ANALCIME—ALBITE EQUILIBRIA

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ABSTRACT. New data are presented that suggest the reaction:

analcime + quartz = albite + liquid water

is in equilibrium near 190°C or possibly at even lower temperatures. On the basis of these data, a phase diagram showing the field of stability of the assemblage analcime–quartz is constructed. The ΔG° of the above reaction estimated from these data is 330 calories, and factors that may influence equilibria such as salinity, silica activity, solid solutions, and order–disorder are considered. Experimental difficulties associated with studies of zeolite equilibria are considered in the light of entropy data.

INTRODUCTION

Since the work of Coombs (1954), the examination of sedimentary rocks of many types has continued to show the importance of zeolites as rock-forming minerals in zones of diagenesis and the lowest grades of metamorphism. As there are a large variety of zeolites, in particular calcium zeolites, and as these minerals take the place of the plagioclase feldspars, they must be considered important indicators of physical conditions and perhaps, of environmental kinetic factors. In particular, they may provide information concerning thermal gradients in sedimentary piles. Zen (1961) has correctly emphasized that whether or not zeolites are dominant in a given environment depends on the ratio of partial pressure of carbon dioxide and water and hence on the quantity of carbonate and clay in the original sediments.

To achieve the most significant physico-chemical analysis of mineral assemblages, one essential primary step involves determination of the conditions under which the observed assemblages are in equilibrium. Despite a large experimental effort, the situation with zeolites is still confused, a result of the inadequacy of accepted common methods of study. The sodium zeolites, or the system NaAlSi₄O₈–SiO₂–H₂O, present a simple and fundamental case, and most of the discussion which follows will be concerned with this system.

THE SYSTEM NaAlSi₄O₈–SiO₂–H₂O

The dominant phases encountered in natural environments and experimentally and the reactions between them are:

mordenite → analcime + quartz + water

NaAlSi₅O₁₂·3.5H₂O → NaAlSi₄O₁₀·H₂O + 3SiO₂ + 2.5H₂O

and

analcime + quartz → albite + water

NaAlSi₄O₁₀·H₂O + SiO₂ → NaAlSi₃O₈ + H₂O

Some experimental data on these reactions were summarized in Coombs and others (1959), and certain salient features appear from these data.

A. In synthesis experiments analcime tends to grow metastably relative to albite, and the synthesis field of analcime diminishes with time in the direction of lower temperatures. Typical synthesis boundaries are shown in figure

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1. Reaction rate studies indicate that these boundaries must be at higher temperatures than the equilibrium boundary.

B. Saha (1959) has shown that depending on the composition of the system analcimes may be synthesized with compositions across the range, \( \text{NaAlSi}_{1.8}\text{O}_3\cdot0.75\text{H}_2\text{O} \rightarrow \text{NaAlSi}_{2}\text{O}_6\cdot\text{H}_2\text{O} \rightarrow \text{NaAlSi}_{3}\text{O}_8\cdot1.5\text{H}_2\text{O} \). Whereas the data in Deer, Howie, and Zussman (1963, p. 343) show only slight variation in analcime composition, studies of sedimentary types (Wilkinson and Whetten, 1964) indicate a range similar to that found by Saha. It would appear that typical “igneous” analcimes are closer to the ideal formula and on account of their frequent spectacular development and ease of clean separation have been selectively studied.

C. Synthesis fields obtained experimentally are dependent on the reactivity of silica in the system. When silica activity is high as obtained from glass or amorphous silica, sodium mordenite occupies almost all the zeolite field. If quartz is the form of silica used, sodium mordenite is not observed. As the attainment of equilibrium in the \( \text{SiO}_2\cdot\text{H}_2\text{O} \) system is catalyzed by hydroxyl ions, high silica activities are transient in alkaline solutions. In systems with high initial silica activity, the field of mordenite increases as pH decreases. In sedimentary rocks, there is little indication that sodium mordenite is common. Thus both sodium zeolites tend to appear mostably in synthesis experi-
ments, and such experimental data suggest regions of stability that are too extensive.

