Pressure induced transitions in inorganic hydrates.

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ABSTRACT

A study was made to determine the effect of pressure on a number of inorganic compounds in order to determine the possibility of inducing dehydration, and/or new phase transformations, and fitting compressibility data to a recently developed equation of state for plastics.

The application of high pressure dehydrated

Ca(CNS)_2·4H_2O at 0.5 kilobars,

ThCl_4·8H_2O over the range 2.2 to 4.6 kilobars,

Zr(SO_4)_2·4H_2O over a broad range of pressure,

Zn(SO_4)_2·7H_2O at 4.6 kilobars, and

Na_2SO_4·7H_2O at 8.9 kilobars.

There also resulted new reversible phase transitions in

Na_2S_2O_3·5H_2O at 18.5 kilobars,

MgS_2O_3·6H_2O at 7.7 kilobars,

ZnSO_4·6H_2O at 2.2 kilobars, and 16.2 kilobars,

K_2(MoO_4)_2·5H_2O at 10.3 kilobars,

BeSO_4·4H_2O at 10.3 kilobars,

ZrOCl_2·6H_2O at 5.6 kilobars;

Mg(CNS)_2·4H_2O at 5.8 kilobars,

Th(SO_4)_2·8H_2O at 9.8 kilobars, and

ZnSO_4·7H_2O at 2.1 kilobars.

The expression \(-\Delta V/V_0 = m + n\ln P\) was found to fit the 77°F compressibility data of the following compounds up to 22.6 kilobars within
a confidence level of ninety-nine percent.

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CHAPTER I

INTRODUCTION

One of the simplest ways of purifying a compound is to recrystallize it from a suitable solvent. The crystals separating from the solution may consist of the pure compound or they may contain a solvent of crystallization. For most salts water is a convenient solvent so that crystals containing water (hydrates) have been known from the earliest days of chemistry. As a matter of fact many inorganic compounds are obtained naturally as hydrates and this is one reason why a great interest is being shown in them.

Little is known about the temperature behavior (under atmospheric conditions) of the crystalline inorganic compounds reported here. What happens to them when they are subjected to very high pressure is almost completely unknown. The study of hydrates under pressure has assumed importance because of the light it can throw on certain geological phenomena that might have been responsible for making our earth what it is today.

The object of this project was to make a preliminary determination of pressures at which these compounds may lose their water, to ascertain new pressure induced phase transitions in these hydrates and to apply an equation of state recently developed for plastics.
A. Dehydration

A review of literature in any field of high pressure work must begin with P.W. Bridgman's contribution. This field is no exception. Larsen and Bridgman (4) were the first to investigate the dehydration or inorganic compounds as a result of high pressure. Their work was confined to certain selected minerals and mixtures and the attempt was not primarily directed towards study of dehydration but towards formation of what Bridgman called "stress minerals". Moreover the stress applied was not purely compressive but an intentional combination of compression and shear. In fact Bridgman called the compressive pressure the "confining pressure" and went on to say that the study was done because of a suspicion that shear action hastens reactions that proceed extremely slowly at room temperature. Opal was dehydrated to quartz and gypsum to anhydrous calcium sulphate in Bridgman's study using a "piston and anvil" apparatus. Kiyama and Yanagimoto (14) reproduced Bridgman's work on dehydration of gypsum to a soluble anhydrite under similar conditions. Kiyama and Yanagimoto later obtained the same change without any deliberate shear action at a compacting pressure of 5,000 atmospheres compared to Bridgman's confining pressure of 50,000 atmospheres. Kiyama and Yanagimoto (14) successfully dehydrated CuSO$_4$·5H$_2$O under a pressure of 4,500 atmospheres at room temperature. Dehydration of CuSO$_4$·5H$_2$O is a controversial matter. H. David and S. Hamman (8) tried to duplicate the dehydration and could not, even at pressures as high as 30,000 atmospheres. It is not...
known what kind of apparatus David and Hamman used. The author attempted the CuSO$_4$$\cdot$5H$_2$O dehydration (up to 27 kilobars) without any positive result. The dehydration of gypsum at 5.2 kilobars was observed however.

Levshists, Genshaft et al (15) examined the pressure dehydration of MgSO$_4$$\cdot$7H$_2$O by a method very similar to the one used in the present work. It was a preliminary study and a confirmation of dehydration by X-ray analysis was postponed for some future date. To date this has not been reported.

In addition to inorganic hydrates, organic compounds have also been subjected to pressure to see if dehydration can be induced. Kiyama and Yanagimoto (13) have produced urea from ammonium carbonate by the application of pressure at room temperature. This reaction is essentially a dehydration reaction. Bengelsdorf (1) has reported the dehydration of acetone and cyclohexanone under pressures of the order of 50,000 atmospheres.

B. Phase Transitions

The study of phase transitions with pressure also owes much to Bridgman. In numerous papers (3) he describes phase transitions in more than two hundred materials. After Bridgman, experimental work to determine high pressure transitions in inorganic compounds was generally not attempted except in cases where it was suspected that Bridgman's work needed rechecking due to improvements in technique. Any new work in this field has been essentially confined to naturally occurring minerals, an area relatively untouched by Bridgman's extensive work.

C. Equation of State

Khoubesserian and Stager (12), in testing the range of appli-
cability of Weir's equation (19) for plastics, developed a new equation of state

\[- \frac{\Delta V}{V_0} = B(T_C - 20) + (C + D\Delta T_C) \ln P + E\]

which fitted their data for various organic polymeric substances. This relationship was found to be valid to a confidence level of ninety-nine percent up to a pressure of 22.6 kilobars. This equation reduces to

\[- \frac{\Delta V}{V_0} = m + n \ln P\]

for constant temperatures.
CHAPTER III
EXPERIMENTAL AND THEORETICAL CONSIDERATIONS

A. Aims and Objectives

This project was visualized as a two stage study. The aims for the first stage were:

- dehydration of inorganic compounds at room temperature by the application of pressure,
- discovery of new phase transformations in hydrates brought about by pressure, and
- testing of the validity of the correlation $-\frac{\Delta V}{V_0} = m + n\ln P$

for compounds showing no dehydration or phase transformations.

The second stage of the project will attempt to determine the mechanism of dehydration by compression, the structure of pressure induced phase transformations in hydrates, and the role of water in such transitions. During the later stage it is also proposed to test the validity of the complete equation of state (12)

$$-\frac{\Delta V}{V_0} = B(T_c - 20) + (C + D \chi T_c) \ln P + E$$

B. Dehydration

1. Dehydration in a Confined Space

LeChatelier's principle states that a system in equilibrium when subjected to a stress will move in the direction of stress relief. This constitutes the basis for dehydration studies with pressure.
Consider the general equation

\[ M \cdot xH_2O \rightarrow M + xH_2O \]

where \( M \cdot xH_2O \) is any hydrate. LeChatelier's principle states that the above change will be favoured by an increase in pressure if it results in a decrease of overall volume. That is to say \( \Delta V_M < 0 \) where \( \Delta V_M = \) molar volume of the anhydrous salt + molar volume of water of crystallisation - molar volume of the hydrate.

Molar volume is defined as the ratio of the molecular weight of a compound and its specific gravity. In the case in which \( \Delta V_M > 0 \) dehydration will have to be done in an apparatus which will let water escape from the confined space. An assumption that the molar volume of an anhydrous salt is always less than the molar volume of the hydrate underlies the above statement however.

Bridgman's (4) apparatus for dehydration of gypsum had to have an outlet for exit of water as can be seen from the nature of \( \Delta V_M \)

\[
\text{CaSO}_4 \cdot 2H_2O \rightarrow \text{CaSO}_4 + 2H_2O
\]

\[
V_M = 74 \quad V_M = 56 \quad V_M = 36
\]

\[
\Delta V_M = (56 + 36 - 74) = 18
\]

Similar considerations prompted Kiyama (dehydration of \( \text{CuSO}_4 \cdot 5H_2O \)) and Levshists (dehydration of \( \text{MgSO}_4 \cdot 7H_2O \)) to provide for water outlets in their equipment.
\[
\begin{align*}
\text{CuSO}_4 \cdot 5\text{H}_2\text{O} & \rightarrow \text{CuSO}_4 + 5\text{H}_2\text{O} \\
V_M = 109 & \quad V_M = 44 \quad V_M = 90 \\
\Delta \bar{V}_M = (90 + 44 - 109) = 25 \\
\text{MgSO}_4 \cdot 7\text{H}_2\text{O} & \rightarrow \text{MgSO}_4 + 7\text{H}_2\text{O} \\
V_M = 150 & \quad V_M = 45 \quad V_M = 126 \\
\Delta \bar{V}_M = (126 + 45 - 150) = 21
\end{align*}
\]

In the design of apparatus for this project, clearance was provided between the pistons and the cell wall for the same reason.

