Overhead Slides

for

Atmospheric Chemistry

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by

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The Lectures on Atmospheric Chemistry are currently held as a one semester course at the University of Munich (LMU), Department of Meteorology. This course will be especially useful for students of environmental sciences and meteorology, but also students of physics, geophysics, and physical chemistry are addressed.

The lectures cover issues related to the atmospheric chemistry of the Earth's troposphere and stratosphere. Thereby, a basic knowledge of atmospheric chemistry is conveyed, preparing the students for further in-depth studies. The chemistry of the upper atmosphere (mesosphere and ionosphere) and of other planets is not addressed.

During the lectures, the following collection of overhead slides is supplemented by further viewgraphs containing more illustrations and tables, as well as by more detailed derivations presented on the blackboard.

Acknowledgements

I am grateful to Christoph Brühl, Max-Planck-Institut für Chemie, Mainz, for providing results from simulations of the Mainz 2D Photochemical Model. The figures used in the lectures serve to illustrate the basic global distribution of important trace species. Keep in mind that models can only represent the current state of knowledge; individual results may be subject to changes if this knowledge improves.

I thank Hans Feichter, Max-Planck-Institut für Meteorologie, Hamburg, for providing several global distributions and source strengths of aerosol particles and aerosol precursor gases. Likewise, these are mainly model results, as observations do not cover the globe.

Finally, I have made use of graphics taken from NASAs *Electronic Textbook on Stratospheric Ozone*, set up by colleagues from the Goddard Space Flight Center. This is an excellent introduction to this fascinating subject.

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1. Atmospheric Composition and Transport

Atmospheric pressure and density, Equation of state, Vertical profiles of pressure and temperature, Global temperature field, Partial pressure and mixing ratio, Trace gases, Relative humidity, Dew point and frost point, Thermal equilibrium, Atmospheric aerosols, Principal aerosol sources, types, and modes, Primary and secondary aerosol sources, Concentrations and size of aerosols, Particle size distributions, Lognormal size distributions, Particles interacting with molecules, Radiation, Radiative balance of the Earth, Radiative processes, Absorption and scattering in the atmosphere, Scales of atmospheric motions, Large-scale atmospheric motions, Global circulation, Exchange times between atmospheric compartments

2. Atmospheric Gases and Global Cycles

Biogeochemical cycling, Reservoirs of the Earth system, Nitrogen cycle, Major elements of the nitrogen cycle, Nitrous oxide, Nitrous oxide zonal mean concentrations, Nitrogen oxides, Nitrogen oxide climatology from HALOE, Reactive nitrogen, Ammonia, Ammonia emission inventory, Oxygen cycle, Major elements of the oxygen cycle, Ozone, Atmospheric ozone, Vertical profile of ozone and absorption of UV radiation, Ozone climatology from HALOE, Carbon cycle, Major elements of the carbon cycle, Methane, Methane climatology from HA-LOE, Carbon dioxide, Carbon monoxide, Carbon monoxide zonal mean concentrations, Non-methane hydrocarbons, Sulfur cycle, Major elements of the sulfur cycle, Dimethyl sulfide, Carbonyl sulfide, Sulfur dioxide, Sulfur dioxide emission inventory, Global sulfur emissions, Water vapor, Structure of liquid water, Structure of ice, Water vapor climatology from HALOE, Water vapor in the tropopause region, Hydrological cycle, Halogencontaining compounds, F11, F12, and F22 zonal mean concentrations, Methyl chloride zonal mean concentrations, Hydrochloric acid climatology from HALOE, Bromocarbons, Iodocarbons, Molecular hydrogen, Hydrogen zonal mean concentrations, Hydrogen fluoride, Hydrogen fluoride zonal mean concentrations

