

phase $A_xB_yC_z$ will form over a wider range of conditions if the state of C is not the stable form at the given pressure and temperature, and if other factors such as nucleation do not interfere. This effect, which is not restricted to silica may be large. Consider, for instance, the reaction:



at equilibrium at 25°C where $\Delta G = 0$ and the stable silica phase is quartz. As the free energy of vitreous silica is 3 kcal more positive than that of quartz at this temperature (LATIMER, 1952) if silica is added as glass, ΔG at 25°C will now become -6000 cal and the field of $A(\text{SiO}_2)_6$ will be expanded. The silica (or any other component) may be added in an experimental run in an amorphous state and at the end of the run may be recovered partly or entirely as quartz. Nevertheless, phases may have grown while the silica activity was high and may persist in the final products.

Consider the effect this silica activity has on a typical hydrate boundary. Data from synthetic studies indicate that the reaction:



may be at equilibrium around 350°C and 1000 bars. Solubilities (KENNEDY, 1950a) indicate that the free energy of amorphous silica is about 1500 cal/mole above that of quartz. Thus with amorphous silica the above process will have a ΔG of +3000 cal. The ΔS of dehydration may be of the order of 10-15 cal/water molecule and the equilibrium temperature with respect to amorphous silica may be 100-150°C higher. This is well demonstrated both in direction and magnitude by the data in Table 3.

4.2. Relative importance of silica content and water content

In this paper attention is focused on silica-rich systems. On the basis of entropy it would be expected that the least hydrated phase would also be the high temperature phase. Further, if two assemblages have different amounts of silica bound in silicates it might be anticipated that the assemblage with the greater amount of bound silica would be the more stable. It is a fact that assemblages such as nepheline-quartz, thomsonite-quartz, olivine-quartz are not stable. It might therefore be suggested that the larger silica content of sodium mordenite relative to analcime could conceivably increase its stability and hence make it the higher temperature phase. However, the reaction:



must have a positive entropy change due to the large entropy of free water in the gas or liquid state. This implies that analcime becomes more stable at high temperatures relative to mordenite. Analcime need not be stable at all, but it would be most remarkable if analcime was stable at lower temperatures than mordenite.

The silica-deficient zeolite natrolite ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) is unlikely to occur with free quartz for although its formula suggests intermediate hydration between mordenite and analcime, on the basis of its $\text{Na}/\text{H}_2\text{O}$ ratio it is hydrated to the same extent as analcime but has less silica. Natrolite would be expected to occur only in silica-deficient environments.