon dioxide (approx. −80°). The tubes and their contents were introduced into the bomb and the pressure was raised as expeditiously as possible to the highest value. Five minutes elapsed between the removal of the capsules from the freezing mixture and the pressure on the dihydrate exceeding 7 kilobars. From auxiliary experiments at atmospheric pressure it was found that very little inversion of the salt would take place during the interval required for raising the pressure. A series of readings of pressure and piston displacement was taken when the apparatus came to temperature equilibrium. Rise or fall of pressure, temperature and piston displacement being constant, indicated decomposition or forma-

TABLE II

MELTING POINTS OF $NaCl\cdot 2H_2O$ AT HIGH PRESSURES

Expt.	Temp., °C.	Pressure, bars	Uncertainty, bars
AP503	17.15	3620	± 20
AP505	21.21	5190	± 25
AP513a	23.77	6740	± 50
AP517	23.79	6731	± 50
AP498	24.30	7220	± 50
AP513b	24.66	7500	± 40
AP513c	25.17	8250	±100
AP525	25.10	11800	±250

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[9] (a) Adams, Williamson and Johnston, THIS JOURNAL, **41**, 12 (1919); (b) Adams and Gibson, *Proc. Nat. Acad. Sci.*, **15**, 713 (1929).

tion of the dihydrate and by prolonged observation we were able at temperatures up to 25° to estimate the inversion pressure to within the limits of error given in Col. 4 of Table II. It was also possible to make reliable estimates of the change in volume on inversion at these higher pressures. The results are recorded in Table II and the complete melting curve is illustrated in Fig. 2.

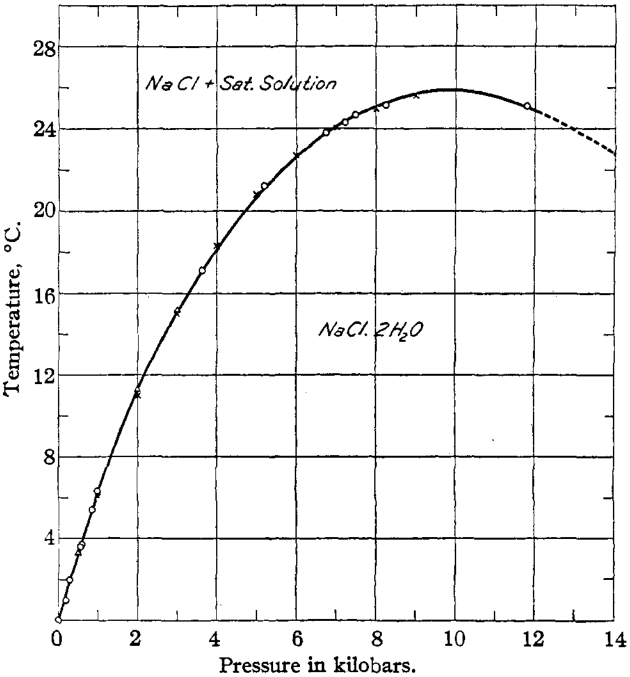

Fig. 2.—The influence of pressure on the incongruent melting of $NaCl \cdot 2H_2O$.

