HIGH-PRESSURE FORM OF ANALCITE
AND FREE ENERGY CHANGE WITH PRESSURE OF
ANALCITE REACTIONS

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ABSTRACT. The compressibility of four natural analcites has been obtained up to
10,000 atm at 25°C. All specimens show abnormal compressibility \( (\partial \beta / \partial p)_T > 0 \) and
one exhibits a reversible transition at about 8400 atm. Abnormal increase of compressibility
with pressure usually precedes a transition, and it is suggested that a similar transition
lies at higher pressures than those investigated for the three remaining specimens.

The compressibility and density data were used with previously obtained data to com-
pute the volume change and free energy change with pressure for the reactions 2 analcite
\( \rightleftharpoons \) nepheline + albite + 2 water, analcite \( \rightleftharpoons \) jadeite + water, and analcite + quartz
\( \rightleftharpoons \) albite + water. The volume change for these reactions proceeding to the right is
negative for all pressures investigated at 25°C.

The analcite exhibiting the transition showed an increase in birefringence after com-
pression, which is attributed either to strain induced by the volume discontinuity or to
retention of a possible lower symmetry of the high-pressure form. Lower symmetry in a
high-pressure form is not uncommon in previously investigated substances.

INTRODUCTION

The stability ranges of minerals have been calculated from their thermo-
dynamic properties in order to obtain a guide for experiment or as a test of
experimental results. One mineral, jadeite, has been the subject of intense
study for many years because of its bearing on problems relating to minerals
and rocks believed to have formed at high pressures. Prior to the successful
synthesis (Coes, 1955) and determination of portions of the field of stability
of jadeite (Griegs and Kennedy, 1956; Robertson, Birch, and MacDonald.
1957), thermochemical data were collected for the purpose of computing the
stability field of jadeite. The principal reactions for which such data were
obtained are

\[
\begin{align*}
nepheline + albite & = 2 \text{jadeite} \quad (1) \\
\text{albite} & = \text{jadeite} + \text{quartz} \quad (2)
\end{align*}
\]

The large amount of data collected by various workers for this purpose has
been summarized by Adams (1953) and by Fyfe and Valpy (1959). In addition
to these anhydrous reactions, others involving water also limit the field
of stability of jadeite:

\[
\begin{align*}
2 \text{analcite} & = \text{nepheline} + \text{albite} + 2 \text{water} \quad (3) \\
\text{analcite} & = \text{jadeite} + \text{water} \quad (4) \\
\text{analcite} + \text{quartz} & = \text{albite} + \text{water} \quad (5)
\end{align*}
\]

Efforts were made, therefore, to acquire the additional data, namely the ther-
mochemical properties of analcite, necessary to compute these reactions. The
low-temperature heat capacity and entropy at 25°C of analcite were obtained
through the courtesy of Dr. K. K. Kelley by King (1955) and preliminary
data on the heat of solution were obtained through the kindness of Dr. F. C.
Kracek (personal communication, 1954). The compressibility, high-tempera-
ture specific heat, thermal expansion, and specific volume data are still to be

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measured. In the meantime, reaction (3) has been investigated experimentally (Yoder, 1950, 1954; Valpy, 1958) at relatively low pressures; reaction (4) was studied at relatively high pressures (Griggs and Kennedy, 1956; Robertson, Birch, and MacDonald, 1957); and data have been obtained by Ellis (1958) and Valpy (1958) on reaction (5).

It is the purpose of the present paper to record the compressibility and density data for several natural analcites. These data are required for calculating the free energy change in reactions (3), (4), and (5) as a function of pressure.

APPARATUS AND SPECIMENS

The apparatus for compressibility measurements has been previously described by Weir (1950), and the equations for calculation have been outlined by Adams, Williamson, and Johnston (1919). The specimen is immersed in Varsol in a pressure vessel fitted with a leak-proof piston. The displacement of the piston is measured at a series of pressures up to 10,000 atm. A similar experiment performed with a steel bar of known compressibility permits the calculation of the compressibility of the specimen.

