

The Fe(III) catalyzed reaction studies that are pertinent to the formation of sulfate in the troposphere are identified in Table XI. The only studies not using two-phase systems (subject to mass transport limitations) are those of Neytzell-de Wilde and Taverner (1958), Karraker (1963), Brimblecombe and Spedding (1974a), and Fuzzi (1978). Hegg and Hobbs (1978) 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 reanalyzed 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 XII. 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  $pH \leq 4.0$ . Fuzzi's (1978) rate expression has been modified by incorporating the dependence on  $[H^+]_0^{-1}$  and is presented in Table XII. 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 measurement; these two studies appear to be the most definitive for the Fe(III) system, and there is no basis to prefer one over the other. Fuzzi (1978) has clearly demonstrated the change in kinetics is due to the formation of colloidal  $Fe(OH)_3$  for  $pH > 4$ , which provides an explanation for the disagreement among earlier investigators. Because of the formation of the  $Fe(OH)_3$  colloid, it is unlikely that a meaningful Fe(III) catalyzed rate expression for use in tropospheric sulfate formation can be stated for conditions in which  $pH > 4$ .