CHEMISTRY OF THE ATMOSPHERE

I.L. Karol and **A.A. Kiselev**
Main Geophysical Observatory, St. Petersburg, Russia

Keywords: Atmospheric composition, gas phase reactions, heterogeneous reactions, catalytic cycles, lifetime

Contents

Summary

The various types of atmospheric reactions are considered. The relevant formulas and necessary parameters for calculation of the most important reaction rates are denoted. There is the common information about atmospheric catalytic cycles. Residence time of an atmospheric compound as the important characteristic of atmospheric chemistry is discussed. Typical residence times of basic atmospheric species for diurnally, annually and globally averaged conditions are illustrated.

The existence of the atmosphere is due to the law of gravitation. Owing to its effect, the air molecules are not capable to move away from the Earth at a great distance. The air density decreases with altitude by the exponential law. As a result, it is about 2.5×10^{19} molecules per cm^3 but 10 and 1000 times lesser at 16 and 50-km altitude, respectively. The atmosphere is a mixture of various gases. On the whole air consists of molecules of nitrogen N_2 and oxygen O_2: their shares are about 78.08 and 20.95%, correspondingly, and do not change with height. Therefore the net share of all the others does not exceed 1%. Among them, about 0.94% falls on the inert gases and about 0.03% is the share of carbon dioxide CO_2. But the main interest of atmospheric chemistry is in many

hundreds of air compounds whose content shares are a few thousandths percent and less. In spite of their apparent trifle, their presence in the atmosphere often has the same importance as one of molecular oxygen that is necessary for the human's and animal's respiration. For instance, a life on the Earth is impossible without an existence of atmospheric ozone O_3 whose molecules number does not exceed 0.0001% of total air molecules. As it is well known, ozone has unique ability to absorb the disastrous solar radiation in ultraviolet (UV) band of 280-320 nm (1 nm = 1×10^{-9} m).

The atmosphere is in permanent development. For example, according to modern estimations, ozone concentration share in the atmospheric air density was increasing during the last decades. The similar behavior of some other air components, such as CO_2, methane CH_4, nitrous oxide N_2O and so on, during the long time period of the Earth's history is observed on the base of ice core measurements (see theme, *Environmental Structure and Function: Climate System* . This gas composition evolution is caused by many natural factors (solar activity variations, decrease of snow cover area, air temperature change, evolution of vegetation and others). Also the anthropogenic impact on the atmosphere intensified during the last centuries because of the sharp increase of fossil fuel amount combustion, of minerals mining output, of agricultural activity in increasing areas and so on. The last decades are characterized by intensive emission of many chemical industry products, such as chlorofluorocarbons (CFCs), halons and ethers, into the atmosphere too.

1. Types of Atmospheric Reactions

The molecules of hundreds of atmospheric species react each other incessantly, demolishing ones and/or producing others. There are several types of atmospheric reactions. The gas phase reactions are the most studied among them.

1.1. Photolysis Reactions

First of them is due to their interaction with the solar UV radiation. The atmospheric species, whose molecules contain several atoms, absorb photons and, as a result, turn into the new excited state

$$XY + h\nu \rightarrow XY^* .$$

If the energy of absorbed quantum exceeds the energy of atomic coupling in the molecule, this molecule disintegrates

$$XY^* + h\nu \rightarrow X+Y$$
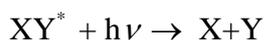
This process is called photodissociation or photolysis. If energy of absorbed quantum is insufficient for photodissociation of a molecule, this molecule returns to its former state after its collision with other air molecules M

$$XY^* + M \rightarrow XY + M$$
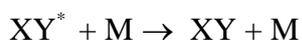
The photodissociation, the reaction with one reactant only, is called as monomolecular or the first-order reaction. Its intensity v is

$$v = -d\left[\mathrm{XY}\right]/dt = d\left[\mathrm{X}\right]/dt = d\left[\mathrm{Y}\right]/dt = J_{\mathrm{XY}}\left[\mathrm{XY}\right]$$

J_{XY} is a coefficient of proportionality between the photodissociation intensity v and reactant concentration $[\mathrm{XY}]$. It depends on both the radiation characteristics and individual properties of reactant.