2. Thermodynamics of Dehydration

Thermodynamics can be used to predict the pressure at which the dehydration of a given compound will take place. This is shown as follows:

\[
G = H - TS
\]

where \( G \) = Gibbs free energy

\( H \) = Enthalpy

\( T \) = Temperature

\( S \) = Entropy

\[
dG = dH - TdS - SdT
\]

\[
dG = dE + PdV + VdP - TdS - SdT
\]

as

\[ H = E + PV \]

where \( E \) = Internal energy

\( P \) = Pressure
\[ V = \text{Volume} \]

for a system in which temperature is kept constant, as was done in this study, the above expression becomes

\[ dG = dE + PdV + VdP - TdS \]

but \[ dE = TdS - PdV \]

therefore \[ dG = VdP \]

Extending to a system of more than one component

\[ \Delta G = \int_{P_1}^{P_2} \Delta \bar{V}_M \, dP \]

where \[ \Delta \bar{V}_M = \text{molar volume of the anhydrous salt} + \text{molar volume of water of crystallisation} - \text{molar volume of the hydrate} \]

For an equation of state a first order approximation can be used.

\[ \Delta \bar{V}_M = \Delta \bar{V}_M^o (1 - \Delta \bar{B} P) \]

where \[ \Delta \bar{V}_M^o = \text{molar volume of the anhydrous salt} + \text{molar volume of water of crystallisation} - \text{molar volume of the hydrate at atmospheric pressure} \]

and \[ \Delta \bar{B} = \text{compressibility of the anhydrous salt} + \text{compressibility of water} - \text{compressibility of the hydrate} \]

therefore

\[ \Delta G = \Delta \bar{V}_M^o \int_{P_1}^{P_2} (1 - \Delta \bar{B} P) \, dP \]

If compressibilities over the range \( P_1 \) to \( P_2 \) can be assumed constant then
\[ \Delta G = \Delta V^o_M (P_2 - P_1) + \frac{\Delta A}{2} (P^2_2 - P^2_1) \]  
\hspace{1cm} (1) 

Since \( P_1 \) = 1 atmosphere is a negligible quantity

\[ \Delta G = \Delta V^o_M (P_2 + \frac{\Delta A P^2}{2}) \]

If one knows \( \Delta G \), \( \Delta V^o_M \) and \( \Delta A \) then \( P_2 \) can be predicted. In most cases however these quantities were not available and hence an experimental study was undertaken.

Levshists (15) recognized that \(-\Delta V/V_0\) versus pressure curves for a hydrate and the corresponding anhydrous compound are different and used the fact for confirming the dehydration of \( \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \). The same fact was used in this study for verifying dehydration. The alternative of taking out the sample from the cell and analyzing it chemically, was not adopted, as it would have led to contamination of the compound by oil from the constant temperature bath.

C. Phase Transformations

Polymorphism in crystalline materials is the rule rather than the exception. The profusion of crystal forms of any one substance is related to the small difference in internal energy between the forms and it is just because of this that pressure has been used so successfully in inducing polymorphic changes. For the purpose of this study only the first order polymorphism involving changes in volume was considered. With the type of equipment visualized attention was focussed on the so called rapid transitions. The following types of transformations were expected to be encountered:
1. Transformations of Secondary Coordination:
   a. Displacive Transformation

   The atoms of any crystal can theoretically be displaced in such a way that the contact between atoms that may be said to touch is maintained and yet the structure becomes distorted so that noncontacting atoms are displaced with respect to each other. Such transformations are found in crystals having atoms with low coordination numbers.

   b. Reconstructive Transformation

   It is possible to destroy the crystal network completely and rebuild it in such a way that although the secondary coordination is not the same, the primary is identical. It thus amounts to unlinking and relinking, with the relinking done in a manner to preserve the first coordination. Pressure is found to be an effective tool in such transformations. The presence of water in the molecule and consequent solvation is expected to promote this reorganization.

2. Transformations of First Coordination

   Pressure is also known to have caused transformations involving the first coordination. The well known case of a face centred cubic (fcc) structure (NaCl type) changing to a body centred cubic (bcc) form (CsCl type) is an example. The compound KCl has fcc crystals at room temperature and atmospheric pressure but at a pressure of 20.2 kilobars has crystals that are bcc.

3. Transformations of Bond Type

   Transformations involving changes in the type of bonds are known. Examples are diamond to graphite and grey tin to white tin. The bonds in one type may be metallic and in others non-metallic.
4. Detection of First Order Phase Transitions

The study of the phase transitions involving volumetric changes is concomitant to the study of compressibilities. The discontinuity in a mathematical function is used to detect a phase transition. Considering any property \( \pi \) of a material it is known from thermodynamics that

\[
\pi = f(P, T)
\]

where \( P \) is the pressure and \( T \) is the temperature, or

\[
\pi = g(P)
\]

at constant temperature. If a phase is characterized by a continuous function, then a discontinuity in this function, with respect to pressure will indicate the appearance of a new phase.

If

\[
\pi = -\frac{\Delta V}{V_0} = g(P)
\]

then as soon as a new phase appears, \(-\frac{V_0}{V_0}\) versus pressure curve will show a discontinuity.

5. Prediction of Pressure of Transition

At the point of equilibrium where two phases coexist, the thermodynamic potential is equal when \( G_1 = G_2 \).

\[
E_1(T, P) - TS_1(T, P) + PV_1 = E_2(T, P) - TS_2(T, P) + PV_2
\]

Bradley (2) argues that at high pressure the entropy terms may be neglected in comparison with the rest. Therefore

\[
P = \frac{E_2 - E_1}{V_1 - V_2}
\]

\[
E_1 + PV_1 = E_2 + PV_2
\]
where $E_1$ and $E_2$ are the internal energies for phase I and II respectively.

$V_1 = \text{molar volume of phase I}$

$V_2 = \text{molar volume of phase II}$

$P$ is the pressure at which the new phase appears.

Jacobs (10) calculated the value of $P$ for simple crystals like Rubidium Iodide. The calculated pressure did not agree with the experimentally determined value although it did provide an insight into the phenomenon. Considerations of Jacobs' paper show that it is not possible to go beyond the stage

$$P \approx \frac{E_2 - E_1}{V_1 - V_2}$$

as theoretical calculations of internal energy and molar volume in the case of complex molecules are extremely difficult.

D. A Correlation for Pressure-Volume Data

It was expected that a number of hydrates would have no transformations. A number of anhydrous compounds were to be used for purposes of comparison. It is well known that at high pressure, compressibilities of various materials tend to be the same, probably because at high pressure, compressibilities approach zero. It was in view of this that it was decided to test the validity of the correlation

$$-\frac{\Delta V}{V_o} = m + n \ln P.$$ 

Khourbesserian's equation (12)

$$-\frac{\Delta V}{V_o} = B(T_c - 20) + (C + D \Delta T_c) \ln P$$ 

could be tested if temperature was also varied.
CHAPTER IV
DESIGN OF THE PRESSURE CELL

Table I

<table>
<thead>
<tr>
<th>Member</th>
<th>Internal Diameter</th>
<th>External Diameter</th>
<th>Material</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>inches</td>
<td>inches</td>
<td></td>
<td>inches</td>
</tr>
<tr>
<td>Inner cylinder</td>
<td>0.250</td>
<td>1.257</td>
<td>Carboloy &quot;55A&quot;</td>
<td>1.000</td>
</tr>
<tr>
<td>Ring No. 1</td>
<td>1.249</td>
<td>1.671</td>
<td>Alco S Rockwell C = 50</td>
<td>1.000</td>
</tr>
<tr>
<td>Ring No. 2</td>
<td>1.667</td>
<td>2.223</td>
<td>&quot;</td>
<td>1.000</td>
</tr>
<tr>
<td>Ring No. 3</td>
<td>2.219</td>
<td>2.957</td>
<td>&quot;</td>
<td>1.000</td>
</tr>
<tr>
<td>Pistons</td>
<td>0.249</td>
<td>0.249</td>
<td>Carboloy &quot;883&quot;</td>
<td>1.000</td>
</tr>
</tbody>
</table>

The maximum pressure that can be attained in a cylinder piston type of assembly is limited by the strength of the piston. By the use of a multiring support on the cylinder it can be made to withstand very high pressures. However it is not possible to strengthen the neck of the piston, though one can reinforce the rest of the piston. The term "neck of the piston" means the portion of the piston at its entry into the cylinder. These pistons were made of General Electric Carboloy grade "883". Though Carboloy "883" can withstand pressures as high as 60 kilobars, it was decided never to subject the material to more than a pressure of 40 kilobars. A decision was made to prolong the life of the pistons, by choosing a working limit of 23 kilobars. This was based on an observation of Christiansen (5).
The pressure cell was thus designed to withstand a maximum pressure of 40 kilobars. There is no direct method of calculating the support needed for developing such a pressure. It was therefore decided on the basis of experience gained by Khoubesserian (12) to start with a carbide cylinder of the following dimensions: inner diameter = 0.250 inches, outer diameter = 1.257 inches, length of the cylinder = 1.000 inches. The length was chosen to be one inch as one-half inch samples were visualized for compression.

