



Fig. 6. Plot of SiO_2/Na ratios and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in albite solutions, where all quantities are expressed in ppm. Dashed lines: SiO_2/Na ; solid lines: $\text{SiO}_2/\text{Al}_2\text{O}_3$.

mental runs in which partial valve failures allowed the collection rate to exceed 100 milliliters per hour. The results, quoted on table 3B show that the soda and alumina contents are greatly depressed, as might be expected, but that the silica content is markedly enhanced. Examination of the temperature and pressure records of these runs indicates that, after an initial sharp fluctuation, temperatures and pressures were maintained near the quoted values, though fluctuations were much larger than those in the runs believed to approach equilibrium.

DISCUSSION OF RESULTS

The absence of Ca in the solutions confirms the qualitative work of Euler and Hellner (1958) who found sodium to be preferentially leached from plagioclase by supercritical steam. The soda to potash ratio on the other hand is always less in the solutions than that in the starting material. It varies from 60 in the starting material down to 30 in some of the solutions. Additional work in progress by the author shows that in solutions derived from mixtures of soda and potash feldspars this ratio

always tends toward a fixed value of the order of one determined by the temperature and pressure, regardless of the proportions of soda and potash feldspar. The low values of potash in these solutions probably indicate complete leaching of potash from the starting material.

The enhancement of silica in solutions collected under non-equilibrium conditions cannot be explained by any theory of solution known to the author. Together with the solubility equations derived below, it seems to indicate that the feldspar lattice breaks down in the presence of water, and various parts react with water at different speeds.

The most notable features of the equilibrium solubility of albite in this range are (1) the non-stoichiometric composition of the solutions, (2) the difference in behavior of silica, soda, and alumina, and (3) the remarkable stability of highly supersaturated solutions at room temperature and pressure. These phenomena can be explained by a theory of solution in dense reacting fluids developed by Franck (1956). Assume the solute, designated by the subscript 1, to form complexes. Formation of such complexes can be represented schematically by



where n may have values from zero up to m , the maximum association number. If the solute dissolves non-stoichiometrically, it can be represented by two or more "species" chosen to represent the bulk chemical composition of the solute and the non-stoichiometric behavior of the solution. It will be shown below that the chemically analyzed components may be used as species, no matter what the actual composition of the complexes may be. The composition of the complexes is not elucidated by this treatment. Using the virial equation of state, the chemical potential μ for a species in a reaction mixture is, to terms linear in the mole volume V ,

$$\mu_1/RT = -\ln F_1 + \ln x_1/V + \sum_j 2x_j (B_{1j}/V) \quad (2)$$

(Fowler and Guggenheim, 1938, chap. 8), where F_i is the volume independent part of the potential, x_i the mole fraction of species i in the mixture, and B_{ij} the second virial coefficient. At equilibrium, for the reaction of equation (1)

$$n \mu_2 + \mu_1 = \mu_{12_n} \quad (3)$$

Now if the solution is very dilute $x_2 \sim 1$ and $V \sim V_2$. Substituting (2) into (3) and setting $x_2 = 1$,

$$\ln (x_{12_n}/x_1) = \ln (F_{12_n}/F_1 F_2^n) - n \ln V_2 + (2/V_2) (B_{1,2} + n B_{2,2} - B_{12_n,2}) \quad (4)$$

where interactions between solute species are assumed negligible because of the diluteness of the solutions.

Assuming that the association of each of the n molecules of 2 with 1 is accompanied by the same change in enthalpy and entropy,

$$\ln (F_{12_n}/F_1 F_2^n) = (n/RT) (H_{21} - T S_{21}) \quad (5)$$

where H_{21} and S_{21} are respectively the change of enthalpy and entropy