THERMODYNAMIC DATA

Entropy data are now available for some of the phases, and these data suggest the source of part of the experimental problem. For the reaction:

\[
\text{analcime (near NaAlSi}_{2}\text{O}_{8}\cdot\text{H}_{2}\text{O}) + quartz \rightarrow \text{albite} + \text{liquid water (3)}
\]
\[
\Delta S^0_{298} = +1.005 \text{ e.u.}
\]
\[
\Delta V^o = -1.92 \text{ cm}^3
\]

(entropy and volume data from Robie, ms; and Robie and Bethke, ms). It must be stressed that the above values are quite anomalous when compared with values for similar reactions in the majority of hydrate systems. Normally, any anhydrous products and liquid have a much larger entropy than the equivalent hydrate. Fyfe, Turner, and Verhoogen (1958) give values for twenty-three reactions. The average is +7.1 entropy units, and the variation within ±2 e.u. The anomaly with analcime resides in the very low density of the zeolite and the open structural sites in which the water is situated. Entropy change of the reaction:

\[
\text{analcime} \rightarrow \text{dehydrated analcime} + \text{liquid water}
\]

which is only +2.6 e.u. indicates that the water molecules must lose little of

![Diagram](image-url)

Fig. 2. Diagram illustrating the rate of change of \(\Delta G\) of reaction for dehydration reactions involving one water molecule. Line A–B is for a normal hydrate, line C–D with entropy values from the analcime–albite reaction.
their degrees of freedom on entering the zeolite lattice. The volume change is equally anomalous for the same reasons.

These figures lead to very different free energy-temperature relations than those encountered in most dehydration reactions. The situation is indicated in figure 2 where relative free energies of an average dehydration reaction and the analcime reaction are indicated across an equilibrium temperature. Such behavior implies that at significant distances from equilibrium, the free energies of zeolite reactions will be much smaller than normal dehydration processes. All processes, such as rates of nucleation of new phases and growth of new phases, will be correspondingly slower, and when this is coupled with the low temperatures at which the reactions occur and hence a low density of fluctuations, it is not surprising that reactions involving nucleation and growth of stable assemblages are quite sluggish and that synthesis methods of establishing equilibrium are disappointing. With the very large array of calcium zeolites the lack of success in establishing equilibrium relations is not surprising. The most common natural zeolite, laumontite, has not been synthesized.

It should be noted that while we may have considerable confidence in the entropy data listed by Robie (ms), the heat of formation and free energy of formation of analcime do not appear to be reasonable.

\[
\begin{align*}
\text{nepheline + albite + 2 liquid water} & \rightarrow 2 \text{ analcime} \\
\Delta G^\circ_{298} &= +1690 \text{ cals} \\
\Delta S^\circ_{298} &= -1.3 \text{ e.u.}
\end{align*}
\]

These figures imply that analcime is not stable relative to nepheline and albite at any temperature above 298° K at low pressures, an implication contradicted by direct experiments of Greenwood (1961).

For the reaction:

\[
\begin{align*}
\text{jadeite + liquid water} & = \text{ analcime} \\
\Delta G^\circ_{298} &= +1540 \text{ cals} \\
\Delta S^\circ_{298} &= +7.42 \text{ e.u.}
\end{align*}
\]

These figures suggest that analcime replaces jadeite only at moderate temperatures and do not agree with present experimental data. As the free energy for jadeite, nepheline, and albite provides reasonable figures for equilibrium reactions in the anhydrous system, it appears that the free energy of analcime is in considerable error. A very approximate estimate of \(\Delta G^\circ_{298}\) for reaction (4) may be made from the data of Greenwood (1961) and indicates a value of the order of —5000 cals.

The thermodynamic data thus suggest that analcime is always a metastable phase at low temperatures. This is known to be incorrect in the system nepheline–albite–H\(_2\)O, but there is no direct evidence in the system albite–H\(_2\)O. To this writer’s knowledge direct transformation of albite to analcime and quartz has not been observed in rocks. The nearest approach has been observed by Coombs and Speden (see Coombs and others, 1959, p. 58-64) where plagioclase is replaced by thomsonite and analcime in the absence of quartz, and plagioclase is replaced by heulandite–analcime in the presence of quartz. Further, it could be claimed that an igneous plagioclase solid solution is metastable and the component NaAlSi\(_2\)O\(_5\) is in a state of higher free energy than pure albite. This could favor analcime formation. Althaus and Winkler (1962)
report the conversion of albite to analcime by addition of sodium hydroxide, but this experiment does not answer our question as the alkali will remove silica from the albite, and the reaction to form analcime plus a solution of sodium silicate is to be expected.