A few additional comments are appropriate with regard to the calibration, by means of the Ice VI—L transition, of the manganin-resistance pressure gage used in the apparatus. The temperature of the room in which the equipment was installed was regulated to 20° ± 0.5°C, and the temperature variation in the apparatus is presumed to be less than 0.1°C, so the value used for the Ice VI—water transition was 8710 atm (Bridgman, 1912). For thermodynamical purposes the accuracy of this value is not very great (Bridgman, 1912; Adams, 1931), since the value is extremely sensitive to changes in temperature (0.1°C = 15.4 atm). An appreciation of the precision may be gained from figure 1. The values given by Bridgman have been generally accepted subject to later correction, if any. For the present study, errors as great as ± 20 atm have negligible influence on the accuracy of the volume changes measured.

The specimens of analcite investigated were selected on the basis of composition or availability of especially large single crystals. Two specimens (Golden, Colo., and Wasson's Bluff, Nova Scotia) consisted of crystal fragments and were contained in an open, thin steel vial. (The compressibility of steel has been determined by Bridgman, 1940, 1949.) Two other specimens (Seisser Alp, Austria, and Fassa Thal, Austria) were used in the form of cores drilled from exceptionally large single crystals. The core assembled from each specimen was 1.5 cm in diameter and approximately 10 cm long. No container was required for these specimens.

Representative chemical analyses of specimens from the same localities are given in table 1. These analyses are 1.47 to 2.48 percent higher in SiO₂ than the ideal composition. a common feature of analyzed analcites (see Saha, 1959, p. 310, fig. 4). These high SiO₂ values cannot be attributed to improper analytical technique because the Al₂O₃ + SiO₂ totals are also higher than expected. The material from Golden, Colo., purified by the writers, was analyzed with extreme care by E. H. Oslund (Rock Analysis Laboratory, Univer-
Fig. 1. Melting curve for ice VI used as a standard for pressure gage calibration. Circles are data of Bridgman (1912) and triangles his preferred values at fixed points; cross is data of Adams (1931, p. 3778). The extreme sensitivity of the melting behavior to temperature and the dispersion of the data are emphasized.

Table 1

Representative chemical analyses of analcites from the same four localities as those investigated

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Golden Colorado</td>
<td>Wesson's Bluff</td>
<td>Seisser Alp Austria</td>
<td>Fassa Thal Austria</td>
</tr>
<tr>
<td>Ideal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>54.58</td>
<td>56.05</td>
<td>57.06</td>
<td>56.49</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>23.16</td>
<td>22.36</td>
<td>21.48</td>
<td>21.89</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>9.03</td>
<td>9.13</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>FeO</td>
<td>0.02</td>
<td>—</td>
<td>0.13</td>
<td>—</td>
</tr>
<tr>
<td>MgO</td>
<td>0.02</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CaO</td>
<td>0.00</td>
<td>0.16</td>
<td>0.56</td>
<td>0.51</td>
</tr>
<tr>
<td>Na₂O</td>
<td>14.08</td>
<td>13.44</td>
<td>12.20</td>
<td>11.39</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.10</td>
<td>—</td>
<td>0.53</td>
<td>—</td>
</tr>
<tr>
<td>H₂O⁺</td>
<td>8.18</td>
<td>8.13</td>
<td>8.38</td>
<td>8.73</td>
</tr>
<tr>
<td>H₂O⁻</td>
<td>0.01</td>
<td>0.58</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.01</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.15</td>
<td>99.99</td>
<td>99.59</td>
</tr>
</tbody>
</table>

A. \((\text{Na}_{0.35}\text{Mg}_{0.75})(\text{Al}_{0.98}\text{Si}_{1.24})\text{O}_8 \cdot 0.98\ \text{H}_2\text{O})

B. \((\text{Na}_{0.35}\text{Ca}_{0.65})(\text{Al}_{0.98}\text{Si}_{1.24})\text{O}_8 \cdot 1.02\ \text{H}_2\text{O})

C. \((\text{Na}_{0.35}\text{Ca}_{0.65}\text{K}_{0.05})(\text{Al}_{0.98}\text{Si}_{1.24})\text{O}_8 \cdot 1.96\ \text{H}_2\text{O})

D. \((\text{Na}_{0.43}\text{Ca}_{0.57})(\text{Al}_{0.98}\text{Si}_{1.24})\text{O}_8 \cdot 1.66\ \text{H}_2\text{O})
sity of Minnesota) for use in correcting the thermochemical data subsequently obtained on portions of the same sample by King and by Kracek. No excess SiO₂ as quartz was observed in the sample either optically or by means of x-ray diffraction patterns. (From another locality one analyzed analcite known to have a high SiO₂ content was shown as a result of later x-ray study to contain quartz.)

