2.3 Geochemical Reaction Equations

Chemical equilibrium can be dealt with in essentially two ways: the ion association theory (Bjerrum 1926; Fuoss 1935) and the mixed electrolyte theory (Reilly et al. 1971). Nearly all computerized models are based on the ion association theory (Nordstrom et al. 1979). Within this framework the species distribution can be formulated in two distinct but thermodynamically equivalent ways: the equilibrium-constant approach and the Gibbs free-energy approach. In the Gibbs free-energy approach, the species distributions are obtained by minimizing the total Gibbs free-energy function of a given set of species subject to the constraints of mass balance equations. In the equilibrium-constant approach, the set of nonlinear algebraic equations is obtained based on the law of mass action and the principle of mole balance (Morel and Morgan 1972). This set of nonlinear algebraic equations is then solved to yield the species distributions. In the latter approach, equilibrium constants are needed for the data base, whereas in the former approach, free energy values are needed. The equilibrium constant approach is chosen for handling of equilibrium geochemical reactions in HYDROBIOGEOCHEM. In the equilibrium-constant approach, the formation of an aqueous complexed species x_i, an adsorbed species y_i, an ion-exchanged species z_i, or a precipitated (solid) species p_i is described at equilibrium by the law of mass action.

Rate expressions based on collision theory are used to handle the kinetic geochemical reactions. Rate expressions based on Monod kinetics are used to describe biogeochemical reactions. The program has been developed in a modular fashion so that the user may readily incorporate rate expressions based on alternate theories to describe the kinetic reactions.

A general chemical reaction can be represented by

$$\sum_{j \in M} \nu'_{kj} \hat{g}_j < - - - > \sum_{j \in M} \nu''_{kj} \hat{g}_j \ , \quad k \in \text{NRXN} \qquad \textbf{(2.3.1)}$$

where

M = $(N_a + N_s + M_x + M_y + M_z + M_p)$ is the total number of chemical species.

$\nu_{kj}^{/}$ = reactant stoichiometric coefficient of the j-th global species[1] in the k-th chemical reaction.

$\nu_{kj}^{//}$ = product stoichiometric coefficient of the j-th global species in the k-th chemical reaction.

[1] "Global species" refers to all of the species, both components and products, in the simulation. The global species are numbered in the following order: N_a aqueous component species, N_s absorbent component species, M_x aqueous complexed species, M_y absorbed species, M_z ion-exchanged species, M_p precipitated species, M_b aqueous phase microbial specis, and M_a adsorbed phase microbial species.