

negligible part compared to either photochemical or droplet phase mechanisms...." Therefore, such processes will not be considered further here.

It was noted above that, for homogeneous processes, large seasonal changes may be theoretically expected in the oxidation rate, depending on the latitude. The picture is not as clear for heterogeneous reactions. It has been theorized (e.g., Foster, 1969; Freiberg, 1974) that the oxidation rate involving trace metal catalysts should be increased at high ambient ammonia concentrations and relative humidities, both of these factors leading to lower solution acidity and hence higher sulfite ion concentrations (sulfite ions are thought to be the species actually oxidized to sulfate by dissolved O_2). Lower temperatures may also promote oxidation by hydrogen peroxide or trace metal catalysts (Penkett et al., 1979; Freiberg, 1974). Thus, seasonal variations in all these factors (e.g., lower wintertime temperatures and ambient ammonia concentrations) could potentially have an effect on the conversion rate. These effects are difficult to predict. For example, Middleton et al. (1980) have carried out a modelling study into the relative importance of various urban sulfate aerosol production mechanisms, including photochemical reactions followed by sulfuric acid vapour condensation and catalytic, as well as non-catalytic, heterogeneous oxidation. They conclude that the dominant mechanism for sulfate production can depend on the season and time of day. During the daytime in summer, photochemical reactions/sulfuric acid vapour condensation are the most important, followed by liquid-phase oxidation by hydrogen peroxide. At night, however, catalytic and non-catalytic oxidation mechanisms on the wetted aerosol surface become important. In the winter, most of the daytime SO_2 oxidation is predicted to take place by reactions with hydrogen peroxide in droplets at overall rates comparable to those in the summer. However, the above conclusions are based on a large number of assumptions about reaction mechanisms and model input conditions, and should not be regarded as final. For a better assessment of winter/summertime differences in atmospheric chemical transformation rates, the results of actual field studies were consulted (see below).