The analcites having high silica contents are described as belonging to an extensive solid solution series ranging from Na₂O·Al₂O₃·2SiO₂·H₂O hydrous “nepheline” composition) to Na₂O·Al₂O₃·6SiO₂·3H₂O (hydrous “albite” composition). Assuming that the Al and Si ions are distributed over the same position of the analcite structure as assigned by Taylor (1930, 1938), the following general formulas may be deduced for the molecular ratios of interest:

\[
\begin{align*}
1:1:2:1 & \quad \text{Na}_{1.5}(\text{Al}_{1.5}\text{Si}_{1.5})\text{O}_6 \cdot 0.75 \text{H}_2\text{O} \\
1:1:3:1.5 & \quad \text{Na}_{1.2}(\text{Al}_1\text{Si}_{1.8})\text{O}_6 \cdot 0.90 \text{H}_2\text{O} \\
1:1:4:2 & \quad \text{Na}_{1.0}(\text{Al}_{1.0}\text{Si}_{2.0})\text{O}_6 \cdot 1.00 \text{H}_2\text{O} \\
1:1:6:2.7 & \quad \text{Na}_{0.75}(\text{Al}_{0.75}\text{Si}_{2.25})\text{O}_6 \cdot 1.00 \text{H}_2\text{O}
\end{align*}
\]

The parentheses denote equivalent structural positions. The substitution scheme for the high-silica analcites is, therefore, Si→NaAl. It should be noted that the maximum number of sodiums permitted in the structure is 1.50 and the maximum number of H₂O groups is 1.00, although some additional H₂O groups may occupy vacant sodium sites. The formulas written in the form above are given for each analyzed analcite of table 1 calculated on the basis of 14 equivalents (Stevens, 1946).

The specimens on which the compressibility was determined are described in detail below.

Golden, Colorado (U.S.N.M. 84842).—It is presumed that the specimen was collected from Table Mountain, near Golden, Colo. The crystals were chiseled off the walls of a cavity in a basalt flow. The cavity was lined with a 1-2 mm crust of natrolite needles growing perpendicular to the surface. The analcite grew on the natrolite into well-formed crystals not exceeding 2 cm on the largest dimension. The crystals, colorless and transparent, have an index of refraction of 1.485±0.003 and are isotropic to weakly birefringent. The density at 21°C, an average of those of five crystals, was found to be 2.252 before compression. The fragments on which the compressibility measurements were made were of variable size not exceeding 1.5 cm. The powder x-ray diffraction pattern is similar to those of synthetic and some natural analcites believed to be of the cubic type. All the reflections can be indexed on the basis of a cubic cell having \( a_0 = 13.712 \pm 0.005 \) Å. The very weak reflection corresponding to (200) found in the Flinders, Australia, analcite by Coombs (1955) is present. The unit cell dimension was measured from the reflection (11. 5. 2)–(10. 7. 1)–(10. 5. 5) using the (131) and (132) reflections of quartz (2θ = 83.840° and 90.832°, respectively, for CuKα) as internal standards. The unit cell dimension for this analcite specimen as well as the others studied is in accord with that of Gruner (1928), Taylor (1930), Konta (1953), Coombs (1955), and others. The cell dimension is slightly smaller than that for pure synthetic analcite as predicted by Saha.
(1959, p. 304) for other silica-rich analcites. The density calculated from the unit cell dimension of the Golden, Colo., specimen is 2.266, which is somewhat higher than the measured density.

