libria in basic solutions, the Cr + CrN buffer developed by Hallam (ms) can be used. This buffer allows us to control the fugacity of NH_3 and hence the activity of NH_4OH. Preliminary experiments have demonstrated that solutions controlled by this buffer assemblage are quite basic.

The Ag–AgCl buffer combined with a fixed f_{H_2} is probably as close to a pH buffer as we can come in a hydrothermal environment. f_{HCl} is rigorously controlled and in the pure system H–O–Cl the hydrogen ion activity, a_{H^+}, is also controlled, assuming low solubility of the buffer solids in the solution. The fugacities of the uncharged species can be calculated from the relevant equilibrium constants (eq 2 and 3) and the total pressure equation (1). Similarly, the activities of the ionic species can be calculated, using the electrical neutrality equation and the relevant dissociation constants. Using H^+, OH^-, and Cl^- as principal species, we have

$$m_{H^+} = m_{OH^-} + m_{Cl^-} \tag{17}$$

$$HCl \rightleftharpoons H^+ + Cl^- \quad K_2 = \frac{a_{H^+} \cdot a_{Cl^-}}{a_{HCl^\circ}} \tag{18}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad K_3 = \frac{a_{H^+} \cdot a_{OH^-}}{a_{H_2O}} \tag{19}$$

and hence.

$$a_{H^+} = \lambda_{H^+}{}^{1/2} \left[\frac{a_{H_2O} \cdot K_3}{\lambda_{OH^-}} + \frac{a_{HCl^\circ} \cdot K_2}{\lambda_{Cl^-}} \right]^{1/2} \tag{20}$$

If other species are added to the solution, such as K^+, Na^+ or if Ag^+ is present in appreciable amounts, equation (17) contains additional terms, and we cannot solve for a_{H^+} without further information. On the other hand, adding salts may not significantly change equation (1), and in that case we can still calculate the fugacities of all uncharged species. In all cases, however, f_{HCl} remains rigorously specified and buffered.

The Ag–AgCl buffer is directly applicable to the study of ore solutions and of metamorphic solutions, and we expect that it can also be used to investigate igneous solutions.

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