possibility of having a negative total concentration of operational electrons.

2.2.6 Transport of Excess Protons

In a system involving acid-base reactions, an additional parameter describing the acidity of the system is needed. This additional parameter is the proton activity (or the pH value). The pH value may be simulated by using either the electroneutrality equation or proton condition. These two approaches are mathematically equivalent but not computationally equivalent. In coupling the hydrological transport and chemical reactions, it is preferable to use the proton-condition approach, in which the total concentration of the excess protons (H^+ - OH^-) must be known before activity of protons can be computed. Therefore, a transport equation for excess protons is needed to determine the total concentration of excess protons.

Applying the principle of conservation of mass to both oxygen and hydrogen yields two transport equations: one for hydrogen H and the other for oxygen O_2. Adding these two equations with appropriate multipliers produces a transport equation for hydroxide OH. Taking the difference of the transport equation for H and that for OH, one obtains (Miller 1983):

$$\rho_l \theta \frac{\partial T'_H}{\partial t} + L(C'_H) + KT'_H + \rho^* QC'_H = R_j^H + M_j^H. \qquad \textbf{(2.2.70)}$$

which is identical in form to Equation **(2.2.34)** and which describes the transport of excess protons. The algebraic equations defining T_H, C_H, M_H, λ_H and R_H are identical in form to Equations **(2.2.14)** through **(2.2.19)**, with the subscript j replaced by the subscript H.

Because the simulation of pH and/or pe uses transport equations identical in form to Equation **(2.2.34)**, we can treat protons and/or electrons as aqueous components, and no special consideration to distinguish protons and/or electrons from other regular aqueous components is needed. The only thing we must keep in mind is that we use proton activity and electron activity rather than proton concentration and electron concentration as master variables in the geochemical reaction model.

2.2.7 Transport of Gas Component

In HYDROBIOGEOCHEM, one gas phase component may be specified. HYDROBIOGEOCHEM does not simulate the transport of gas within the porous media, but does allow the gas component to react to form aqueous product species, which are subject to transport. This capability was added specifically to provide the capability of simulating a system in which the partial pressure of $CO_{2\,(gas)}$ is specified and the resultant formation and transport of $H_2CO_3^*$, HCO_3^-, and CO_3^{2-} is simulated. This capability could be used to simulate any other gaseous species' interaction with the aqueous phase, as long as the transport of the gaseous species itself is not of significance to the problem.