Wasson’s Bluff, Nova Scotia (U.S.N.M. 96299).—The crystals were chiseled off a fragment of wall rock of a cavity in basalt. No other zeolites were observed in the vug. The surface of the crystals was slightly iron stained. The index of refraction was $1.487 \pm 0.003$ and the birefringence was nil to weak. The largest crystal measured 1.7 cm across; however, only those less than 1.0 cm in diameter were used in the compressibility experiment. The powder x-ray diffraction pattern was similar to that of synthetic and some other natural cubic analcites. A weak reflection corresponding to (200) was observed. The high-angle reflections were somewhat broad; the average unit cell dimension is $13.705 \pm 0.005$ Å. The average density of the sample at $21^\circ$C was 2.234 before compression and 2.235 after compression, and the density obtained by calculation from the unit cell measurement is 2.270.

Seiser Alp, Austria (Harvard Museum 51131).—The sections of core were diamond drilled from a single white crystal approximately 6 cm in diameter. The only contaminant is apophyllite, which is concentrated along fractures through the crystal. It is estimated that there is less than 5 percent apophyllite in the core sections. The index of refraction is $1.486 \pm 0.003$ and the birefringence, nil to weak. The powder x-ray diffraction pattern is in accord with that of synthetic analcite; a reflection corresponding to (200) was not observed. The unit cell dimension is $13.717 \pm 0.005$ Å, and the average density of the core at $21^\circ$C was 2.198 before compression and 2.222 after compression. The density calculated from the unit cell dimension is 2.264.

Fassa Thal, Austria (U.S.N.M. 82457).—The sections of core were drilled from two single crystals, 4 and 4.5 cm in diameter, which grew side by side on a cavity wall. The cores contain apophyllite (10%) and small amounts of the altered vug wall rock. The powder x-ray diffraction pattern is similar to that of other cubic analcites with the exception of the presence of a weak peak corresponding to (200). The index of refraction of these analcite crystals is $1.489 \pm 0.003$ and the birefringence is weak. The unit cell dimension is $13.717 \pm 0.005$ Å and the average measured density of the core sections at $21^\circ$C was 2.093 before compression and 2.226 after compression. The density calculated from the unit cell dimension is 2.264.

RESULTS

The results of the individual measurements of decrease in volume are recorded in table 2 and plotted in figure 2. The relative volume change, $\Delta V/V_o$, is equal to $(V_{2000} - V_p)/V_o$, where $V_o$ is the volume at atmospheric pressure, $V_p$ is the volume at pressure $P$, and $V_{2000}$ is the volume at 2000 atm. The experimental values are well represented by the equation:

$$- \Delta V/V_o = b(P - 2000) + c(P - 2000)^2.$$  

This equation was fitted to the data by the method of least squares and the values of the constants $b$ and $c$ are recorded in table 2. The values of the decrease in volume calculated by means of the equation are recorded for each
Table 2
Results of compressibility measurements of analcite

<table>
<thead>
<tr>
<th>P atm.</th>
<th>Golden, Colorado</th>
<th>Wason's Bluff, Nova Scotia</th>
<th>Seisser Alp. Austria</th>
<th>Fassa Thal, Austria</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\frac{\Delta V}{V_0}$ Exp.</td>
<td>$\frac{\Delta V}{V_0}$ Calc.</td>
<td>$\frac{\Delta V}{V_0}$ Exp.</td>
<td>$\frac{\Delta V}{V_0}$ Calc.</td>
</tr>
<tr>
<td>10,000</td>
<td>0.0345</td>
<td>—</td>
<td>0.0268</td>
<td>0.0262</td>
</tr>
<tr>
<td>9,000</td>
<td>315</td>
<td>—</td>
<td>220</td>
<td>222</td>
</tr>
<tr>
<td>8,000</td>
<td>223</td>
<td>0.0218</td>
<td>176</td>
<td>185</td>
</tr>
<tr>
<td>7,000</td>
<td>162</td>
<td>168</td>
<td>147</td>
<td>149</td>
</tr>
<tr>
<td>6,000</td>
<td>119</td>
<td>123</td>
<td>118</td>
<td>115</td>
</tr>
<tr>
<td>5,000</td>
<td>84</td>
<td>84</td>
<td>84</td>
<td>83</td>
</tr>
<tr>
<td>4,000</td>
<td>54</td>
<td>50</td>
<td>59</td>
<td>54</td>
</tr>
<tr>
<td>3,000</td>
<td>29</td>
<td>23</td>
<td>30</td>
<td>26</td>
</tr>
<tr>
<td>2,000</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1,000</td>
<td>-0.0044</td>
<td>—</td>
<td>-0.0034</td>
<td>—</td>
</tr>
<tr>
<td>V (cc)</td>
<td>9.619</td>
<td>8.577</td>
<td>20.817</td>
<td>17.625</td>
</tr>
<tr>
<td>b $\times 10^b$</td>
<td>1.978$^*$</td>
<td>2,485</td>
<td>2,641</td>
<td>3,673</td>
</tr>
<tr>
<td>c $\times 10^{11}$</td>
<td>27.67$^*$</td>
<td>9.86</td>
<td>12.53</td>
<td>0.108</td>
</tr>
</tbody>
</table>