The design of the cell was based on a paper by Christiansen (5). A three ring assembly with a radial ratio of 1.330 inches was selected where

\[
\text{Radial Ratio} = \frac{\text{Radius of the outer ring}}{\text{Radius of the inner ring}}
\]

The following negative clearances based on diametrical deformations were used for shrink fits.

- Ring No. 1 = 0.008 inches
- Ring No. 2 = 0.004 inches
- Ring No. 3 = 0.004 inches

With these dimensions the theoretical pressure to which the cell could be subjected was calculated to be 41 kilobars (Appendix I).

Two 0.249 inch diameter, one inch long Carboloy "883" pistons were selected for transmitting pressures to the samples in the cell. A 0.5 inch long, 1.0 inch outer diameter jacket of Alco-S steel was press-fitted on these pistons. The negative clearance for pressure fit was 0.002 inches.
CHAPTER V

EXPERIMENTAL APPARATUS

A. Apparatus and Materials

The apparatus used for the experimental investigation is shown in Figures 1 and 2. It consisted of the following distinct units.

1. The Pressure System

The pressure system consisted of a 200 ton "Rodgers Hydraulic Ram" in which the pressure was induced by a Black Hawk "Enerpac" hand pump (Model P-39).

2. The Pressure Measuring Device

The oil pressure in the hydraulic ram was measured with a ten inch Heise Bourdon Gauge (0 to 3000 pounds per square inch range, 5 pounds per square inch graduations).

3. The Displacement Measuring Devices

The decrease in the length of the sample was measured by noting the displacement of Carboloy platen \( C_1 \), on a "Mercer" dial indicator gauge (0 - 0.5 inch range, 0.0001 inch graduations).

4. Constant Temperature Bath

An electrically heated oil bath regulated by a Winsco thermo-regulator, accurate to \( \pm 2^\circ \) was used whenever necessary.

5. The High Pressure Cylinder

A reinforced hollow Carboloy cylinder was used for holding the
Phenolite insulation Disc I, 1" thick and 2" diameter

Carboloy Platen C₂, 1/2" thick and 2" diameter

Steel Gasket, 1" thick and 1" diameter

Piston P, 1" long and 0.249" diameter

Soft steel gasket .006" thick and 0.250" diameter

Sample

Cell, for dimensions see Appendix II

Carboloy Platen C₃, 1/2" thick and 4" diameter

Carboloy Platen C₄, 1/2" thick and 4-1/2" diameter

Phenolite insulation Disc I₂, 1" thick and 4" diameter

FIGURE 1. Pressure Assembly
FIGURE 2. Schematic View of the High Pressure Cell

M.P.: Main Piston
R.P.: Ram Piston
C₁, C₂, C₃, and C₄: Carboloy Platen
C₁, C₂, C₃, and C₄: Carboloy Cylinder
G₁, G₂: Gaskets
I₁, I₂: Insulation Discs
S: Sample
P₁, P₂: Carboloy Pistons
R₁, R₂, R₃: Steel Rings
SJ₁, SJ₂: Steel Jackets

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samples (see Appendix I for the specifications of Carboloy and Appendix II for the design and construction of the cell).

6. The Reinforced Carboloy Pistons

Two 0.249 inch Carboloy "883" pistons were used for transmitting pressure to the sample.

7. Soft Steel Gaskets

Cylindrical discs (0.250 inch diameter and 0.006 inch thick) made of soft steel formed a part of the assembly as shown in Figure 1.

8. Carboloy Platens

Three Carboloy platens C\(_2\), C\(_3\) and C\(_4\) were used for support.

9. Insulation Discs

Two Phenolite discs, I\(_1\) and I\(_2\) were needed for thermally insulating the cell from the hydraulic press.

10. Test Materials

All chemicals investigated were of analytical grade and obtained from British Drug Houses Ltd., Toronto.
CHAPTER VI

EXPERIMENTAL PROCEDURE

A. Cell Calibration for Pressure

Because of the non-hydrostatic nature of the pressure on the sample, and wall friction, the cell had to be calibrated to find a relationship between the oil pressure in the hydraulic ram and the pressure to which the sample was subjected. Certain materials with known first order phase transitions at high pressure were used for this purpose. These are indicated in Table 2.

TABLE II
Calibration Constants at 77°F (20)

<table>
<thead>
<tr>
<th>No</th>
<th>Substance</th>
<th>Decrease in Volume</th>
<th>Pressure in Kilobars</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KNO₃</td>
<td>-</td>
<td>2.3</td>
</tr>
<tr>
<td>2</td>
<td>KBr</td>
<td>10.5%</td>
<td>18.0</td>
</tr>
<tr>
<td>3</td>
<td>KCl</td>
<td>11.0%</td>
<td>20.2</td>
</tr>
<tr>
<td>4</td>
<td>Bismuth</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>I — II</td>
<td>5.0%</td>
<td>25.3</td>
</tr>
<tr>
<td>5</td>
<td>Bismuth</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>II — III</td>
<td>3.0%</td>
<td>26.8</td>
</tr>
<tr>
<td>6</td>
<td>Thallium</td>
<td>1.0%</td>
<td>37.0</td>
</tr>
</tbody>
</table>

The calibration curve obtained is shown in Figure 3. This curve was assumed to be correct over the range of temperatures employed in this study. A reference point was established in the following way:
FIGURE 3. Calibration Curve

Cell Pressure (Kilobars) at 77°F

Line Pressure (P.S.I.G.)
About 0.2 grams of the calibration material powder was placed in the clean bore of the pressure cell. The powder was kept in place by the two Carboloy pistons. Two soft steel gaskets were interposed between the powder and the pistons to prevent the powder from leaking. The assembled cell was placed in the constant temperature bath and allowed to sit there at $77^\circ F$ for about 30 minutes. During this time the cell was expected to come to thermal equilibrium. The pressure on the sample was then raised to 25 kilobars and released. This was repeated 3 times. The sample was then compressed and a transition establishing a reference point was detected as discussed in Chapter VII under data reduction.

B. Blank Calibration for Displacement

The displacement data obtained by the experimental method had to be corrected to take into account the compression of the following: Carboloy plates $C_1$, $C_2$, and $C_3$; insulation disc $I_1$; pistons $P_1$ and $P_2$; and gaskets. Therefore, in order to get the compression of the sample only, blank runs were made at different temperatures, using the cell assembly as shown in Figure 2. Displacement data so obtained were then subtracted from the experimental runs at corresponding temperatures. In this way true salt compression data were obtained.

C. Procedure for an Experimental Run

The cell and pistons were cleaned with water and acetone in turn and then air dried. A gasket was forced into the bore of the cell with an arbor press (see Appendix III, for a diagram of the jig used). Enough powder to form a 0.50" long sample was then poured into the cell and another gasket was forced into it. These soft steel gaskets prevented the powdery material from escaping between the cell wall and

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pistons. The cell was then assembled as shown in Figure 2 and immersed in the oil bath. This system in turn was placed between the rams of the press. Once again at least 30 minutes were allowed to let the system come to thermal equilibrium.

The pressure on the ram was raised to 15 pounds per square inch and released. The cell was taken out and its length measured in order to obtain the sample length at atmospheric pressure. This measurement was done with a combination of a height gauge and dial indicator gauge. The cell was then put back into its previous position and allowed to attain thermal equilibrium.

The experimental readings were taken as follows. The pressure on the ram was increased in increments of five pounds per square inch. A two minute interval was allowed to elapse between two increments. At the end of the first minute, the displacement was noted, at the end of the second minute, the indicator was again read. If there was difference between these observations a first order transition or dehydration of the salt was suspected. In either case the pressure on the Bourdon gauge was seen to fall. If such a thing happened, at the end of the next increment, during the two minute interval, the pressure was maintained at the new value. If no transition or dehydration was encountered the pressure was raised by increments until the sample was under a stress of 23 kilobars. The pressure was then released, the cell taken out, its length measured and the whole procedure repeated. Normally this had to be done about three or four times. The third and fourth run were found to be identical showing lack of hysteresis effect.