3. Gas Phase Reaction Kinetics and Photolysis

Definitions, Collision density, Elementary collision theory, Rate laws, Common types of elementary reactions, Pseudo steady state approximation, Bimolecular reaction kinetics, Uni- and termolecular reaction kinetics, Temperature dependence of reactions, Pressure dependence of reactions, Integrated rate laws, Photochemical processes, Transitions in excited molecules, Primary photochemical processes, Actinic flux, Quantum yield, Photolysis rate coefficients

4. Heterogeneous Reaction Kinetics

Condensation and deposition, Kinetic regime, Diffusion regime, Transition regime, Factors controlling particle growth, Kelvin effect, Solute effect, Dissolution, Characteristic time for equilibration between gas and aerosol phase, Time scale of gas-to-particle transport, Uptake of molecules by liquid particles, Uptake coefficient, Kinetic and diffusive resistances, Diffusion and reaction, Practical use of uptake coefficients, Surface reactions, Adsorption on particle surfaces, Adsorption isotherms, Langmuir isotherm, Surface adsorption and reaction

5. Stratospheric Chemistry

Stratospheric ozone, Ozone zonal mean concentrations, Stratospheric temperature and ozone trends, Processes affecting stratospheric chemistry, Ozone production, Chapman cycle, Analyzing the Chapman cycle, Summarizing the Chapman cycle, Stratospheric ozone and transport, Catalytic ozone destruction, Catalytic ozone loss cycles, Chain reactions, Sources for radical species, NO_x and CIO_x cycles, BrO_x cycles, HO_x cycles, Radicals, reservoirs, and sinks, Coupling the cycles, Creating the reservoir gases, Interchange radicals without ozone loss and further coupling reactions, Molecules with dual roles, Fate of reservoir gases, Chemistry of the lower stratosphere at midlatitudes, Analyzing the budgets of individual cycles, Response of lower stratospheric chemistry to changing levels of NO_x, Stratospheric water vapor, Water vapor zonal mean concentrations, Stratospheric water vapor trends, Chemistry of stratospheric aerosol precursors, Stratospheric aerosol layer, Stratospheric aerosol sources and sinks, Climatological stratospheric aerosol surface area densities derived from satellite observations, Heterogeneous stratospheric chemistry, Effects

of heterogeneous reactions, N₂O₅ hydrolysis, Halogen activation, Effects of major volcanic eruptions, Optical depth of stratospheric aerosols, Chemistry at high aerosol levels, Distribution and partitioning of NO_v, Distribution and partitioning of Cl_v and Br_v, HCl zonal mean concentrations, CIOX zonal mean concentrations, BrX zonal mean concentrations, BrO zonal mean concentrations, Polar ozone chemistry, Ozone columns, Ozone column minima (SH and NH), Vertical profile of an "ozone hole", "Ozone hole" from satellite observations, Summarizing "ozone hole" observations, "Ozone hole" theories, Polar stratospheric clouds, Polar lower stratospheric zonal mean temperatures, PSC frequency of occurrence, PSC characteristics, PSC formation pathways, CIOdimer cycle, Analyzing the dimer cycle, Beyond the gas phase reactions, PSCs liberate active chlorine, PSC chemistry, Denoxification, denitrification, and dehydration, Phase-dependence of reactions, Temporal evolution of chlorine activation, Chlorine partitioning observed during "ozone hole" events, Satellite observations of CIO, Role of methane in polar ozone depletion, Summarizing "ozone hole" photochemistry, Ozone depletion in the Arctic, Future evolution of total chlorine and ozone