* 2000 to 8000 atm only
pressure and may be compared with the experimental values. Since only the points from 2000 to 10,000 atm were used in determining the equation, the equation is valid only within those limits of pressure.

![Graph showing the relative volume change at 25°C as a function of pressure for four natural analcites. The specimen from Golden, Colo., exhibits a volume change at about 8400 atm. All specimens show an anomalous increase in compressibility with pressure.](image)

Fig. 2. The relative volume change at 25°C as a function of pressure for four natural analcites. The specimen from Golden, Colo., exhibits a volume change at about 8400 atm. All specimens show an anomalous increase in compressibility with pressure.

The value of the compressibility $\beta$ which is equal to $-\frac{1}{V_o} \frac{dV}{dP}$ may be obtained by differentiating the above equation:

$$\beta = b - 4000c + 2cP.$$ 

The specific molal volume change is obtained by integrating the compressibility expression between the limits $P_o = 0$ and $P_f = P$:

$$\Delta V = -V_o \left[ (b - 4000c)P + cP^2 \right].$$

This procedure involves the assumption that the expression for $\beta$ is valid in the region 0 to 2000 atm. The change in molal volume of the four specimens of analcite (molecular weight = 220.10; densities given above) is given by the following equations for $T = 298^\circ$K:

Golden, Colo. \hspace{1cm} \Delta V = -0.843 \times 10^{-4} P - 27.04 \times 10^{-9} P^2 \text{cc/mol}
Wasson's Bluff, N. S. $\Delta V = -2.059 \times 10^{-4}P - 9.71 \times 10^{-8}P^2 \text{ cc/mol}$

Seisser Alp, Austria $\Delta V = -2.120 \times 10^{-4}P - 12.41 \times 10^{-8}P^2 \text{ cc/mol}$

Fassa Thal, Austria $\Delta V = -3.628 \times 10^{-4}P - 0.107 \times 10^{-8}P^2 \text{ cc/mol}$

These equations are valid in the region 2000 to 10,000 atm except for the Golden, Colo., specimen, which is valid only in the region 2000 to about 8400 atm. At about 8400 atm the Colorado specimen shows a distinct, reversible volume discontinuity. After compression to 10,000 atm the Colorado analcite crystals were distinctly birefringent and exhibited a large and variable 2V. Macroscopically the fragments were opaque due to a multitude of irregular fractures. There were no observable changes in the index of refraction or x-ray pattern. The other analcite specimens were unchanged after compression.

Several experiments were performed to verify the existence and position of the transition in the Golden, Colo., analcite, and a description of the phenomena involved may be of interest. In routine pressure-volume studies measurements are made on decompression, the pressure being reduced in steps of about 1000 atm. At each decompression the contents of the pressure vessel are adiabatically cooled and a time interval of 10-20 min is required at the lower pressure for attainment of thermal equilibrium. During this interval heat flows into the vessel whose contents, because of high piston friction, are maintained at essentially constant volume; as a result the pressure rises. This “pressure regain” depends on factors such as pressure, rate of decompression, and thermal properties, but in general the range rarely exceeds 10-20 atm. Any thermal phenomenon, as for example absorption of latent heat by an inversion, that occurs during decompression produces an anomalous “pressure regain” and is readily observable by means of the pressure gage. The transition in the Colorado analcite was first observed in this manner, with large anomalies being noted on decompressions from 9000-7950 atm.