In cases where phase transitions or dehydrations were suspected, the pressure was increased about 20 pounds per square inch beyond the
value where change was first suspected and then released. It was followed by repetition of the procedure. A check on the reversibility of the transition was then made. After establishing the nature of the transition, the sample was still subjected to a maximum pressure of 23 kilobars two or three times and observations recorded. This procedure was repeated at an interval of 5°F wherever needed.
CHAPTER VII
REDUCTION OF DATA

A. Treatment of Data for Dehydration and Phase Transformations

The exact determination of pressures at which a dehydration or a phase transition occurs is very difficult to make in the type of equipment that was used for this project. There were two important reasons for the variations in the data.

1. Variation in Frictional Forces

The frictional forces between the walls of the pressure cell and the pistons were bound to change from run to run. Therefore there were always slight variations from the true calibrations. As a consequence the same transition was observed at slightly different pressures over several runs. This error was minimized by averaging data from several runs.

2. Metastability and the Inherent need for a Driving Force

The tendency of one phase to continue as a metastable form into the region where only the other phase is stable under the given conditions is well known. Supercooling is the analogous thermal example. Thus a higher pressure will have to be applied before the transitions can proceed at a noticeable rate. Kennedy et al (11) claim that they avoided these difficulties by rotating their pistons at the first evidence of appearance of any transitions. Friction was thus relieved and the metastable state disturbed. However the slow solid state transitions will proceed at an
observable rate only if pressures in excess of the actual equilibrium pressures are applied. As long as the driving force is small, the rate of a process is slow. Since only two minutes were allowed between two consecutive readings the detection of any discrepancy between the first minute observation and the second minute observation was difficult. Consequently the reported transition pressures will be slightly higher than the true pressures.

3. Criteria Used for Detection of Transformations

The following criteria were used for the detection of transformations.

(a) first drift of displacement with time.
(b) first deviation from continuity on a $-\Delta V/V_o$ vs P graph.
(c) appearance of water outside the cell.

The variables used for plotting graphs were $-\Delta V/V_o$ and P, where

$V_o = \text{volume of the sample at 1 atmosphere,}$

$\Delta V = \text{volume of the sample at pressure } P - \text{volume of the sample at atmospheric pressure,}$

$P = \text{pressure in kilobars.}$

Since the Carboloy cylinder can be assumed to be perfectly rigid for the pressures applied in this study, $I_0$ and $\Delta I$ can be used instead of $V_o$ and $\Delta V_o$. In computing $\Delta I$, blank corrections were applied (already mentioned in Chapter VI).

B. Treatment of Data for Pressure-Volume Correlation

As a first step in evaluating the experimental results for the twelve compounds which showed no transformations the blank corrected displacement data was treated to find their fit to Khoubessarian's (12)
relationship \[-\Delta V/V_0 = m + n \ln P\]. Several runs for the same sample were tested statistically and correlation factors calculated (16) for each run. The results indicated that the relationship was valid to at least a confidence level of 99 percent.
# CHAPTER VIII
## RESULTS

### A. Dehydration

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>Crystal Structure</th>
<th>Dehydration Pressure</th>
<th>Temperature</th>
<th>New Hydrate State</th>
<th>New Crystal Structure</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>ZnSO₄·7H₂O</td>
<td>Rhombic</td>
<td>1 atmosphere</td>
<td>536°F</td>
<td>ZnSO₄</td>
<td>Rhombic</td>
<td>(9)</td>
</tr>
<tr>
<td>1b</td>
<td>ZnSO₄·7H₂O</td>
<td>Rhombic</td>
<td>4.6 kilobars</td>
<td>77°F</td>
<td>ZnSO₄·6H₂O</td>
<td>Monoclinic</td>
<td>Observable by visual inspection and from (-\Delta V/V₀) graph.</td>
</tr>
<tr>
<td>2a</td>
<td>Na₂SO₄·7H₂O</td>
<td>Monoclinic</td>
<td>1 atmosphere</td>
<td>302°F</td>
<td>Na₂SO₃</td>
<td>Hexagonal</td>
<td>(9)</td>
</tr>
<tr>
<td>2b</td>
<td>Na₂SO₄·7H₂O</td>
<td>Monoclinic</td>
<td>8.9 kilobars</td>
<td>77°F</td>
<td>Na₂SO₃</td>
<td>Hexagonal</td>
<td>Water was observed oozing out. A sudden decrease in volume was also found at 8.9 kilobars. Dehydration is apparent on (-\Delta V/V₀) curve.</td>
</tr>
<tr>
<td>3a</td>
<td>Zr(SO₄)₂·H₂O</td>
<td>Rhombic</td>
<td>1 atmosphere</td>
<td>248°F</td>
<td>Zr(SO₄)₂·H₂O</td>
<td>-</td>
<td>(9)</td>
</tr>
<tr>
<td>3b</td>
<td>Zr(SO₄)₂·H₂O</td>
<td>Rhombic</td>
<td>Continuous</td>
<td>77°F</td>
<td>-</td>
<td>-</td>
<td>Loss of water is continuous over the pressure range. (-\Delta V/V₀) curve.</td>
</tr>
<tr>
<td>No</td>
<td>Compound</td>
<td>Crystal Structure</td>
<td>Dehydration Pressure</td>
<td>Temperature</td>
<td>New Hydrate State</td>
<td>New Crystal Structure</td>
<td>Remarks</td>
</tr>
<tr>
<td>----</td>
<td>------------------</td>
<td>-------------------</td>
<td>----------------------</td>
<td>-------------</td>
<td>-------------------</td>
<td>----------------------</td>
<td>-------------------------------------------------------------------------</td>
</tr>
<tr>
<td>4a</td>
<td>ThCl₄·8H₂O</td>
<td>-</td>
<td>1 atmosphere</td>
<td>77°F</td>
<td>-</td>
<td>-</td>
<td>Visual observation as well as $\Delta V/V_0$ curve.</td>
</tr>
<tr>
<td>4b</td>
<td>ThCl₄·8H₂O</td>
<td>-</td>
<td>2.2-4.6 kilobars</td>
<td>77°F</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td>Ca(SCN)₂·4H₂O</td>
<td>-</td>
<td>1 atmosphere</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>5b</td>
<td>Ca(SCN)₂·4H₂O</td>
<td>-</td>
<td>0.5 kilobars</td>
<td>77°F</td>
<td>-</td>
<td>-</td>
<td>Visual inspection and the pressure-volume graph make it apparent.</td>
</tr>
</tbody>
</table>
B. Phase Transformations

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>Crystal Structure</th>
<th>Transition Temperature</th>
<th>Transition Pressure (kilobars)</th>
<th>Percentage</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na$_2$S$_2$O$_3$·SH$_2$O</td>
<td>Monoclinic</td>
<td>77°F</td>
<td>18.5</td>
<td>2.2</td>
<td>Transition is reversible</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>85°F</td>
<td>18.1</td>
<td>2.8</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>90°F</td>
<td>17.7</td>
<td>2.1</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>95°F</td>
<td>17.4</td>
<td>3.1</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100°F</td>
<td>16.6</td>
<td>3.1</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>105°F</td>
<td>16.5</td>
<td>2.6</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>110°F</td>
<td>16.0</td>
<td>2.6</td>
<td>&quot;</td>
</tr>
<tr>
<td>2</td>
<td>ZnSO$_4$·6H$_2$O</td>
<td>Monoclinic</td>
<td>77°F</td>
<td>2.2</td>
<td>2.5</td>
<td>Transition is reversible</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>77°F</td>
<td>16.2</td>
<td>3.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>3</td>
<td>Th(SO$_4$)$_2$·8H$_2$O</td>
<td>Monoclinic</td>
<td>77°F</td>
<td>9.8</td>
<td>1.3</td>
<td>Transition is reversible</td>
</tr>
<tr>
<td>4</td>
<td>MgS$_3$O$_3$·6H$_2$O</td>
<td>Rhombic</td>
<td>77°F</td>
<td>7.7</td>
<td>2.5</td>
<td>Transition is reversible</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>90°F</td>
<td>6.7</td>
<td>2.6</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>105°F</td>
<td>5.2</td>
<td>2.3</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>120°F</td>
<td>4.6</td>
<td>2.2</td>
<td>&quot;</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>135°F</td>
<td>4.0</td>
<td>2.2</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>150°F</td>
<td>3.2</td>
<td>2.2</td>
<td>&quot;</td>
</tr>
<tr>
<td>5</td>
<td>ZnSO$_4$·7H$_2$O</td>
<td>Rhombic</td>
<td>77°F</td>
<td>2.1</td>
<td>1.0</td>
<td>Transition is reversible</td>
</tr>
<tr>
<td>No</td>
<td>Compound</td>
<td>Crystal Structure</td>
<td>Transition Temperature</td>
<td>Transition Pressure (kilobars)</td>
<td>$\Delta \left[ \Delta V/V_0 \right]$</td>
<td>Remarks</td>
</tr>
<tr>
<td>----</td>
<td>-------------------</td>
<td>-------------------</td>
<td>------------------------</td>
<td>--------------------------------</td>
<td>----------------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>6</td>
<td>ZrOCl$_2$·8H$_2$O</td>
<td>Tetragonal</td>
<td>77°F</td>
<td>5.6</td>
<td>1.6</td>
<td>Transition is reversible</td>
</tr>
<tr>
<td>7</td>
<td>BeSO$_4$·4H$_2$O</td>
<td>Tetragonal</td>
<td>77°F</td>
<td>10.3</td>
<td>3.1</td>
<td>Transition is reversible</td>
</tr>
<tr>
<td>8</td>
<td>K$_2$(MoO$_4$)·5H$_2$O</td>
<td>Unknown</td>
<td>77°F</td>
<td>10.3</td>
<td>2.8</td>
<td>Transition is reversible</td>
</tr>
<tr>
<td>9</td>
<td>Mg(SCN)$_2$·4H$_2$O</td>
<td>Unknown</td>
<td>77°F</td>
<td>5.8</td>
<td>5.9</td>
<td>Transition is reversible</td>
</tr>
</tbody>
</table>
C. Pressure Volume Correlation