Change in Volume at Higher Pressures.—At higher pressures the volume change on inversion, Δv, which is proportional to the slope of the p–t curve, becomes very small. Even with the volume of the system under pressure reduced to a minimum, we had difficulty in fixing the inversion pressure and temperature at the higher pressures, and, indeed, it was almost impossible to obtain results by direct measurement between 8 and 11 kilobars. As one of the most interesting features of this work was the investigation of the possibility of a maximum on the melting curve, we decided to measure as accurately as possible the difference between the specific volume of $NaCl \cdot 2H_2O$ and its decomposition products at pressures up to 12,000 bars. The maximum on the melting curve would occur at the pressure where Δv is zero. Two methods were used to estimate Δv. Method 1 consisted of determining the rise in pressure at constant volume or the increase in volume at constant pressure by direct observations near the actual inversion point at any temperature. Results were obtained in this way below 8 kilobars and are given in the second column of Table III. Method 2, being rather novel and depending on the fact that a mixture of sodium chloride and its saturated solution will remain in a metastable state several thousands of bars above the inversion point, will now be discussed in some detail. The piston displacements for a given amount of dihydrate at pressures from 6 to 12 kilobars were compared with the piston displacements for the decomposition products of the same sample of dihydrate (sodium chloride and saturated solution) at the same pressures obtained at the same temperature in such a way that errors due to hysteresis in the bomb were reduced to a minimum. The procedure may be illustrated by an example. A quantity of $NaCl{\cdot}2H_2O$ was placed in the bomb at 23.3°. The pressure was raised to exactly 12,400 bars and then reduced to 30 bars below 12,000 bars. A pause was made for temperature readjustment, and then the pressure was raised to as near 12,000 bars as possible. A reading of the piston displacement was taken. Similar observations of displacement and pressure at intervals of 1000 bars were made down to 7000 bars. The pressure was now lowered to 5700 bars, which is 500 bars below the inversion pressure at 23.3°. Readings were noted and a rise of pressure which was allowed to go on only for a short time indicated that $NaCl{\cdot}2H_2O$ was decomposing. The pressure was again raised to 12,400 bars and a second series of measurements was taken. The first run was made merely to put the apparatus through a definite hysteresis cycle. At the end of the second series the inversion was allowed to go to completion. Incidentally the rise of pressure at constant piston displacement gave a measure of Δv at 5700 bars.

After the reaction was entirely finished the pressure was again raised to 12,400 bars and a third series of pressures and piston displacements was observed.

This was followed by a fourth series of observations made in exactly the same way. By noting the differences between two successive runs made with the material in the bomb in the same state of aggregation we were able to make corrections for the small systematic difference between two successive series. The differences between the corrected piston displacements before and after the inversion when multiplied by the cross section area of the hole in the bomb and divided by the weight of dihydrate used gave the approximate change in volume per gram accompanying the inversion at pressures from 6 to 12 kilobars. Three experiments were made at temperatures of 23.3, 23.7 and 24°. In each case an additional value of Δv at 6000 bars was obtained by observation of the total rise in pressure during the inversion. In the experiments at 23.3 and 23.7° uncertainty arose as to the exact amount of dihydrate in the bomb. The results were calculated in such a way that the values of Δv at 7000 bars were made equal to that obtained in the experiment at 24°. All the results on volume changes are recorded in Table III.

TABLE III

INCREASE IN VOLUME OF $NaCl \cdot 2H_2O$ ON MELTING AT VARIOUS PRESSURES

Pressure, bars	Δv, cc./g., Method 1	Δv, cc./g., Method 2		
		1	2	3
3620	0.0165			
5190	.0101			
6000		0.0069	0.0074	0.0071
7000		(.0046)	(.0046)	.0046
7220	.0054			
8000		.0027	.0026	.0027
9000		.0012	.0010	.0006
10000		− .0004	− .0008	− .0009
11000		− .0021	− .0019	− .0024
12000		− .0032	− .0034	− .0036

Discussion of Results

Interpolation Formulas.—Two cubic equations

$$t = 7.047p - 0.7655p^2 + 0.035244p^3 \qquad (1)$$

$$t = 0.06 + 6.512p - 0.5529p^2 + 0.06056p^3 \qquad (2)$$

were found to express the melting temperature as a function of pressure. The temperature, t, is expressed in degrees centigrade and the pressure, p, is in kilobars. Equation 1 being passed through the points at lower pressures gives more accurately the initial slope of the pressure–temperature curve, but it does not represent the data very well above 4.5 kilobars. Equation 2, we consider, expresses the results accurately between 4 and 8 kilobars. Indeed, it applies very well to atmospheric pressure, which is surprising when it is mentioned that the lowest point used in computing this equation was that at 17.15° and 3.620 kilobars.

In Fig. 2 the circles represent the observed points, the crosses, points calculated from Equation 1, and the triangles, points calculated from Equation 2. Both equations are purely interpolation formulas and are not suited for extrapolation.