Some very small discontinuities in volume may be pinpointed by their associated thermal effects. However, if the transition involves a change in volume sufficiently large, an anomalous piston displacement will also be noted in the pressure interval encompassing the inversion. For the Colorado analcite an anomalous piston displacement was observed to be greater between 9000-8000 atm than between 8000-7000 atm. Studies made on decompression in 185 atm steps between 9000-8000 atm (table 3) show that the transition is not as sharp as indicated by figures 2 and 3. It occurs between 8200 atm and 8600 atm with a midpoint at about 8400 atm. Presumably a structurally perfect and chemically pure analcite would invert sharply at about 8400 atm.

It will be noted that the recorded measurements were made on decompression because it is known that metastability is encountered less frequently under these conditions. Observations made on compression, however, showed that the inversion took place readily at about 8400 atm so that the region of indifference is probably small.

Concerning the high-pressure phase of the Colorado analcite it may be said that its compressibility is much lower than any of the low-pressure analcites. The discontinuity in volume, approximately 0.5 cc/mol, cannot be evaluated with great precision since it occurs over a finite pressure range.
Decompression data for Golden, Colorado, analcite: piston displacements in the pressure region of the polymorphic transition

<table>
<thead>
<tr>
<th>P, atm (185 atm interval)</th>
<th>Piston Position in inches</th>
<th>Differences in Piston Position in inches</th>
</tr>
</thead>
<tbody>
<tr>
<td>7890</td>
<td>0.0742</td>
<td>*</td>
</tr>
<tr>
<td>7705</td>
<td>0.0620</td>
<td>0.0122</td>
</tr>
<tr>
<td>7520</td>
<td>0.0497</td>
<td>0.0123</td>
</tr>
<tr>
<td>8075</td>
<td>0.0667</td>
<td>0.0125</td>
</tr>
<tr>
<td>8260</td>
<td>0.1003</td>
<td>0.0136</td>
</tr>
<tr>
<td>8445</td>
<td>0.1136</td>
<td>0.0133</td>
</tr>
<tr>
<td>8620</td>
<td>0.1276</td>
<td>0.0140</td>
</tr>
<tr>
<td>8815</td>
<td>0.1394</td>
<td>0.0118</td>
</tr>
<tr>
<td>9600</td>
<td>0.1502</td>
<td>0.0108</td>
</tr>
<tr>
<td>(185 atm interval)</td>
<td>(185 atm interval)</td>
<td>(185 atm interval)</td>
</tr>
</tbody>
</table>

* transition zone.

Volume change and free energy change with pressure for analcite reaction (3)

The volume change for the reaction 2 analcite → nepheline + albite + 2 water at 25°C may be obtained by the following equation:

$$\Delta V = V_{Na} + V_{Ab} + 2V_{W} - 2V_{Anal}$$

where the subscript Ne refers to nepheline; Ab, albite; W, water; and Anal, analcite. The volume data for water at 25°C (Adams, 1931, p. 3780), for nepheline and albite (Yoder and Weir, 1951, p. 692), and the present data for the Colorado analcite at 298°CK are as follows:

$$V_{Na} = 54.120 - 1.113 \times 10^{-4}P + 0.28 \times 10^{-9}P^2 \text{ cc/mol}$$

$$V_{Ab} = 100.399 - 2.123 \times 10^{-4}P + 2.17 \times 10^{-9}P^2 \text{ cc/mol}$$

$$V_{W} = 18.016 - 4.463 \times 10^{-4}P + 14.51 \times 10^{-9}P^2 \text{ cc/mol}$$

$$V_{Anal} = 97.735 - 0.843 \times 10^{-4}P - 27.04 \times 10^{-9}P^2 \text{ cc/mol}$$

The compressibility data for water were fitted by the method of least squares and adequately represent the determined values within the experimental error. The $\Delta V$ for the reaction at 25°C is, then:

$$\Delta V = -4.919 - 10.476 \times 10^{-4}P + 85.55 \times 10^{-9}P^2 \text{ cc/mol.}$$