**EXPERIMENTAL**

An attempt has been made to obtain information on reaction (3) using a sensitive method for detecting small amounts of reaction. In any heterogeneous process:

assemble A → assemble B,

if rates of solution are moderately rapid, but if the rate of growth of any member is slow and rate controlling, then synthesis methods and the study of mixtures may be unrewarding. The study of weight changes of single crystals may be a useful and sensitive method of measuring the direction of the reaction, for changes greater than ten micrograms can be measured significantly (see Fyfe and Hollander, 1964).

In the present case, changes in weight of single plates of albite (from Amelia, Virginia) weighing about 0.5 grams were studied. The crystals were immersed in solutions presaturated with analcime and quartz. A mass of small crystals of analcime and quartz were placed in 20 cubic centimeters of liquid

<table>
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<th>°C</th>
<th>Change in weight (micrograms)</th>
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<td>-123</td>
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<tr>
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<td>-  67</td>
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<td>5</td>
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Fig. 3. Plot of experimental data from table 1 (see text).

water. Albite plates were suspended from the top of the vessel in the vapor phase, and Fyfe and McKay (1962) have shown that weight changes under such conditions are negligible. After four days, the vessel was inverted so that the albite was immersed in the solution, presumably in the presence of some of the crystals. This position was maintained for an additional four days and the albite crystals were then washed and weighed. The results are shown in table 1 and figure 3. In general, changes of 10 micrograms can be considered uncertain. Washing and handling of crystals normally led to an increase in weight in the sixth figure so that any zero correction lies in the positive direction. If we ignore all changes less than 10 milligrams it appears that the transition from gains to losses is in the region of 190 ± 10°C. These results might suggest that above 190° solutions are supersaturated with respect to albite and undersaturated below. It could be claimed that as rates of solution or reaction are falling at low temperatures and saturation might not be achieved, the losses at low temperatures may have less significance. This could be so, but the consistent gains above 200°C cannot be explained on this basis, and the conclusion can be drawn that these results only set an upper limit on the position of equilibrium. The material causing the gain in weight of the albite is assumed to be albite but while the parent is known to be the low temperature ordered form, this cannot be said for the material added. If this is a partially disordered form, the boundary will again be observed at temperatures above the true equilibrium temperature.
The data discussed above suggest that reaction (3) may be in equilibrium near 190°C. This temperature in no way contradicts the large number of synthesis experiments that indicate a boundary below 280°C and is probably more consistent with field observation as will be discussed below.

If we assume that the interpretation of the data is valid we may make an estimate of $\Delta G^\circ_{298}$ of reaction (3). We assume equilibrium with liquid water at 190°C and pressure of 12 atmospheres. $\Delta S^\circ_{298}$ is 1 e.u., and using the method of Crawford and Fyfe (1965), $\Delta S$ at 190°C is estimated to be approximately 3 e.u. Taking an average value of 2 e.u. over the temperature interval $\Delta G^\circ_{298}$ would be 330 calories. Pressure correction to 1 atmosphere will be trivial, and the error in $\Delta G^\circ_{298}$ can hardly exceed 100 calories.

From this $\Delta G^\circ$ we may make a reasonable deduction of the form of the entire phase diagram. At 190°C the $\Delta S$ is near 3 e.u. and $\Delta V$, 0.58 cm$^3$, the initial boundary slope is positive and steep at 212 atmospheres per °C. This slope will become negative in sign at pressures above those when $\Delta V = 0$, approximately 400 atmospheres. At 25°C, when $\Delta G^\circ$ is 330 calories and $\Delta V^\circ = -1.92$ cm$^3$ by evaluating the integral of $\Delta VdP$, one obtains an equilibrium pressure near 4200 atmospheres. The initial boundary slope at 25°C is negative and about 5 atmospheres per degree. The phase diagram must thus be of the form shown in figure 4. Entropy estimates are so approximate that further refinement on the basis of the present data is not justified. On figure 4 we have

![Phase diagram](image_url)

Fig. 4. Phase diagram for the system NaAlSi$_3$O$_8$-$\text{H}_2\text{O}$. Two possible curves are given for the jadeite reaction from Fyfe and Vulpy (1959). A geothermal gradient of 20°/km is shown as a dotted line.
plotted a geothermal gradient of 20°/km. The intersection with the analcime reaction occurs at 150°C or near 7.5 kilometers. Coombs, 1959, found the transition on the range 5 to 8 kilometers in reasonable agreement with these data. The coincidence may lead to a little more confidence in the significance of these results.

