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Kinetic regimes and limiting cases of gas uptake and heterogeneous reactions in atmospheric aerosols and clouds: a general classification scheme

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Heterogeneous reactions are important to atmospheric chemistry and are therefore an area of intense research. In multiphase systems such as aerosols and clouds, chemical reactions are usually strongly coupled to a complex sequence of mass transport processes and results are often not easy to interpret.

Here we present a systematic classification scheme for gas uptake by aerosol or cloud particles which distinguishes two major regimes: a reaction-diffusion regime and a mass-transfer regime. Each of these regimes includes four distinct limiting cases, characterized by a dominant reaction location (surface or bulk) and a single rate-limiting process: chemical reaction, bulk diffusion, gas-phase diffusion or mass accommodation.

The conceptual framework enables efficient comparison of different studies and reaction systems, going beyond the scope of previous classification schemes by explicitly resolving interfacial transport processes and surface reactions limited by mass transfer from the gas phase. The use of kinetic multi-layer models instead of resistor model approaches increases the flexibility and enables a broader treatment of the subject, including cases which do not fit into the strict limiting cases typical of most resistor model formulations. The relative importance of different kinetic parameters such as diffusion, reaction rate and accommodation coefficients in this system is evaluated by a quantitative global sensitivity analysis. We outline the characteristic features of each limiting case and discuss the potential relevance of different regimes and limiting cases for various reaction systems. In particular, the classification scheme is applied to three different data sets for the benchmark system of oleic acid reacting with ozone. In light of these results, future directions of research needed to elucidate the multiphase chemical kinetics in this and other reaction systems are discussed.

Reference: Berkemeier, T., Huisman, A. J., Ammann, M., Shiraiwa, M., Koop, T., and Pöschl, U.: Kinetic regimes and limiting cases of gas uptake and heterogeneous reactions in atmospheric aerosols and clouds: a general classification scheme, Atmos. Chem. Phys. Discuss., 13, 983-1044, doi:10.5194/acpd-13-983-2013, 2013.