Neither dehydration nor any phase transformation could be found in the following compounds to a pressure of 22.6 kilobars at 77°F. P V data obtained at 77°F was correlated by Khoubesserian's (12) expression

\[-\Delta V/V_0 = m + n \ln P\]

The values for m and n are given below.

Table V

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal Structure</th>
<th>Average, m</th>
<th>Average, n</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3K_2S_2O_3 \cdot H_2O$</td>
<td>Monoclinic (9)</td>
<td>0.0040</td>
<td>0.022</td>
</tr>
<tr>
<td>$(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$</td>
<td>Monoclinic (9)</td>
<td>0.0020</td>
<td>0.022</td>
</tr>
<tr>
<td>$BaS_2O_3 \cdot H_2O$</td>
<td>Rhombic (9)</td>
<td>0.0020</td>
<td>0.017</td>
</tr>
<tr>
<td>$(NH_4)_2Cr(SO_4)_2 \cdot 12H_2O$</td>
<td>Cubic (9)</td>
<td>0.0030</td>
<td>0.029</td>
</tr>
<tr>
<td>$Ce(NO_3)_3 \cdot 6H_2O$</td>
<td>-</td>
<td>0.020</td>
<td>0.026</td>
</tr>
<tr>
<td>$(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$</td>
<td>-</td>
<td>0.0020</td>
<td>0.022</td>
</tr>
</tbody>
</table>

| Anhydrous Salts                           |                     |            |            |
| $Na_2SO_3$                                | Hexagonal (9)       | 0.0000     | 0.019      |
| $Na_2S_2O_3$                              | Monoclinic (9)      | 0.0060     | 0.017      |
| $(NH_4)_2SO_3$                            | Monoclinic (9)      | 0.0120     | 0.029      |
| $PbS_2O_3$                                | -                   | 0.0120     | 0.018      |
| $ThCl_4$                                  | Rhombic (9)         | 0.0070     | 0.018      |
| $ZnSO_4$                                  | Rhombic (9)         | 0.0150     | 0.032      |
CHAPTER IX
DISCUSSION OF RESULTS

A. General

When this study was undertaken it was recognized that this would be the first step towards the solution of certain problems. How does pressure cause and initiate chemical change? Does application of pressure always result in new phases with closer packing of ions, atoms or molecules? Is there an equation of state which will predict the behavior of all materials at high pressure? It was never conceived that the answers will be forthcoming immediately. The objective was to gain more information in order to be able to ask the questions more precisely.

The overall study attempts to: first, dehydrate inorganic compounds by the application of pressure, and find the mechanism of dehydration; second, discover new phase transformations in hydrates brought about by pressure, and determine the role played by water in these transformations; and finally to fit a newly developed equation of state

\[-\Delta V/V_0 = B(T_c - 20) + (C + D(T_c))\ln P + E\]

to hydrates exhibiting no transformations.

This equation was developed for plastics and has been found to be valid to 22.6 kilobars and 205°F.
The results obtained as a consequence of this preliminary study are discussed under three headings, Dehydrations, Phase Transformations Under High Pressure, and Correlation of Pressure-Volume Data.

B. Dehydrations

Of the nineteen hydrates examined only five showed any degree of dehydration up to a pressure of 22.6 kilobars at a temperature of 77°F. These nineteen compounds are listed below according to their crystal structure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal Structure</th>
<th>Dehydrated Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr((SO_4)_2\cdot4H_2O)</td>
<td>Rhombic</td>
<td>((NH_4)_2Cr(SO_4)_2\cdot12H_2O) Cubic</td>
</tr>
<tr>
<td>ZnSO(_4\cdot7H_2O)</td>
<td>Rhombic</td>
<td>BeSO(_4\cdot4H_2O)</td>
</tr>
<tr>
<td>MgS(_2O_3\cdot6H_2O)</td>
<td>Rhombic</td>
<td>ZrOCl(_2\cdot8H_2O)</td>
</tr>
<tr>
<td>BaS(_2O_3\cdotH_2O)</td>
<td>Rhombic</td>
<td>ThCl(_4\cdot3H_2O)</td>
</tr>
<tr>
<td>Na(_2SO_4\cdot7H_2O)</td>
<td>Monoclinic</td>
<td>Ca(SCN)(_2\cdot4H_2O)</td>
</tr>
<tr>
<td>ZnSO(_4\cdot6H_2O)</td>
<td>Monoclinic</td>
<td>K(_2)(MoO(_4))_5H_2O</td>
</tr>
<tr>
<td>Th(SO(_4)_2\cdot8H_2O)</td>
<td>Monoclinic</td>
<td>Mg(SCN)(_2\cdot4H_2O)</td>
</tr>
<tr>
<td>Na(_2S_2O_3\cdot5H_2O)</td>
<td>Monoclinic</td>
<td>Ce(NO(_3)_3\cdot6H_2O)</td>
</tr>
<tr>
<td>Zr(SO(_4)_2\cdot4H_2O)</td>
<td>Monoclinic</td>
<td>(NH(_4)_2Mn(SO(_4)_2\cdot6H_2O</td>
</tr>
<tr>
<td>(NH(_4)_2Co(SO(_4)_2\cdot6H_2O</td>
<td>Monoclinic</td>
<td></td>
</tr>
</tbody>
</table>

Of the above nineteen compounds the five that show dehydration are:

\[ \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \]
\[ \text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O} \]
\[ \text{Zr(SO}_4)_2 \cdot 4\text{H}_2\text{O} \]
\[ \text{ThCl}_4 \cdot 8\text{H}_2\text{O} \]
\[ \text{Ca(SCN)}_2 \cdot 4\text{H}_2\text{O} \]

The dehydration of the above compounds is discussed below.
1. Dehydration of ZnSO$_4$·7H$_2$O

Figure 4 shows graphically what happens to ZnSO$_4$·7H$_2$O when it is compressed. The compound undergoes a reversible phase transition at 2.1 kilobars. The reversibility was tested by raising the pressure to 3.4 kilobars and releasing it three times. At 4.6 kilobars the salt showed dehydration as could be seen from the water that oozed out of the cell. This was also clear from the discontinuity in the $-\Delta V/V_0$ curve at 4.6 kilobars and 77°F. The pressure was then raised to 10 kilobars and released. On reapplication of pressure a reversible transition at 2.1 kilobars was detected but the discontinuity at 4.6 kilobars could not be repeated. Another reversible transition at 16.2 kilobars and 77°F was found.

Figure 5 shows the behaviour of ZnSO$_4$·6H$_2$O, the lower hydrate, under pressure. There is one reversible transition at 2.2 kilobars and another at 16.2 kilobars. These two figures suggest that both ZnSO$_4$·7H$_2$O and ZnSO$_4$·6H$_2$O have phase transformations which just happen to occur at about the same pressure 2.1-2.2 kilobars. At 4.6 kilobars the heptahydrate loses a molecule of water and then behaves like the hexahydrate. That the decrease in volume over the two transitions for the converted hexahydrate and the actual hexahydrate does not agree is understandable. The dehydration probably is not complete at the centre of the pellet. This view is supported by the fact that repetition of compression does show a trend towards such an agreement.