At 2000 atm and 25°C $\Delta V$ is equal to -6.672 cc/mol and at 3000 atm and 25°C, -7.825 cc/mol. The important contribution water makes to the volume change is seen in figure 3. The free energy change with pressure at constant temperature is given by the equation:

$$\frac{\partial (\Delta F)}{\partial P} \bigg|_T = -0.119 - 0.254 \times 10^{-4}P + 2.071 \times 10^{-9}P^2$$

with $\Delta F$ in cal/mol, P in atm, and $T = 298^\circ$K.\(^3\)

\(^3\) 1 cc · atm = 0.024206 cal.
Fig. 3. Relative volume change at 25°C as a function of pressure for phases in the reactions:

\[
\begin{align*}
2 \text{ analcite} & = \text{nepheline} + \text{albite} + 2 \text{ water} \\
\text{analcite} & = \text{jadeite} + \text{water} \\
\text{analcite} + \text{quartz} & = \text{albite} + \text{water}
\end{align*}
\]

Analcite data from Golden, Colo., specimen; nepheline, albite, and jadeite (Yoder and Weir, 1951); quartz (Adams and Gibson, 1929); water (Adams, 1931).

The analcite reaction takes place at 570°C at 2000 atm water pressure (Yoder, 1950, p. 323). The density of water at this pressure and temperature is 0.6294 (Kennedy, 1950, p. 561) and the molal volume is 28.624 cc/mol. If the thermal expansions of analcite, nepheline, and albite are assumed to be essentially the same, then the reaction would take place with a positive volume change under these conditions. This is the normal volume change in dehydration reactions.
Volume change and free energy change with pressure for 
analcite reaction (4)

The volume change for the reaction analcite = jadeite + water at 25°C may be obtained from the following equation:

\[ \Delta V = V_{jd} + V_w - V_{anal} \]

where the subscript Jd refers to jadeite. The volume data for jadeite are given by Yoder and Weir (1951, p. 691) and the others are as indicated above. The \( \Delta V \) for the reaction at 25°C is, therefore:

\[ \Delta V = -19.289 - 4.069 \times 10^{-3}P + 41.42 \times 10^{-9}P^2 \text{ cc/mol.} \]

At 2000 atm and 25°C \( \Delta V \) is equal to \(-19.937 \text{ cc/mol, and at 8000 atm and 25°C, -19.893 cc/mol.} \) The change for free energy with pressure for the reaction is:

\[ \left. \frac{\partial (\Delta F)}{\partial P} \right|_T = -4.669 - 0.098 \times 10^{-4}P + 1.003 \times 10^{-9}P^2 \]

with \( \Delta F \) in cal/mol, P in atm, and \( T = 298^\circ \text{K.} \)

The reaction was studied experimentally by Griggs and Kennedy (1956) (see also Robertson, Birch, and MacDonald, 1957) and dT/dP was found to be negative. Since the volume change and the entropy change are both negative, Fyfe and Valpy (1959) suggested that the slope of the pressure-temperature curve should be initially positive. The present data, taking into account possible pressure transitions, support in part this suggestion.

Volume change and free energy change with pressure for analcite reaction (5)

The volume change for the reaction analcite + quartz = albite + water at 25°C may be obtained from the following equation:

\[ \Delta V = V_{Ab} + V_w - (V_{anal} + V_{Qtz}) \]

where the subscripts Ab and Qtz refer to albite and quartz respectively. The volume change for quartz is given by Adams and Gibson (1929, p. 717, table 3), and the others are as indicated above. The \( \Delta V \) for the reaction at 25°C is, then:

\[ \Delta V = -1.950 - 5.180 \times 10^{-4}P + 43.24 \times 10^{-9}P^2 \text{ cc/mol.} \]

At 2000 atm and 25°C the \( \Delta V \) is \(-2.813 \text{ cc/mol, and at 8000 atm and 25°C the} \Delta V \text{ was found to be -3.327 cc/mol.} \) The change of free energy with pressure for the reaction is:

\[ \left. \frac{\partial (\Delta F)}{\partial P} \right|_T = -0.047 - 0.125 \times 10^{-4}P + 1.047 \times 10^{-9}P^2 \]

with \( \Delta F \) in cal/mol, P in atm, and \( T = 298^\circ \text{K.} \)

