

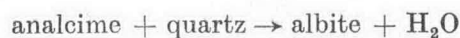
with emphasis on the limitations of the assumption that entropies of constituent oxides are additive. To the writers' knowledge, the entropy of only one zeolite has been determined, namely analcime for which KING (1955) reports a value of 56.0 cal/deg mole. This entropy is very high compared with the sum of the entropy of the oxides, 44.6 cal/deg mole. However, a large entropy is to be expected since the molar volume of analcime is large. Following the arguments used in Fyfe *et al.* (1958) we estimate an entropy of 57.0 cal/deg mole which includes a volume correction and a correction for randomness in the Al-Si arrangement (Beattie, 1954). Similarly wairakite would be expected to have a large entropy which is in accord with its ready nucleation and growth (cf. cristobalite). Further, the apparent molar volume of water in analcime is much larger than with most hydrates. The large entropy of analcime leads to some unusual features of its breakdown. At 25°C, the ΔS of the reaction: analcime + quartz \rightarrow albite + water (liquid) is +0.95 cal/deg mole, a value very near zero. For most dehydration reactions removal of one water molecule to give liquid water at 25°C is accompanied by an entropy increase of 7 cal/deg mole (an average of twenty-four cases). The small change noted above indicates the danger of using average figures with zeolites. In fact it could be possible to have negative entropies of dehydration at low temperatures and pressures.

4.5. Osmotic conditions

Data indicate that zeolites will be stable minerals in a low temperature environment or under conditions of moderate depth of burial. In these environments open pores must be common. In hydrothermal areas such as Wairakei, New Zealand, the pressure measured in fissures is often that of the water column and is therefore related to rock pressure in the ratio of water density to rock density. It is thus necessary to consider conditions where the pressure on the solid phases is greater than the pressure in the fluid phase and in particular conditions where $P_{H_2O} \simeq \frac{1}{3} P_{load}$. For this to be relevant it is necessary that alteration produces a zeolitized rock which is still porous yet in which the zeolites support the load of overburden. In contrast the zeolites in a cavity in a basalt grow in an environment where clearly $P = P_{H_2O}$. At great depths continuous pore systems must become unstable unless some fluid can support them. If the porosity is low and water is being expelled on a large scale by dehydration reactions the most likely conditions are $P_{H_2O} \simeq P_{load}$.

For phase changes in hydrate systems where density relations are "normal", if the pressure on the solid phases is greater than the pressure in the gas phase the vapour pressure of the solid will be increased (Fyfe *et al.*, 1958). If molar volumes of all phases are known the extent of the effect can be estimated.

Consider the effect on the analcime-albite boundary. In Fig. 7 curve A is our boundary based on synthesis for the experimental conditions that $P = P_{H_2O}$. At 1000 atm it passes through $280^\circ C \pm 10^\circ$. If at the equilibrium temperature at 1000 atm we add 2000 atm rock load ($P_{load} = 3P_{H_2O}$) then the free energy of the reaction:



becomes

$$2000 \times \Delta V_{solids} \times 0.024 \text{ cal}$$