Maximum on Melting Curve.—From direct observations of melting we can say definitely that at 8000 bars sodium chloride dihydrate becomes the stable phase in contact with a saturated solution at 25°. The question as to whether the melting curve passes through a maximum and whether at some higher pressure sodium chloride is again stable at 25° may be answered from considerations of the volume changes. In Fig. 3 we have plotted points representing Δv per gram at different pressures as measured by our first method (triangles), and as determined by the second method (circles). The two series are fairly consistent, although the second method appears to give values which are somewhat lower than those given by the first. The curve passed through these points cuts the pressure axis at 9500 bars, showing that the melting curve passes through a maximum at this pressure. It should be mentioned that the values of Δv at the higher pressures are calculated on the assumption that the effect of temperature on the change in volume during the inversion is negligible when compared with the effect of pressure.

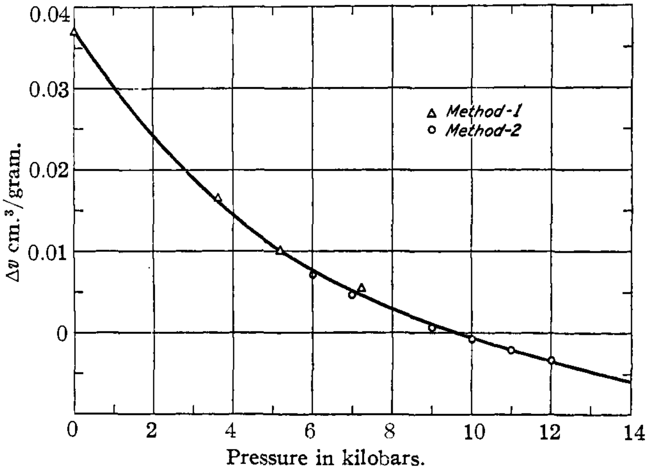

Fig. 3.—Volume change accompanying the melting of 1 g. of $NaCl\cdot 2H_2O$ at various pressures. Above 9500 bars the volume change is negative.

Confirmation of the maximum on the melting curve was obtained by direct observation of the decomposition of $NaCl\cdot 2H_2O$ at 12,500 bars and 25.1°. The pressure on the sample was first raised to 12,500 bars and dropped to 10,000 bars, where it was held until equilibrium was established. The pressure was then raised by steps of 500 bars and at each pause was carefully watched and its trend noted. Below 12,000 bars and above 10,000 bars the creep of pressure after the primary rise was always upward—there was no tendency to fall. This phenomenon will be referred to later. At 12,000 bars the pressure drifted down slowly but steadily and in the course of four hours dropped 80 bars. That this drop was due to the decomposition of $NaCl\cdot 2H_2O$ was shown when the pressure was finally lowered to 7000 bars (1000 bars below the low-pressure equilibrium value at 25°) and the total rise at constant volume was about one-third that which would be obtained from the particular sample of uninverted dihydrate. As the pressure rose at constant volume at 11,500 bars, we were able to place the pressure coördinate of the melting curve at 25.1° between 11,500 and 12,000 bars.

The Compressibility of $NaCl\cdot 2H_2O$.—The volume of sodium chloride at any pressure is known from compressibility measurements,[9a] and recently the specific volumes of saturated sodium chloride solutions have been determined to 12 kilobars.[10] As we have measured around 25° the differences in volume between $NaCl\cdot 2H_2O$ and its decomposition products, it is possible to calculate the specific volume of the hydrate at pressures between 6 and 12 kilobars. It is assumed that the solubility of sodium chloride is not greatly altered by pressure in this range. The results are recorded in Fig. 4 where v_0, the specific volume, is plotted against the pressure. The slope of this curve, when divided by the specific volume of $NaCl\cdot 2H_2O$ at ordinary pressure, gives the fractional decrease in volume per bar increase of pressure, or the compressibility β. The average value of β between 6 and 12 kilobars is 4.8×10^{-6} reciprocal bars. This may be compared with 3.6×10^{-6}, the value of β for sodium chloride at 9 kilobars.