6. Tropospheric Chemistry

Key aspects of tropospheric chemistry, Atmospheric ozone, NO_x zonal mean concentrations, CH₄ zonal mean concentrations, OH-mediated chemistry, NO_x–O₃ photochemical cycle, Photostationary state relationship, Ozone photolysis, Production of OH radicals, Recycling of OH radicals, Catalytic oxidation of CO, Interconversion of HO_x species, HO_x destruction, HO_x zonal mean concentrations, HNO₃ zonal mean concentrations, Temporary HO_x reservoirs, Nighttime nitrogen chemistry, CO-NO_x reaction chain, Degradation of formaldehyde, Methane oxidation, Summary of HO_x-related chemistry, Role of tropospheric NO_x for ozone production, Budget of tropospheric ozone, Urban photochemistry, Definitions, Alkanes and alkenes, Aromatics and aldehydes, Peroxyacyl nitrates, Other organic compounds, Ozone production in the presence of hydrocarbons, Condensed reaction mechanisms for organic chemistry, Relative roles of VOC and NO_x in ozone formation, Ozone isopleth plot, Hydrocarbons in the free troposphere, Net upper tropospheric ozone production rates, Heterogeneous tropospheric chemistry, Chemistry of marine

clouds, Basic HO_x chemistry in clouds, Chemistry of continental clouds, Nitrogen chemistry in clouds, Sulfur chemistry in clouds, Heterogeneous reactions with aerosol particles, Hydrolysis of N₂O₅, Heterogeneous loss of HO_x, Heterogeneous Production of HNO₂, Reactions with sea salt particles, Ozone destruction in the Arctic tropospheric boundary layer, Reactions with mineral particles, Tropopause altitudes, Water vapor in the tropopause region, Heterogeneous chemistry in the tropopause region, Denitrification of the upper troposphere, Tropospheric

chemistry and climate

Introductory Textbooks

- J.H. Seinfeld and S.N. Pandis Atmospheric Chemistry and Physics Wiley Interscience, 1326pp, 1998.
- B.J. Finlayson-Pitts and J.N. Pitts, Jr. Atmospheric Chemistry: Fundamentals and Experimental Techniques John Wiley, 1098pp, 1986.
- R.P. Wayne
 Chemistry of Atmospheres
 Clarendon Press Oxford, 447pp, 1996.
- D.J. Jacob Introduction to Atmospheric Chemistry Princeton Univ. Press, 267pp, 1999.
- P. Fabian Atmosphäre und Umwelt Springer, 144pp, 1992.

Review Articles and Other Useful References

World Meteorological Organization and United Nations Environment Programme, Scientific Assessments of Ozone Depletion, WMO/UNEP Reports No. 37+44, 1995+1998.

G.P. Brasseur et al (Eds.), Atmospheric Chemistry in a Changing World. IGBP Information and Synthesis Series, Springer Verlag, to be published 2002.

http://see.gsfc.nasa.gov/education/SEES /strat/class/S-class.htm

S. Solomon, Stratospheric ozone depletion: A review of concepts and history, *Rev. Geophys., 37*, 275–316, 1999.

Th. Peter, Microphysics and heterogeneous chemistry of polar stratospheric clouds, 785–822, 1997.

J. Staehelin, N.R.P. Harris, C. Appenzeller, and J. Eberhard, Ozone trends: A review, *Rev. Geophys.*, *39*, 231–290, 2001.

R. Atkinson, Atmospheric chemistry of VOCs and NO_x, *Atmos. Environment, 34*, 2063–2101, 2000.

D.R. Crosley (Ed.), Measurement of HO_x radicals in the atmosphere, *J. Atmos. Sci.*, *52*, 3297–3441, 1995.

L. Jaeglé, D.J. Jacob, W.H. Brune, and P.O. Wennberg, Chemistry of HO_x radicals in the upper troposphere, *Atmos. Environment*, 35, 469–489, 2001.

D.J. Jacob, Heterogeneous chemistry and tropospheric ozone, *Atmos. Environment, 34*, 2131–2159, 2000.

R.P. Wayne, G. Poulet, P. Biggs, J.P. Burrows, R.A. Cox, P.J. Crutzen, G.D. Hayman, M.E. Jenkin, G. Le-Bras, G.K. Moortgat, U. Platt, and R.N. Schindler, Halogen oxides: Radicals, sources and reservoirs in the laboratory and in the atmosphere, *Atmos. Environment*, *29*, 2677–2881, 1995.