Usually, for the photodissociation rate J_{XY} calculation the Behr-Lambert-Bouger law is used

$$J_{\mathrm{XY}}(z,\varphi) = \int_{\lambda} I(\lambda)\alpha_{\mathrm{XY}}(\lambda)\Phi_{\mathrm{XY}}(\lambda)\exp\{-\sec\varphi[\alpha_{\mathrm{O}_2}(\lambda)V_{\mathrm{O}_2}(z)+\alpha_{\mathrm{O}_3}(\lambda)V_{\mathrm{O}_3}(z)]\}B(\lambda,z,\varphi)d\lambda$$

where $I(\lambda)$ is the solar radiation intensity at the upper atmospheric boundary; α_{XY}, α_{O_2} and α_{O_3} are photon absorption cross sections by molecules of compound XY, O_2 and O_3, respectively; $\Phi_{\mathrm{XY}}(\lambda)$ is the quantum yield of compound XY; V_{O_2} and V_{O_3} are the total columns of O_2 and O_3 above level z; $B(\lambda,z,\varphi)$ is correction coefficient due to the photon reflection and scattering by air molecules, aerosols and ground surface; φ is latitude; λ is the wavelength. The integration by λ is along the radiation absorption band of compound XY. The photodissociation rate is in s^{-1}.

The photodissociation of air compound molecules leads to the production of free atoms and radicals, whose important characteristic is their extremely high chemical reactivity. Among the most important free atoms and radicals are atoms of oxygen, nitrogen, chlorine, bromine and radicals - hydroxyl OH, perhydroxyl $\mathrm{HO_2}$, nitric oxide NO, nitrogen dioxide $\mathrm{NO_2}$, chlorine oxide ClO and many others. It is evident that the photodissociation process occurs during enlightened time of the day only. Thus, the concentrations of free radicals and atoms, as products of air molecules photolysis, have significant diurnal variations.

1.2. Bimolecular Reactions

The reactions between two reactants X and Y are called as bimolecular or second-order ones

$$\mathrm{X} + \mathrm{Y} \rightarrow \text{ products}.$$
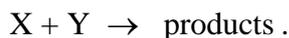
This reaction intensity is

$$v = -d\left[\mathrm{X}\right]/dt = -d\left[\mathrm{Y}\right]/dt = k\left[\mathrm{X}\right]\left[\mathrm{Y}\right]$$

where k is a coefficient of proportionality between the reaction intensity v and product of reactant concentrations $[X]$ and $[Y]$, t is a time. Coefficient k is called as the reaction rate. In 1899, for the first time, basing on the experimental data, Arrhenius proposed the dependence of the reaction rate on temperature

$$k = A \exp[-E/(RT)]$$

where T is temperature in Kelvin, R is gas constant. The parameters, Arrhenius A - factor and activation energy E, are obtained in the laboratory studies. In the overwhelming majority of cases the activation energy E is positive and, thus, the reaction rate increases with temperature growth. But reactions with negative activation energy exist also and then, opposite, the temperature increase is accompanied by decrease of these rates. Sometimes the reaction rates are defined by other formulas, e.g. the recommended rate for important atmospheric reaction between carbon monoxide CO and hydroxyl is $1.5 \times 10^{-13}(1 + P_{atm})$ where P_{atm} is atmospheric pressure in millibar divided to 1000. Also the rate of other atmospheric reaction between nitric acid HNO_3 and hydroxyl is calculated by formula

$$k(M,T) = k_0 + \frac{k_3[M]}{1 + \dfrac{k_3[M]}{k_2}}$$

where $k_0 = 1.01 \times 10^{-14} \exp(785/T)$, $k_2 = 4.1 \times 10^{-16} \exp(1440/T)$, $k_3 = 2.66 \times 10_{-33} \exp(725/T)$.

Reaction rate k of bimolecular reaction is expressed in $cm^3 \, s^{-1}$.

