

have pointed out that Karraker (1963) did not investigate the catalyzed oxidation in which dissolved O_2 is the oxidant, but instead the redox system associated with the couple $Fe(III) + e^- \rightarrow Fe(II)$ in an oxygen-free system. Thus, Karraker's work is not considered applicable. Neytzell-de Wilde and Taverner (1958) reported that the sulfate formation rate was second order for $[S(IV)]$, but Karraker (1963) has re-analyzed their data and has shown instead that the order is unity. As noted for the $Mn(II)$ system, Neytzell-de Wilde and Taverner (1958) did not present a rate expression and constant for the $Fe(III)$ system; an estimate derived from their paper is presented in Table 2-9. Brimblecombe and Spedding (1974a) have reported a rate expression and constant measured at a constant $pH = 4$; unfortunately, they used a plastic reaction vessel, which could have released organic inhibitors into the system, causing the rate to be diminished. (At $pH = 4$, their rate is 0.25 of that of Neytzell-de Wilde and Taverner, 1958, and 0.1 of that of Fuzzi, 1978) Fuzzi (1978) did not note the similarity of his observations and those of Neytzell-de Wilde and Taverner (1958), especially the dependence of the rate on the initial inverse H^+ concentration for $pH < 4.0$. Fuzzi's (1978) rate expression has been modified by incorporating the dependence on $[H^+]_0^{-1}$ and is presented in Table 2-9. Note that Fuzzi's (1978) modified rate constant is 2.5 times greater than that of Neytzell-de Wilde and Taverner (1958), which is good agreement for this type of