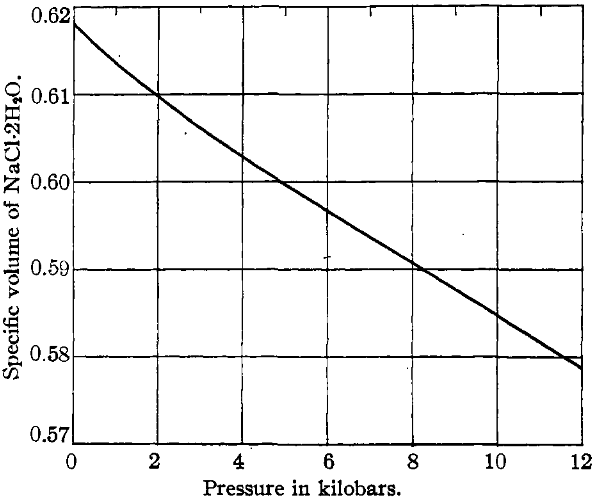

Fig. 4.—The specific volume of $NaCl\cdot 2H_2O$ as a function of pressure.

Heat of Inversion from the Melting Curve.—The initial slope of the melting curve is shown by Equation 1 to be 7.05° per kilobar. The volume change at atmospheric pressure is 0.037 cc. per gram of $NaCl\cdot 2H_2O$, and hence by the Clausius–Clapeyron equation the heat of fusion per gram, Δh, is 34.4 cal. In the same way, obtaining Δv from the curve in Fig. 3 and dt/dp from Equation 2, we find that at 5 and 7 kilobars Δh is 36.4 and 33.1, respectively. The heat of fusion is not greatly influenced by pressure—a fact which is in accord with Bridgman's[11] observations on various materials.

[10] Adams, unpublished data.

[11] Bridgman, *Phys. Rev.*, 3, 190 (1914).

Secondary Increase of Pressure.—On all occasions when a charge of dihydrate was held at a pressure and temperature in the vicinity of the maximum on the melting curve a very curious phenomenon was observed. The pressure had been raised to somewhat above 10,000 bars, and, contrary to what was expected, it continued to drift slowly *upward* for an hour or more, the total increase of pressure being as much as 20 bars. The normal behavior of a system the pressure of which has just been increased is, of course, to show at first a small decrease of pressure—even in a pressure-tight apparatus. The immediate cause of this decrease may be the cooling subsequent to the heating by compression, or, in a multi-phase system, the transformation of one phase to another in accordance with the conditions of equilibrium. Similarly, a decrease of pressure is usually followed by a secondary increase. In the simple case of a mixture of solid and liquid in equilibrium an increase of pressure causes the production of more solid (in rare instances more liquid), and since this is accompanied by a decrease of volume, the pressure falls, finally coming back, if the primary increase is not too great and the substance is a pure material, exactly to the original pressure.

The abnormal behavior of the sodium chloride dihydrate, which at first seemed very puzzling, may be explained as follows. Suppose that a mixture of the dihydrate and its decomposition products is held at a temperature and pressure corresponding to the point *O* in Fig. 5, and that the pressure on the system is suddenly increased. The temperature will increase with the pressure, approximately isentropically, as shown by the dotted line. The material will then begin to cool, and the secondary pressure change will be the sum of two effects: (1) the effect due to cooling and (2) the effect due to transformation from one form to the other. In the present case the problem is much simplified because the inversion takes place relatively slowly so that during the time required for the temperature to return to its original value (about five minutes) very little of the material has changed its state. On the diagram, therefore, the temperature and pressure reach the point *a* while there is still present a mixture of the dihydrate and its decomposition products. Since at this point dihydrate is the stable phase, solution and salt will react to form dihydrate, which under the given conditions has the smaller volume, and hence the pressure will fall. Suppose, on the

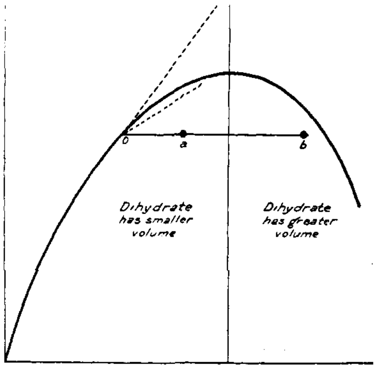

Fig. 5.—Diagram to accompany explanation of secondary increase of pressure.

