

MULTI-PHASE PROCESSES IN CLOUDS

S. E. Schwartz
Environmental Chemistry Division
Department of Applied Science
Brookhaven National Laboratory
Upton, NY 11973-5000

September 1999

Published in
Proc. Workshop on Modelling the Transport and Scavenging
of Trace Constituents by Clouds in Global Atmospheric Models
(Cambridge, UK, Aug. 1-4, 1995), Rasch, P., Ed., Appendix 51,
World Climate Research Programme, Cambridge, UK, 1999.

By acceptance of this article, the publisher and/or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper.

Research by BNL investigators was performed under the auspices of the U.S. Department of Energy under Contract No. DE-AC02-98CH10886.

ABSTRACT

Uptake and reaction of gases in clouds are key atmospheric processes governing the transformation and removal of gaseous atmospheric constituents. Cloud droplets serve as a sink for soluble gases (such as HNO_3) and also as a medium for reaction of less soluble gases such as SO_2 by which the material can be transformed to the much more soluble sulfate ion. Material incorporated into cloudwater can be removed in precipitation or, if the cloud evaporates rather than precipitating, returned to the atmosphere in gaseous or aerosol form, depending on volatility.

Reactive uptake of a gas into cloud water can be described as the following processes in series: mass transfer of the gaseous substance to the surface of cloud droplets, across the interface, and within the cloud droplets, the latter taking place in parallel with aqueous-phase chemical reaction. For cloud droplets of diameter less than about $50\ \mu\text{m}$ the principal means of mass transport on both sides of the interface is molecular diffusion; for larger droplets mass transport is enhanced by convection induced by droplet motion relative to the surrounding air. Mass transfer across the interface occurs only by molecular collision, at a rate given by the kinetic theory of gases times a "mass accommodation coefficient."

The rate of reaction is governed by the concentrations of dissolved materials--gaseous and/or nonvolatile solutes--together with the appropriate rate expression. The composition of any given droplet reflects the composition of the aerosol particle on which it formed and any subsequent chemical reaction and is not necessarily the same as that of other droplets; likewise, therefore, also the reaction rate. Cloud droplets are typically separated by 100 times their own diameter (for liquid water volume fraction $\sim 1 \times 10^{-6}$) so that to good approximation cloud droplets can be considered noninteracting. However volatile solutes tend to redistribute themselves toward establishing phase equilibrium between any given droplet and the surrounding gas phase, and this process together with the ensuing reactions tend to homogenize the composition of droplets and the rates of reactions in the droplets.

Quantitative description of reactive uptake requires knowledge of situational parameters (liquid water content, drop size distribution, concentrations of reagent species) and physical-chemical properties of reagent gases (solubilities, diffusion coefficients, mass-accommodation coefficients, reaction rate laws). Expressions have been developed to evaluate such reaction rates under varying assumptions, for example that the composition is dependent on cloud drop size but homogeneous in a given drop-size cut. Evaluation of the reaction rate is greatly simplified if the aqueous concentration(s) of the reagent gas(es) can be evaluated according to Henry's law equilibrium. Although in the absence of aqueous-phase reaction this phase equilibrium is rapidly attained (characteristic time of seconds), the equilibrium assumption does not necessarily hold when there is rapid reaction of a dissolved gas in solution depleting the aqueous-phase concentration. Readily applicable criteria have been developed for ascertaining whether phase equilibrium can be assumed. In the case of oxidation of SO_2 by H_2O_2 and O_3 this phase equilibrium can be assumed under most conditions pertinent to atmospheric interest; a key exception is the reaction of SO_2 with O_3 at high pH.

This talk will review the theory governing uptake and reaction of gases in cloudwater and present examples of evaluations of rates of multiphase processes illustrating the above approaches.