The small size of the sample made it impossible to obtain the degree of dehydration of the sample by weighing. A further complication in the same method arose from the seepage of oil into sample upon dis-
FIGURE 4. ZnSO₄·7H₂O at 77°F

(1) Run 1
(2) Run 2
(4) Run 4
FIGURE 5. $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ at 77°F
mantling of the cell. An X-ray study however would establish the nature beyond doubt. This is to be taken up in the next stage of work.

2. Dehydration of $\text{Na}_2\text{SO}_3\cdot 7\text{H}_2\text{O}$

The compound $\text{Na}_2\text{SO}_3\cdot 7\text{H}_2\text{O}$ was found to lose water at a pressure of 8.9 kilobars. There was a sudden change of volume as is apparent from Figure 6. Repeated compression to 8.9 kilobars seems to yield a compound whose compression behaviour is very similar to that of the anhydrous salt as can be seen from Figure 6. Thus it is reasonable to assume that the hepta-hydrate changes to the anhydrous form.

3. Dehydration of $\text{Zr(SO}_4)_2\cdot 4\text{H}_2\text{O}$

Zirconium sulphate octahydrate was not found to lose water at any specific pressure. The dehydration was seen to be continuous as is clear from Figure 7. A shrinkage after every run was also apparent. It was not possible to obtain $\text{Zr(SO}_4)_2\cdot 4\text{H}_2\text{O}$ or $\text{Zr(SO}_4)_2$ samples and hence it was not possible to say anything about the new state of the dehydrated compound.

4. Dehydration of $\text{ThCl}_4\cdot 8\text{H}_2\text{O}$

The salt $\text{ThCl}_4\cdot 8\text{H}_2\text{O}$ is a little known compound. Even an accurate density of the material is not known. Dehydration studies at elevated temperatures and atmospheric pressure have not been attempted. The crystal structure of the hydrate has yet to be explained.

Dehydration with pressure presents some interesting features. Water was seen to escape from the cell in the pressure range 2.2-4.6 kilobars. This can also be seen from the irregular nature of the curves (figures 8a and 8b). The most surprising thing however was the repetition of the behaviour in the same range over a number of runs for the same sample.
FIGURE 6. $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_3$ at $77^\circ\text{F}$

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FIGURE 7. \[ \text{Zr(SO}_4\text{)}_2 \cdot \text{H}_2\text{O at 77°F} \]
FIGURE 8a. ThCl$_4$·8H$_2$O at 77°F
FIGURE 8b. ThCl₄•8H₂O at 77°F
The compound shows a smooth -$\Delta V/V_0$ curve beyond 4.6 kilobars. Repeated compression changes the octahydrate into an anhydrous form as is illustrated by the comparison of compression curves for ThCl$_4$•$8$H$_2$O converted and actual ThCl$_4$ (Figures 8a, 8b, 8c, and 8d).

In the absence of X-ray studies it is hard to say anything with certainty about the behaviour of ThCl$_4$•$8$H$_2$O in the 2.2 to 4.6 kilobar range. A hypothesis however can be advanced. It can be assumed that ThCl$_4$•$8$H$_2$O undergoes a transition at 2.2 kilobars. The new phase (Phase II) which extends between 2.2-4.6 kilobars loses water. At 4.6 kilobars another phase appears in which water is held tightly. If both these transitions are reversible, the loss of water between 2.2-4.6 kilobars is easily explained. Repeated compression will eliminate phase II completely and the hydrate will behave like ThCl$_4$.

5. Dehydration of Ca(SCN)$_2$•$4$H$_2$O

Water was observed to ooze out of the cell at 0.5 kilobars. The second run on the same sample did not produce the same result. This is also clear from the comparison of runs number 1, 2, 3, and 4 on Figure 9. The smoothness of runs 2, 3, and 4 indicate that dehydration is almost complete at the end of the first compression to 22.6 kilobars. The second and third runs differed slightly from each other, but the third and fourth did not. This was because by the end of the second run the material had settled into a new pattern. As it was not possible to obtain the anhydrous form nothing can be said about the degree of dehydration.

6. Mechanism of Dehydration

How does dehydration take place? In the absence of X-ray diffraction analysis of the material under pressure, it is difficult to make
FIGURE 8c. ThCl₄·8H₂O and ThCl₄ at 77°F

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FIGURE 8d. Dehydration of ThCl$_4$.8H$_2$O at 77°F.
FIGURE 9. Ca(SCN)$_2$.4H$_2$O at 77°F
a clear cut statement but the following views can be considered.

Since the pressure is not hydrostatic, compression does result in generation of shear stresses. Shear stresses could cause a collapse of the crystal lattice. Such collapsing of the crystal lattice has been observed in temperature dehydration studies of ZnSO$_4$·7H$_2$O and CuSO$_4$·5H$_2$O by Frost et al. (7). It is assumed that the collapsed state corresponds to an amorphous structure. Water in these zeolitic intermediates is held in tunnels and cavities of the rigid framework. Application of pressure should therefore result in squeezing out of water from these tunnels.

Any accidental liberation of water from the equipment will cause nucleation and growth of new stable crystalline form. If by any chance traces of lower hydrate or anhydrous compounds are present, the rate of nucleation will be accelerated and dehydration will proceed at an observable rate. This has been found to be true in the case of CaSO$_4$·2H$_2$O, as shown by Kiyama (14).

The structure of the intermediate resulting from a collapsed lattice is a matter of controversy however. The amorphous zeolitic mass may be really disorganized or it might consist of highly dispersed microcrystals of a size below the limit required for X-ray diffraction analysis.

From the thermodynamic point of view the accidental escape of water is extremely important as can be seen from the equation

\[ M \times H_2O \rightarrow M + XH_2O \]

In the case of the five hydrates examined for this study, the molar volume on the right hand side is greater than that on the left hand side, and hence higher pressure would not favour the reaction to the right.
But the escape of water will shift the equilibrium to the right.

Why do some hydrates show dehydration at ordinary temperature and high pressure, and others do not? A look at the Gibbs free energy function $G$ explains it.

Since the hydrates examined for this study are stable at room temperature, $\Delta G$ for the change, $M \cdot XH_2O \rightarrow M + XH_2O$, is $> 0$, but

$$\Delta G = \Delta V_M^0 (P_2 - P_1) - \Delta B(P_2^{1/2} - P_1^{1/2})$$

(equation (1) in Chapter III), and if at any stage $\Delta B(P_2^{1/2} - P_1^{1/2}) > P_2 - P_1$ (assuming $\Delta V_M^0 > 0$, which it is in most cases), $\Delta G$ will change its sign and thus dehydration will proceed. In most cases however such a thing will happen in vacuum or at high pressures if $\Delta B$ is negative.

C. Phase Transformations Under High Pressure

The following hydrates showed phase transitions.

<table>
<thead>
<tr>
<th>Hydrate</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S$_2$O$_3 \cdot 5$H$_2$O</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Th(SO$_4$)$_2 \cdot 6$H$_2$O</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>ZnSO$_4 \cdot 7$H$_2$O</td>
<td>Rhombic</td>
</tr>
<tr>
<td>BeSO$_4 \cdot 4$H$_2$O</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Na$_2$S$_2$O$_3 \cdot 5$H$_2$O</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>ZnSO$_4 \cdot 6$H$_2$O</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>MgS$_2$O$_3 \cdot 6$H$_2$O</td>
<td>Thombic</td>
</tr>
<tr>
<td>ZrOCl$_2 \cdot 8$H$_2$O</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>K$_2$(MoO$_4$)$_2 \cdot 5$H$_2$O</td>
<td>Unknown</td>
</tr>
<tr>
<td>Mg(SCN)$_2 \cdot 6$H$_2$O</td>
<td>Unknown</td>
</tr>
</tbody>
</table>

1. Monoclinic Systems

a. Sodium Thiosulphate Pentahydrate

Monoclinic crystals of sodium thiosulphate pentahydrate are known to undergo a phase transformation at 118°F at atmospheric pressure

$$Na_2S_2O_3 \cdot 5H_2O \xrightarrow{118°F} Na_2S_2O_3 \cdot 2H_2O + 3H_2O.$$

A reversible phase transition at 18.5 kilobars and 77°F was found during
this study (Figure 10a). The percentage \( \frac{\Delta (-\Delta V/V)}{V_o} \) was 2.2. At 110°F the transition pressure was 16.0 kilobars (Figure 10b). Figure 10c and Table IV summarize the effect of temperature on the transition pressure. The material when compressed to 19.3 kilobars at 110°F showed a very sudden contraction. This contraction invariably damaged the pressure cell, and in spite of several attempts, pressure beyond 19.3 kilobars could not be attained. This contraction could be due to one of the following reasons.