other hand, that starting again with a mixture at *O*, the pressure is suddenly increased, attaining at the same temperature the pressure indicated by *b*. Here, as before, dihydrate is the stable phase, and more will be formed, but the pressure being now beyond the maximum, the dihydrate occupies more volume and the pressure therefore will rise. A secondary increase of pressure has been discussed by Tammann[12] in connection with the existence of maximum melting points, but Bridgman in a careful analysis of the problem points out that the conditions of equilibrium in a system make it impossible for Tammann's secondary increase of pressure to occur. According to Bridgman,[13] in a system composed of phases in equilibrium, and each in condition of internal stability, thermodynamical considerations require that the secondary pressure reaction be a decrease rather than an increase. That this result, however, does not contradict the opposite conclusion obtained as above from elementary principles becomes apparent when we recall that Bridgman's equation is valid only for *infinitesimal* changes and is not necessarily applicable to the *finite* changes here under discussion. It is only because we have increased the pressure a considerable distance beyond the equilibrium curve and into that part of the field which lies beyond the maximum that the secondary increase of pressure occurs. Expressed in other terms: we are here dealing with a non-equilibrium process, whereas the thermodynamical equations refer only to equilibrium states and their immediate vicinity. It should be noted that the above considerations apply equally well to the melting curve of a substance which does not decompose at its melting point.

Heat of Inversion from the Solubility Curves.—No direct measurements of the latent heat of the incongruent melting of $NaCl\cdot 2H_2O$ are available but it is possible to calculate this heat of inversion from solubility measurements of sodium chloride in water and from the known values of the chemical potential of sodium chloride in aqueous solution. The relation is

$$\Delta h = T(b_3 - b_2)\frac{\partial \mu_2}{\partial x_2}\frac{x_0 - x_2}{1 - x_2} \qquad (3)$$

Here Δh is the heat absorbed, when one gram of $NaCl\cdot 2H_2O$ inverts to a mixture of sodium chloride and saturated solution of sodium chloride in water, T is the absolute temperature, x_0 is weight fraction of sodium chloride in $NaCl\cdot 2H_2O$, x_2 is the weight fraction of sodium chloride in the saturated solution which is in equilibrium with sodium chloride and $NaCl\cdot 2H_2O$, b_3 is the slope dx_2/dT of the solubility curve for $NaCl\cdot 2H_2O$ as the solid phase, b_2 is dx_2/dT for the solubility curve with sodium chloride as the solid phase, and μ_2 is the chemical potential of Gibbs (or partial free energy of Lewis) referred to one gram of sodium chloride in solution.[14] In the expression

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[12] G. Tammann, "Kristallisieren und Schmelzen," p. 87.

[13] P. W. Bridgman, *Phys. Rev.*, **3**, 192 (1914).

[14] If it is desired to express the above equation in terms of activity and mole frac-

$\partial\mu_2/\partial x_2$ the temperature is constant. The derivation of the equation will be given in another paper from this Laboratory.

From a careful plot of the solubility data of sodium chloride in water as given in the "International Critical Tables," b_3 is found to be 0.00138 and b_2 0.00001. The solubility of sodium chloride, x_2, at the inversion point is 0.263, and x_0 is 0.619. The absolute temperature of the inversion, T_1, is 273.2°, and the value of $\partial\mu_2/\partial x_2$, as determined from freezing point, e. m. f., solubility and vapor-pressure data, and corrected to $t = 0.1°$, is taken as 165 calories. Substituting these numerical quantities in Equation 3 we have

$$\Delta h = 30 \text{ cal.}$$

for the heat absorbed by the incongruent melting of one g. of $NaCl \cdot 2H_2O$.

This result is to be compared with 34 cal., the value obtained from the initial slope of the p–t curve and the volume change at $p = 1$. The agreement is none too close, but considering the complexity of the calculation, and the large variety of data involved, it is an interesting confirmation. Probably about equal weight should be given to the value of Δh obtained from the solubility curve and that derived from the initial slope of the melting curve.

Summary

The temperature of the incongruent melting of $NaCl \cdot 2H_2O$ has been determined up to 12,000 bars (or c. g. s. atmospheres) by direct measurement and also indirectly from measurements of the volume changes. The melting curve starts at 0.1° at atmospheric pressure with an initial slope of 7.05° per kilobar. The slope decreases rapidly with increasing pressure, finally becoming zero, so that the curve passes through a maximum at 9500 bars and 25.8°.

