

oxidation for all major pathways, where each is represented as a linear process. For example, the oxidation rate of SO_2 by an HO radical in the gas phase to form H_2SO_4 has the form

$$d[\text{H}_2\text{SO}_4]/dt = k_2[\text{HO}][\text{SO}_2] \quad (4-2)$$

If the HO concentration in the atmosphere is constant, then the rate can be expressed as

$$d[\text{H}_2\text{SO}_4]/dt = k_2'[\text{SO}_2] \quad (4-3)$$

where k_2' is a pseudo first-order rate constant. This rate is linear in SO_2 concentration. That is, changes in SO_2 concentration will directly effect the H_2SO_4 formation rate. Thus, for the rate of H_2SO_4 formation to have a linear dependence on the ambient SO_2 concentration:

- (a) the rate expression must have a first-order dependence on SO_2 ambient concentration,
- (b) the SO_2 must not be a limiting reactant (that is, its concentration must greatly exceed those of the oxidizers so that it is not completely consumed), and
- (c) k_2' must remain constant.

If all the major processes are linear, then their rates are additive and k_5 is the sum of the pseudo first-order rate constants for these processes. However, if one or more major H_2SO_4 formation processes cannot be expressed in a linear form such as in equation 4-3, then k_5 is not constant and equation 4-1 is, in principle, not an adequate representation for modeling the H_2SO_4 formation in the atmosphere.