Additional factors influencing the temperature of equilibrium.—Given that \( \Delta G^0 \) for reaction (3) is near 330 calories, it is possible to consider a number of factors that may influence the temperature of reaction. For example, if the albite in a natural sediment is not ordered but represents albite frozen from a higher temperature of formation, we must consider the reaction:

\[
\text{albite (disordered)} + \text{liquid water} \rightarrow \text{analcime} + \text{quartz}.
\]

If albite was statistically disordered, then its entropy would exceed the fully ordered variety by \( R \ln \frac{4!}{3!} \) or 2.76 e.u. The entropy of equilibrium and disordered albite must approach at temperatures near the melting temperature. At low temperatures the free energy of disordered albite will exceed that of equilibrium albite by an amount dependent on the area between the entropy, temperature curves. This difference could be as large as 1000 calories for perfect disordering but reasonably can be assumed to be of the order of a few hundred calories. The free energy could account for the extended fields of analcime in synthesis experiments where disordered albite is the normal product. Depending on the balance of reaction rates, it would even be possible to have a reaction path:

\[
\text{high albite} \rightarrow \text{analcime} \rightarrow \text{low albite}.
\]

In natural situations when volcanic glasses are involved, all reactions involving loss or gain of silica, will be affected by the form and free energy of the silica in the environment, high silica assemblages being favored by the glasses. Using data from Robie (ms), for the reaction:

\[
\text{analcime} + \text{cristobalite} \rightarrow \text{albite} + \text{liquid water}
\]

\( \Delta G^0_{298} \) will be -241 calories. If we use data for the free energy of the quartz–cristobalite transition from Fournier and Rowe (1962) then \( \Delta G^0 \) becomes -570 calories. Thus albite could be stable at 25°C in the presence of a highly metastable form of silica or solutions highly supersaturated with silica. Since Saha (1959) has shown that analcimes may have compositions approaching albite in alumina—silica ratios, the silica effect can be evaluated only with exact knowledge of the analcime composition and the silica free energy in a given environment.

Natural solutions are frequently saline, and the presence of large salt concentrations will diminish the chemical potential of water in the solution. Consider the reaction:

\[
\text{analcime} + \text{quartz} \rightarrow \text{albite} + \text{NaCl solution}
\]

at 100°C. In pure water we would estimate \( \Delta G = 225 \) calories. For equilibrium we would have \( \Delta G = -RT \ln P \) and \( P = 0.738 \) atmospheres. Such a vapor pressure lowering would be achieved in saturated sodium chloride solutions at 100°C, and hence albite could replace analcime–quartz in such
solutions. At 25°C, the vapor pressure lowering in saturated sodium chloride solutions is not sufficient to stabilize albite, but from data in Robinson and Stokes (1959, p. 510) many saturated salt solutions or mixtures could achieve stabilization.

Frequently, albite may be presented to a low temperature solution as a solid solution in the form of plagioclase or alkali feldspar. Where such solid solutions are stable, the free energy of mixing would lead to additional restriction of the field of stability of analcime. But present data suggest that the component NaAlSi₅O₈ in such frozen solid solutions produced in igneous rocks would have a higher chemical potential than pure albite. If the solid solutions are thus metastable, then depending on kinetic factors, the analcime field could be expanded through a reaction such as:

\[2(\text{Na},\text{K})\text{AlSi}_3\text{O}_8 + \text{H}_2\text{O} \rightarrow \text{NaAlSi}_3\text{O}_6 \cdot \text{H}_2\text{O} + \text{KAlSi}_3\text{O}_8 + \text{SiO}_2.\]

Such a reaction occurring in the albite field would again produce a metastable assemblage, but at the temperatures involved, such metastable reactions cannot be considered impossible. Finally, it may be noted that pH will have no intrinsic influence on the equilibrium temperature of reaction (3) although pH may have a profound influence on kinetic factors leading to metastable assemblages.

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