The volume change was measured at one bar in a dilatometer, and at various pressures up to 12,000 bars by two different methods. From the volume change and slope of the melting curve the heat of fusion at several pressures was calculated. The density of $NaCl \cdot 2H_2O$ at 0.1° and one bar

tions, this can be done by making use of the relation $d\overline{F}_2 = M_2 d\mu_2 = RT \text{ d } \ln a_2$ at constant temperature, in which $\overline{F}_2$ is the partial molal free energy, M_2 the formula weight, a_2 the activity of component 2, and R is the gas constant. The transformed equation is

$$\Delta H = 3RT^2(B_3 - B_2)\,\frac{\text{d} \ln a_2}{\text{d}X_2}\,\frac{X_0 - X_2}{1 - X_2}$$

in which ΔH is the heat observed when one mole of $NaCl \cdot 2H_2O$ inverts, X_2 is the mole fraction of sodium chloride in the equilibrium solution, X_0 is the mole fraction of sodium chloride in $NaCl \cdot 2H_2O$, B_3 and B_2 are the values of $\text{d}X_2/\text{d}t$ along the $NaCl \cdot 2H_2O$ and sodium chloride curves, respectively, and a_2 is the activity of sodium chloride in solution. Moreover, the activity coefficient γ may be used in place of a_2 by making the substitution, $\text{d} \ln a_2/\text{d}X_2 = \nu \text{ d} \ln (m\gamma)/\text{d}X_2$, ν being the number of ions into which one molecule of the solute is assumed to dissociate.

was found to be 1.630, and its mean compressibility between 6000 and 12,000 bars at about 22°, 4.8×10^{-6} per bar. A method for calculating the heat of fusion from solubility data gives a value which is in fair agreement with that determined from the initial slope of the melting curve, the average value being 32 cal. per g. of $NaCl \cdot 2H_2O$.

A secondary pressure increase, that is, a continued rise of pressure following a sudden increase, was observed at pressures near the maximum on the curve, and an explanation is given for this phenomenon.

WASHINGTON, D. C.

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

THE SEPARATION OF YTTERBIUM BY ELECTROLYTIC REDUCTION.
OBSERVATIONS ON THE RARE EARTHS. XXXVI

BY ROBERT W. BALL[1] WITH L. F. YNTEMA

RECEIVED AUGUST 2, 1930 PUBLISHED NOVEMBER 5, 1930

Recently it was found that europium can be separated from a mixture of samarium, europium and gadolinium chlorides by electrolytic reduction in acid solution in the presence of the sulfate ion.[2] Europous sulfate, $EuSO_4$, precipitated as a white, finely crystalline compound, stable when heated in air at 65° and insoluble in dilute acids. It was readily oxidized by dilute nitric acid.

In 1929 Klemm and Schüth[3] reported the preparation of ytterbous chloride, $YbCl_2$, similar to samarous chloride, $SmCl_2$,[4,5] and europous chloride, $EuCl_2$[6,7] by treatment of ytterbium oxide, Yb_2O_3, with a stream of Cl_2–S_2Cl_2 at 600–620°.

These facts suggested the possibility of separating ytterbium from the other rare earths of the yttrium group by electrolytic reduction in the presence of the sulfate ion.

Experimental

I. Electrolysis of Rare Earths with Low Ytterbium Content.—Ten grams of pink yttrium group oxides, containing yttrium and erbium with small percentages of thulium and ytterbium, were dissolved in hydrochloric

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[1] An extract from a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.

[2] Yntema, THIS JOURNAL, **52**, 2782 (1930).

[3] Klemm and Schüth, *Z. anorg. allgem. Chem.*, **184**, 352 (1929).

[4] Matignon and Cazes, *Compt. rend.*, **142**, 83 (1906).

[5] Jantsch, Rüping and Kunze, *Z. anorg. allgem. Chem.*, **161**, 210 (1927).

[6] Urbain and Burion, *Compt. rend.*, **153**, 1155 (1911).

[7] Jantsch, Alber and Grubitsch, *Monatsh.*, **53**, **54**, 305 (1929).