Atmospheric Chemical Mechanisms From First Principles to Applications

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abstract

The atmosphere is a dynamic system in which gas particles continuously interact with vegetation, oceans, biological and anthropogenic sources. Atmospheric Chemical Transport Modeling (ACTM) of air pollutants involves four major processes:

- emissions,
- transport of air pollutants,
- diffusion, and
- transformation of chemical compounds during transport, i.e. chemical reactions (the chemical mechanism) and depositions.

The gas-phase chemical mechanism is one of the most important components in ACTM. It is therefore important that the gas-phase mechanism includes all the relevant atmospheric chemical reactions, and that the utilized rate constants and product yields for the gas-phase reactions, and the quantum yields and absorption cross sections for the photolysis reactions are of high accuracy.

Highly complex chemical mechanisms are especially needed to model the concentration of ozone and other air pollutants in the polluted troposphere due to the influence of emissions from nitrogen oxides and volatile organic compounds. Different chemical databases which describe this chemistry have therefore been developed over the years, such as those from NASA Panel for Data Evaluation and IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, and the Master Chemical Mechanism v3. These databases encompass thousands of reactions and chemical species. Due to this large number of reactions and species it is not possible to use an explicit atmospheric chemical mechanism for practical purposes, the computational time will be too long. Therefore, lumped (reduced) chemical mechanisms have been developed during the last couple of decades in order to describe the complex chemical composition of the troposphere.

This presentation will give a description of the development of atmospheric chemical mechanisms from first principles to applications in 3-dimensional ACTM. Therefore, the presentation will cover the following subjects:

1. the utility of chamber experiments to develop atmospheric chemical mechanisms,

2. construction of lumped atmospheric chemical mechanisms, and
3. 3-dimensional ACTM.

Chamber experiments can be used for development of explicit chemical mechanisms and evaluation of lumped chemical mechanisms. Both aspects will be discussed and the utility and limitations of chamber experiments will be outlined.

The knowledge of the atmospheric chemical composition, reactions and corresponding rate constants have to be included in the lumping procedure when lumped atmospheric chemical mechanisms are developed. A broad description of the most commonly used method will be given.

Finally, an atmospheric chemical mechanism will be applied to 3-dimensional ACTM with the purpose of simulating the secondary pollutant ozone. Secondary pollutants are formed by chemical processes from primary pollutants and normal atmospheric constituents. Primary pollutants are emitted by anthropogenic sources.