The reaction was investigated by Ellis (1958) and by Valpy (1958) and equilibrium was found, for example, at 285°C and 1000 atm (Fyfe and Valpy, 1959, p. 317; Fyfe, Turner, and Verhoogen, 1958, p. 168, 176). The entropy change of the reaction at 298°C is approximately \(-7.4 \text{ cal/mol/degree using} \ S_{Ab} = 49.2, S_{Qtz} = 10.0 (Kracek et al., 1951), S_{ice} = 9.4 (Latimer, 1951), \)
and Free Energy Change with Pressure of Analcite Reactions

and $S_{\text{anal}} = 56.0$ (King, 1955). The initial slope of the pressure-temperature curve is, therefore, expected to be positive. This conclusion is in accord with the experimental observations.

High-pressure polymorph of analcite

In all four samples of analcite the compressibility is anomalous, that is, the compressibility increases with increasing pressure. This is clearly recognized in figure 2 and by the negative sign of the $P^2$ term of the molal volume change equations. Such behavior is known in relatively few substances; SiO$_2$, glass, cerium, and chromium (Bridgman, 1931, p. 168; 1946, p. 22). In cerium the anomalous compressibility increase terminates at a transition to a more stable, high-pressure phase. A transition was realized in the Golden, Colo., analcite, and it is believed that the remaining three samples would invert to a denser form at pressures somewhat greater than 10,000 atm. The failure of the latter samples to invert at the same pressure may be attributed to impurities, as was demonstrated in the case of impure cerium (Bridgman, 1931, p. 236). The representative chemical analyses show significant differences in the composition; the specimens from Golden, Colo., appear to approach most closely the ideal composition.

Of particular interest is the probable structure of the new, high-pressure form of analcite observed in the Golden, Colo., specimen. The transition between the low- and high-pressure forms is reversible and apparently non-quenchable; therefore, direct observation of the structure of the high form is possible only above 8400 atm.

An x-ray powder pattern of the high-pressure form of analcite at 10,000 bars was made using a beryllium bomb similar to that designed by Lawson and Riley (1949, p. 15, fig. 4). The patterns obtained, however, were not of sufficient quality to permit observation of detailed changes, if any, from the low-pressure form. The shattering of the crystals observed after compression constitutes additional evidence that the volumes of the two forms are quite different. The increase in birefringence of the crystals after compression also suggests either that the crystals retained some of the strain induced by the compression or that a possible lower symmetry of the high form was retained. The unit cell size and the character of the x-ray powder pattern obtained at atmospheric pressure on the sample after compression were unchanged. Careful attention was given to the (332), (422), (440), and (640) peaks, which have been observed to split in the birefringent Løven, Norway, analcite (Coombs, 1955, p. 703). Since the increase in birefringence was not observed in those specimens which did not invert, the effect must be associated with the inversion. It is not uncommon for the higher pressure modification of a substance to have a lower symmetry (Bridgman, 1931, p. 248-249).

Many workers have suggested that the birefringence observed in natural analcite crystals can be attributed to internal lattice strain connected in some way with the water content or to twinning of individuals of lower symmetry (Taylor, 1930, p. 12-13). On the other hand, some natural birefringent analcites contain the requisite amount of water and are not twinned (Stewart, 1941, p. 7). One natural analcite from Brewster Co., Texas (Lonsdale, 1928;
Milton, 1936), was believed by A. N. Winchell to have an x-ray powder "pattern which does not correspond to an isometric structure but is not greatly different from one." On the prospect that the Texas analcite might have the high-pressure form, having failed to invert for some unknown reason, material from the same locality collected by Dr. J. T. Lonsdale was examined. The powder x-ray diffraction pattern was similar to that of the Flinders type with spacings consistent with cubic symmetry and having a very weak reflection corresponding to 200. Until the structure of the high form is established the birefringence of the compressed analcite can be attributed to either the strain induced by the volume discontinuity or the retention of possible lower symmetry of the high form not readily observable in x-ray powder patterns. Agents other than pressure may also account for the birefringence in some natural analcites.

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