i. Appearance of a New Phase

The appearance of a new phase III with molar volume much smaller than the molar volume of the phase II of the pentahydrate, might have led to a sudden contraction. Such a sudden contraction could cause damage to the cell resulting in leakage of the material into cracks so formed.

ii. Dehydration of the Pentahydrate

The pentahydrate might have been dehydrated to either a lower hydrate form or an anhydrous form. Escape of water will cause sudden contraction and damage to the cell. The only way to settle the question will be an X-ray diffraction analysis.

b. Zinc Sulphate Hexahydrate

Zinc sulphate hexahydrate showed two reversible transitions at 77°F (Figure 11), one at 2.2 kilobars and the other at 16.2 kilobars. The average percentage \( \frac{\Delta (-\Delta V/V)}{V_o} \) for the first transition was 2.5 and for the second transition was 3.0. The cell used was not designed for high temperature work otherwise a phase diagram with a possible triple point could be obtained.
FIGURE 10a. Na$_2$S$_2$O$_3$·5H$_2$O at 77°F
FIGURE 10b. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ at 110°F
FIGURE 10c. $\text{Na}_2\text{S}_2\text{O}_3\cdot5\text{H}_2\text{O}$, Phase Diagram

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FIGURE 11. ZnSO$_4$·6H$_2$O at 77°F
c. Thorium Sulphate Octahydrate

Thorium sulphate octahydrate showed a reversible transition at 9.8 kilobars and 77°F (Figure 12). The percentage $\Delta -\Delta V/V_0$ was 1.3.

2. Rhombic Systems

a. Magnesium Thiosulphate Hexahydrate

The compound $\text{MgS}_2\text{O}_3\cdot6\text{H}_2\text{O}$ was found to have a reversible phase transition at 7.7 kilobars and 77°F (Figure 13a). The percentage $\Delta -\Delta V/V_0$ was 2.5. The temperature-pressure data for this transformation to 150°F are given in Figure 13b and Table IV.

b. Zinc Sulphate Heptahydrate

A reversible phase transition at room temperature and 2.1 kilobars was detected (Figure 14). The percentage $\Delta -\Delta V/V_0$ was less than 1.0.

3. Tetragonal Systems

a. Zirconyl Chloride Octahydrate

The salt $\text{ZrOCl}_2\cdot8\text{H}_2\text{O}$ had a reversible phase transition at 77°F and 5.6 kilobars (Figure 15). The $\Delta -\Delta V/V_0$ was found to be 1.6 percent.

b. Beryllium Sulphate Tetrahydrate

A phase transition was found at 77°F and 10.3 kilobars (Figure 16). The $\Delta -\Delta V/V_0$ was found to be 3.1 percent.

4. Unknown Structures

a. Potassium Molybdate Pentahydrate

A reversible phase transition was shown by this compound at 10.3 kilobars and 77°F. The percentage $\Delta -\Delta V/V_0$ was 2.8 (Figure 17).

b. Magnesium Thiocynate Tetrahydrate

This hydrate had a reversible transition at 5.8 kilobars and
FIGURE 12. $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ at 77°F

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(1) Run at 77°F
(2) Run at 150°F

FIGURE 13a. Mg$_2$O$_{3}$·6H$_2$O

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FIGURE 13b. MgS₂O₃·6H₂O, Phase Diagram

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FIGURE 14. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ at 77°F

(1) Run 1

(2) Run 2

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FIGURE 15. ZrOCl$_2$·8H$_2$O at 77°F
FIGURE 16. BeSO$_4$·4H$_2$O at 77°F
FIGURE 17. $\chi_2(\text{NaNO}_3)\cdot 5\text{H}_2\text{O}$ at 77°F
The change in $-\Delta V/V_0$ was found to be 5.9 percent (Figure 18).

5. Mechanism of Phase Transformations and Structure of New Phases

What are these new phases and what is the role played by water in these phase transformation. This study does not provide the answers. The very complexity of the structures is staggering.

So far it has been assumed that pressure will result in lattices that are more closely packed. A dilatational mechanism involving changes from face centred cubic to body centred cubic has been used to explain the 20.2 kilobar transition in KCl (17).

The monoclinic systems ZnSO$_4$·6H$_2$O, Th(SO$_4$)$_2$·6H$_2$O, Na$_2$S$_2$O$_3$·5H$_2$O, rhombic systems MgS$_2$O$_3$·6H$_2$O, ZnSO$_4$·7H$_2$O, tetragonal systems BeSO$_4$·4H$_2$O, ZrOCl$_2$·6H$_2$O have and the unknown K$_2$(MoO$_4$)$_2$·5H$_2$O and Mg(SCN)$_2$·4H$_2$O presumably have structures which can exist in more than one configuration. But in the absence of X-ray analysis it is not possible to say that these transitions involved only changes of the type, open configuration $\rightarrow$ closed configuration within the same system.

Could solvation by the so called water of crystallization play a part? It is possible that under pressure, water might slip from the crystal lattice, solvate the rest and thus provide the mobility needed for rearrangement. The question, what are these new arrangements, still remains to be answered. Future work in this field can be carried on to verify ideas about solvation and find these rearrangements.

D. Correlation of Pressure-Volume Data

Khoubesserian (12) developed an equation of state for plastics in a range of 22.6 kilobars and $205^\circ$F. This equation

$$-\Delta V/V_0 = B(T_C - 20) + (C + D\times T_C)\ln P + E$$
FIGURE 18. \( \text{Mg(SCN)}_2 \cdot 4\text{H}_2\text{O} \) at 77°F
reduces to

\[-\Delta V/V_0 = m + n \ln P\]

at constant temperature, thus providing an expression for correlating pressure-volume data. It was one of the aims of this project to test the validity of this equation for those compounds which did not show abrupt discontinuities in their \(-\Delta V/V_0 - P\) curves. Twelve out of twenty-five salts examined fell into this category. These consisted of six anhydrous salts used to compare the behaviour of pressure dehydrated compounds and six hydrates. The twelve compounds were

\[
\begin{align*}
\text{Na}_2\text{S}_2\text{O}_3 & \quad (\text{NH}_4)_2\text{Mn(SO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \\
\text{PbS}_2\text{O}_3 & \quad (\text{NH}_4)_2\text{Co(SO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \\
(\text{NH}_4)_2\text{S}_2\text{O}_3 & \quad (\text{NH}_4)_2\text{Cr(SO}_4\text{)}_2 \cdot 12\text{H}_2\text{O} \\
\text{Na}_2\text{SO}_3 & \quad \text{Ce(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \\
\text{ZnSO}_4 & \quad 3\text{K}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O} \\
\text{ThCl}_4 & \quad \text{Ba}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}
\end{align*}
\]

The pressure cell was not designed to withstand higher temperatures it was therefore not possible to test the fit of P-V-T data to the equation of state. However the P-V data obtained at 77°F were fitted to

\[-\Delta V/V_0 = m + n \ln P\]

Statistically the fit was found to be very good as indicated in Figures 19, 20, 21, 22, 23, 24, and 25. The confidence level of the fit was above 99 percent, and the correlation coefficients in any case did not go below 0.90. The fit in the lower range of pressure involved leaving 2 or 3 points out of the proposed line. This was expected however because frictional forces at the cylinder walls were significant in this region, and therefore accurate measurement of cell pressure in this range.
FIGURE 19. Compression Diagram for Na$_2$S$_2$O$_3$ and PbS$_2$O$_3$ at 77°F.
FIGURE 20. Compression Diagram for (NH₄)₂S₂O₃, 3K₂S₂O₃·H₂O, and BaS₂O₃·H₂O at 77°F
FIGURE 21. Compression Diagram for $\text{Na}_2\text{SO}_3$ at 77°F
FIGURE 22. Compression Diagram for ZnSO$_4$ at 77°F
FIGURE 23. Compression Diagram for ThCl₄ at 77°F
FIGURE 24. Compression Diagram for (NH₄)₂Cr(SO₄)₂·12H₂O, (NH₄)₂Co(SO₄)₂·6H₂O and (NH₄)₂Mn(SO₄)₂·6H₂O at 77°F
FIGURE 25. Compression Diagram for Ce(NO$_3$)$_3$·6H$_2$O at 77°F
was not possible. Since in computing the straight line constants, 26 experimental points were used, the effect of 2 or 3 slightly inaccurate points at the low pressure end was considered negligible.