-
-
-

TO ACCESS ALL THE **24 PAGES** OF THIS CHAPTER,
Visit: http://www.eolss.net/Eolss-sampleAllChapter.aspx

Bibliography

Brasseur G.P. (1999). Atmospheric chemistry and global change. Cambridge University Press, UK. [This book contains the recent results of studies devoted to various aspects of atmospheric chemistry].

DeMore W.B., Sander S.P., Golden D.M., Hampson R.F., Kurylo M.J., Howard C.J., Ravishankara A.R., Kolb C.E., Molina M.J. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling (1997). Jet Propulsion Laboratory Publication, Pasadena, California, USA, 266 pp. [This contains the sets of numerous atmospheric gas phase and heterogeneous reactions and their recommended rates].

Scientific Assessment of Ozone Depletion: 1998 (1999). WMO Global Ozone Research and Monitoring Project, Report No. 44, Geneva, Switzerland. [This is devoted to the various aspects of ozone problem

including its monitoring, photochemistry and climatic forcing, prediction of atmospheric composition evolution, and others].

Wuebbles D.J., Edmonds J. (1991). Primer of greenhouse gases. Chelsea, Michigan, Lewis Publishers, 160p. [This book is devoted to review of the major greenhouse gases: their sources, sinks, atmospheric photochemistry, evolution in the atmosphere].

Biographical Sketches

I.L.Karol was born in 27 July 1927 in Leningrad, USSR. In 1944 he entered and in 1949 he graduated from the Hydrodynamics Dept. of Leningrad State University, Mathematics and Mechanics Faculty. Post graduate studies he passed from 1949 to 1952, when he received scientific degree of Candidate in Math & Physics after presenting the candidate these in mathematical physics. After three years of lecturing in mathematics at the Ural University in Sverdlovsk, in 1956 he entered in the Institute of applied Geophysics USSR Academy of Sciences in Moscow as a senior scientist. In 1959 he was transferred to Institute of Experimental Meteorology of USSR Hydrometeorological Service in Obninsk, near Moscow, where he was nominated as chief of laboratory in 1970. Since 1972 he is with Main Geophysical Observatory of USSR Hydromet. service in Leningrad (now St. Petersburg) after receiving the USSR scientific degree of the Doctor in Math & Physics, presenting in 1970 the these, which was published in 1972 as book by Gidrometeoizdat Publishing House "Radioactive isotopes and global transport in the atmosphere". This book was translated into English and published in 1974. From 1953 I.L.Karol published 10 scientific monographs and more than 140 papers individually and with coauthors. The original papers are dealing with modeling of global atmospheric composition and climate changes due to natural and anthropogenic causes. During several periods he served as a member of various international commissions and committees of the International Association of Meteorology and Atmospheric Physics, of the World Meteorological Organization, of the World Climate Research Program Joint Scientific Committee. Since 1974 he is the USSR (now Russian) co-leader of the joint project: "Composition of the atmosphere and climate changes" of the US-Russian Cooperation in the Environmental Protection. He was the author and co-authors of numerous scientific reports, which he presented at international and national scientific meetings during all his scientific career.

A.A.Kiselev was born in 26 April 1953 in Leningrad, USSR. In 1970 he entered and in 1975 he graduated from the Hydrodynamics Dept. of Leningrad State University, Mathematics and Mechanics Faculty Post graduate studies he passed from 1977 to 1981, in 1986 he received scientific degree of Candidate in Math & Physics after presenting the candidate these in geophysics. In 1975 he entered in the Main Geophysical Observatory of USSR Hydrometeorological Service in Leningrad as a junior scientist. Since 1990 he took position of senior research scientist in Main Geophysical Observatory. From 1975 A.A.Kiselev published about 30 papers individually and with coauthors. He is contributor of the Intergovernmental Panel on Climate Change Reports of 1990 and 1999. The original papers are dealing with modeling of photochemical processes in the atmosphere, of global atmospheric composition change due to natural and anthropogenic causes.