Metastability in Near-Surface Rocks of Minerals in the System Al_2O_3-SiO_2-H_2O[1]

Lawrence M. Anovitz[2], Dexter Perkins[3] and Eric J. Essene[4]

[2] Department of Geosciences, The University of Arizona Tucson, Arizona 85721

[3] Department of Geology and Geological Engineering and the North Dakota Mining and Mineral Resources Research Institute The University of North Dakota, Grand Forks, North Dakota 58202

[4] Department of Geological Sciences, The University of Michigan Ann Arbor, Michigan 48109

Abstract: Gibbs free energies for phases in the system Al_2O_3-SiO_2-H_2O have been calculated from reversed experiments in order to correct earlier values and to calculate a phase diagram consistent with more recent experiments. An internally consistent diagram could not be calculated that agreed with all published experiments, and choices of preferred data were made. The following Gibbs free energies, relative to the elements at STP (298.15 K, 1 bar), have been derived: $\Delta G^{\circ}{}_f$(diaspore) = −921.19 kJ/mole $\Delta G^{\circ}{}_f$(pyrophyllite) = −5266.47 kJ/mole $\Delta G^{\circ}{}_f$(kaolinite) = −3800.18 kJ/mole $\Delta G^{\circ}{}_f$(andalusite) = −2442.04 kJ/mole $\Delta G^{\circ}{}_f$(kyanite) = −2443.66 kJ/mole $\Delta G^{\circ}{}_f$(sillimanite) = −2439.63 kJ/mole $\Delta G^{\circ}{}_f$(gibbsite) = −1154.9 kJ/mole $\Delta G^{\circ}{}_f$(bayerite) = −1153.0 kJ/mole $\Delta G^{\circ}{}_f$(boehmite) = −918.4 kJ/mole $\Delta G^{\circ}{}_f$(nordstrandite) = −1154.1 kJ/mole $\Delta G^{\circ}{}_f$(halloysite) = −3783.2 kJ/mole $\Delta G^{\circ}{}_f$(dickite) = −3798.8 kJ/mole The above values were calculated assuming literature values for corundum, quartz, and H_2O (v).

Examination of available thermodynamic, experimental, and observational data on the aluminum hydroxides gibbsite, boehmite, bayerite, and nordstrandite suggests that these minerals are metastable with respect to diaspore + water at STP and at higher temperatures. Similarly, halloysite and dickite are metastable with respect to kaolinite at these conditions. The occurrence of these minerals in soils must therefore be ascribed to nonequilibrium processes, and the use of equilibrium phase diagrams to explain their occurrence is inappropriate.

Key Words: Aluminum hydroxide • Dickite • Gibbs free energy • Halloysite • Kaolinite • Metastability • Phase equilibria • Pyrophyllite