

for determining the reaction order. Also, the results for investigations using supported droplets may be biased due to radical chain termination at the liquid-solid interface.

The Mn(II) catalyzed reaction kinetics have been investigated for over 75 years, the studies pertinent to the formation of sulfate in the troposphere are presented in Table 2-6. One of the first critics of Mn(II) catalysis studies was Titoff (1903), who remarked: "in Bigelow's (1898) work the reaction occurred between two phases, and the retardation could be determined by a change in the boundary layer or by a decrease in the solution rate of oxygen". Unfortunately, that comment applies to all but three of the Mn studies in Table 2-6, which are: Hoather and Goodeve (1934), Neytzell-de Wilde Taverner (1958), and Coughanowr and Krause (1965). It is odd that each of these investigators did not present rate expressions and rate constants derived from their data, and instead left to the reader the task of extracting that information. Estimates of their rate expressions are presented in Table 2-7. There is agreement that the Mn(II) catalyzed rate is independent of dissolved O_2 , SO_2 , HSO_3 , and SO_3^{2-} concentrations.

Clearly, Hoather and Goodeve (1934) and Coughanowr and Krause (1965) are in good agreement. However, Neytzell-de Wilde and Taverner (1958) observed a first-order dependence on $[Mn(II)]$. There appears to be no basis to discount any of the three investigations, yet it appears that serious errors