The fact that an expression developed for plastics will fit the data for inorganic hydrates and anhydrous compounds of diverse crystal structure is surprising. However it supports the hypothesis that beyond a certain pressure, compressibilities of all materials will be similar. This may be due possibly to an equivalence of van der Waal forces in all substances beyond a certain pressure.
CHAPTER X

CONCLUSIONS

Compression without the use of deliberate shear action has been found effective in dehydrating \( \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \), \( \text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O} \), \( \text{Zr(SO}_4)_2 \cdot \text{H}_2\text{O} \), \( \text{ThCl}_4 \cdot 8\text{H}_2\text{O} \), and \( \text{Ca}(\text{SCN})_2 \cdot \text{H}_2\text{O} \).

A hypothesis that pressure causes destruction of hydrate lattices leading to the formation of an amorphous zeolitic mass has been proposed. It has been suggested that the so-called water of crystallization is held in the cavities and tunnels of this non-crystalline mass and dehydration is effected by the squeeze action of pressure. This is in line with Frost's (7) hypothesis about temperature dehydration.

Ten new reversible phase transitions in nine hydrates have been discovered at room temperature. In addition there are indications of two new pressure-induced phase changes in \( \text{ThCl}_4 \cdot 8\text{H}_2\text{O} \) at 2.2 and 4.6 kilobars. There is evidence of an irreversible transition in \( \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} \) at 110°F and 19.3 kilobars. Also a possibility of a triple point in \( \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} \) has arisen.

A mechanism for phase transitions has been proposed. Water dislocated under pressure is thought to solvate the compound thus providing the mobility needed for rearrangement into a new phase.

Pressure and volume data for six hydrates and six anhydrous salts were correlated by an expression.
\[-\frac{\Delta V}{V_o} = m + n\ln P\]

thus completing the first stage of testing the validity of an equation of state developed for plastics under high pressure.
CHAPTER XI

SCOPE OF WORK IN FUTURE

As a result of work done for this project the following guidelines can be laid down for future work.

Construction of a pressure cell capable of withstanding a temperature of at least 400°F.

Use of an air thermostate instead of a constant temperature oil bath, in order to avoid contamination of the sample on dismantling the cell.

Drawing of pressure-temperature diagrams for the reversible phase transformations and dehydrations discovered in this study.

Completion of the second stage of testing of Khoubesserian's equation of state. This will involve obtaining P V and T data for the twelve compounds investigated during this study.

Development of a pressure cell with a window transparent to X-rays. A cell like this can be used in determining the role of amorphous intermediates in pressure dehydration of inorganic compounds. X-ray analysis will also help in determining the structure of pressure induced phases and aid in understanding the solvating role of water in these transitions.
APPENDIX I

SPECIFICATIONS FOR GENERAL ELECTRIC "CARBOLOY"

| Grade | Chemical Compositions (% by weight) | Hardness (Rockwell A) | Density (gm/cc) | Transverse Rupture Strength (psi) | Ultimate Strength in Compression (psi) | Ultimate Strength in Tension (psi) | Elastic limit in Compression (psi) | Elastic limit in Tension (psi) |
|-------|------------------------------------|-----------------------|-----------------|-----------------------------------|----------------------------------------|-----------------------------------|----------------------------------|--------------------------|--------------------------|
|       | WC 87.0                            | 88.3                  | 14.20           | 328,000                           | 530,000                                | 210,000                           | 78,000                           | 88,000                   | 220,000                   |
|       | C₉ 13.0                            |                       |                 |                                   |                                        |                                   |                                  |                          |                          |
|       | WC 94.0                            | 92.0                  | 14.95           |                                   |                                        |                                   |                                  |                          |                          |
|       | C₉ 6.0                             |                       |                 |                                   |                                        |                                   |                                  |                          |                          |

Use

- Cell Cylinder
- Cell Pistons
APPENDIX II

DESIGN CALCULATIONS FOR THE PRESSURE CELL

Since the modulus of elasticity of tungsten carbide is much greater than that of steel, the carbide cylinder can be assumed to be a completely rigid body for calculation purposes.

Seely and Smith (18) describe a method of calculating the optimum dimensions of external support rings. If \( d_0 \) is the outer diameter of the carbide cylinder and \( d_1, d_2 \) and \( d_3 \) are the outer diameters of the steel rings then \( d_1 = m d_0, \) \( d_2 = m^2 d_0, \) and \( d_3 = m^3 d_0, \) where \( m = \) a constant 1.33. Therefore with \( d_0 = 1.257, \) \( d_1 = 1.671'' \), \( d_2 = 2.223'' \), and \( d_3 = 2.957'' \). Christiansen et al (5) used the following expression

\[
\pi_i(f) = \sigma_t \left[ \frac{2^m T-f+1}{m^2 + 1} - 1 \right]
\]

for calculating the internal pressure of any ring. The symbols are defined as
- \( \pi_i \) = internal pressure on any ring
- \( f \) = ring number
- \( \sigma_t \) = maximum tangential stress, \( 15 \times 10^6 \) psi for Alco S steel and \( 42.5 \times 10^6 \) psi for Carboloy 55A
- \( m = 1.33 \)
- \( T = \) total number of rings, 3 in this case

The above formula gives the internal pressure on the innermost ring.

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(labelled ring 1) as \( p_1 = 16.2780 \times 10^4 \text{psi} \)

This also is the external support on the carbide cylinder. For calculating the pressure that could be developed safely inside the Carboloy cylinder, Lame and Clapeyram's (6) equation

\[
p_1 = \sigma_k \left( \frac{b^2 - a^2}{a^2 + b^2} \right) + 2b^2 P_o \]

can be employed. In this expression

\[
b = \text{outer diameter of the Carboloy cylinder} \\
a = \text{inner diameter of the Carboloy cylinder} \\
P_o = \text{external pressure on the Carboloy cylinder} \\
p_1 = \text{internal pressure on the first ring} \]

The safe pressure for the cell is 41 kilobars. The equations given below were used for calculating the diametrical deformations.

For internal diametrical deformation:

\[
u_{1(\text{f})} = \frac{\sigma_t a}{E(m^2 - 1)} \left\{ (1 - \mu) \left[ \left( \frac{2m^2}{m^2 + 1} \right)^{T-f+1} - 1 + m^2 - m^2 \left( \frac{2m^2}{m^2 + 1} \right)^{T-f} \right] \right. \\
\left. + (1 + \mu)m^2 \left( \frac{2m^2}{m^2 + 1} \right)^{T-f+1} - \left( \frac{2m^2}{m^2 + 1} \right)^{T-f} \right\}
\]

where \( u_{1(\text{f})} \) = internal diametrical deformation of any ring \( \text{f} \)

\( a \) = inside diameter of the ring

\( E \) = modulus of elasticity, \( 30 \times 10^6 \) for Alco S steel

\( \mu \) = Poisson's ratio, 0.28.

For external diametrical deformation:
where \( u_{of} \) = external diametrical deformation of any ring \( f \)

\[ b = \text{external diameter of any ring } f. \]

The following internal and external deformations were obtained.

### TABLE VI

<table>
<thead>
<tr>
<th>Ring No</th>
<th>Internal Diametrical Deformation</th>
<th>External Diametrical Deformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.008</td>
<td>0.0045</td>
</tr>
<tr>
<td>II</td>
<td>0.0088</td>
<td>0.0077</td>
</tr>
<tr>
<td>III</td>
<td>0.0119</td>
<td>not needed</td>
</tr>
</tbody>
</table>

Interference (or negative clearance) for any ring \( f \) is defined as

\[ \text{internal deformation of ring } f - \text{external deformation of ring } f - 1. \]

Based on this definition, the negative clearances are given in the following table.

### TABLE VII

<table>
<thead>
<tr>
<th>Ring No</th>
<th>Interference or Negative Clearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.008</td>
</tr>
<tr>
<td>II</td>
<td>0.004</td>
</tr>
<tr>
<td>III</td>
<td>0.004</td>
</tr>
</tbody>
</table>
With these negative clearances the cell members have the dimensions as listed in the table below.

<table>
<thead>
<tr>
<th>Member</th>
<th>Outer Diameter</th>
<th>Inner Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbide Cylinder</td>
<td>1.257&quot;</td>
<td>0.250&quot;</td>
</tr>
<tr>
<td>Ring I</td>
<td>1.671&quot;</td>
<td>1.249&quot;</td>
</tr>
<tr>
<td>Ring II</td>
<td>2.223&quot;</td>
<td>1.667&quot;</td>
</tr>
<tr>
<td>Ring III</td>
<td>2.219&quot;</td>
<td>2.957&quot;</td>
</tr>
</tbody>
</table>
FIGURE 26. Arbor Press Jig
APPENDIX IV

EXPERIMENTAL DATA

The original experimental data is available on computer cards from the Department of Chemical Engineering, University of Windsor, Windsor, Ontario.
BIBLIOGRAPHY


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