

TABLE 2-7. Rate Expression for the Manganese-Catalyzed Oxidation

Expression ^{a,b,c}	pH	Investigators
$\frac{d[\text{SO}_4^{2-}]}{dt} = 44 [\text{Mn(II)}]^{1.7} [\text{S(IV)}]^0 [\text{H}^+]^0$	3,4	Adapted from Hoather Good-eve (1934)
$\frac{d[\text{SO}_4^{2-}]}{dt} = 1.7 \times 10^{-5} [\text{Mn(II)}] [\text{S(IV)}] [\text{H}^+]_0^{-1} \sim 2.2$		Adapted from Neytzell-de Wilde and Taverner (1958)
$\frac{d[\text{SO}_4^{2-}]}{dt} = 8 [\text{Mn(II)}]^2 [\text{S(IV)}]^0$	$\sim 3-4$	Adapted from Coughanowr and Krause (1965); dependence on pH not reported

^aThe units are: liter, mole, second.

^bConcentrations shown with zero power (e.g., $[\text{S(IV)}]^0$) indicate that the investigators found the rate to be independent of those species. Note that any concentration to the zero power is equal to unity.

^cThe term $[\text{H}^+]_0^{-1}$ indicates that the rate is dependent only on the inverse of the initial H^+ ion concentration; changes in H^+ concentration after the reaction is in progress do not affect the rate.

(10-100 minutes) of the experimental runs were sufficiently long that it is reasonable that the rate of oxidation was measured after the establishment of the radical chains, and not during the induction period.

The Fe(III) catalyzed reaction studies that are pertinent to the formation of sulfate in the troposphere are identified in Table 2-8. 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)