

GLOBAL VARIATIONS IN THE CHEMISTRY OF ATMOSPHERIC WATER

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Keywords: ppm, ppb, super saturation, tropospheric and stratospheric clouds, Henry law coefficient, aqueous-phase chemical reactions, equilibrium constant of chemical reactions, rate constant of aqueous-phase chemical reactions, reservoir species, reactive uptake coefficient, free radicals, transient metal ions.

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Summary

As neither evaporation nor condensation of water vapor in the atmosphere could have changed over many thousands of years, the global variations in the chemistry of the atmospheric water should be related exclusively to man-made air-borne pollutants over the last one to two hundred years. Among these pollutants, methane, nitrogen and sulfur oxides and chlorinated substances have increased markedly during the last two centuries. Stratospheric ozone loss ('ozone hole') over Antarctica in springtime due to catalytic reactions induced by minute quantities of ozone-destroying chlorine radicals liberated through heterogeneous chemical processes has received much attention. Aqueous-phase tropospheric oxidation processes of sulfur dioxide emitted on a large scale by both natural and anthropogenic sources lead to acid rain. The production of formic acid, by aqueous-phase oxidation of formaldehyde, is also an important contributor to the acidity of precipitation at remote sites.

1. Introduction

For thousands of years the climate of the Earth underwent little variation, i.e. the conditions of circulation of water were kept practically unchanged. In the last one and a half centuries, however, the chemical composition of the atmosphere has changed dramatically. For example, observations have indicated an increase in the concentrations of trace gases such as nitrous oxide (N_2O), methane (CH_4), sulfur (mainly SO_2) and halogen-containing (mainly chlorofluorocarbons) compounds. The rapid changes in the trace components were caused by human activity starting in the first half of the nineteenth century, when large-scale combustion of fossil fuels, primarily coal and oil for energy and transportation, found universal application. The temporal development of the increased emission can be clearly followed from snow cores taken from Greenland and other polar regions. The SO_4^{2-} and NO_3^- concentrations in Greenland have strongly increased from 1788-1800 ($42 \mu\text{g}$ of $\text{SO}_4^{2-} \text{ g}^{-1}$ and $65 \mu\text{g}$ of $\text{NO}_3^- \text{ g}^{-1}$ respectively) compared to present Greenland snow samples (1976-1977: $120 \mu\text{g}$ of SO_4^{2-} and $120 \mu\text{g}$ of $\text{NO}_3^- \text{ g}^{-1}$ respectively). In addition to gaseous compounds, particles are also emitted from anthropogenic and natural sources. The fraction of aerosols emitted by anthropogenic sources is about 10% of the overall anthropogenic air pollution, on a mass basis. These are mainly metal oxides, as present in fly ash. For instance snow deposited in Greenland since 1955 contains more than 10 times as much lead (Pb) as snow that fell prior to 1850. Although no data are available for iron, this is the metal with highest level of emission. Manganese (Mn), copper (Cu) and other transient metal ions (TMI) are emitted in much smaller quantities but they are of great importance for atmospheric water chemistry because of their high catalytic activity. In the last few decades of the twentieth century both coal and oil have been gradually replaced by natural gas (CH_4). Although its usage as an energy-carrier is safer than coal or black oil, some ecological problems, in particular NO_x emission in the atmosphere, still remain. Another problem is the leakage of CH_4 from pipelines. Long-term observations indicate an average yearly increase close to 1% up to about the mid-1980s. This, together with its long residence time, has made methane the most abundant organic compound in the atmosphere among. The current content of methane in the atmosphere is as high as ≈ 2 ppm. Analysis of air trapped in ice cores has shown that the content of atmospheric methane during the present interglacial, until about 200 years ago, was two to three times lower than the present level.

2. Background

Junge was the first to declare, in the early 1960s, the potential importance of aqueous phase oxidation of SO_2 within droplets in atmospheric clouds or fogs. The known dramatic drop in stratospheric ozone over the Antarctic in springtime (the 'ozone hole') has been attributed to the chemical reactions proceeding in water-based aerosols (ice particles made up from water or trihydrate of nitric acid, ternary solutions $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$, etc). Today there are grounds to suspect that the background sulfate aerosol layer (The Junge Layer) is responsible for global ozone depletion. If we ignore the dramatic temporary (2-3 years) ozone depletion caused by the eruption of Mt. Pinatubo (1991), the average measured trend in global ozone depletion since the early 1980s was approximately 3% per decade (ten years). Contact between wet sea-salt particles and the surrounding gas is now considered to be a source of molecular halogens (chlorine, bromine), whose dissociation in sunlight starts the catalytic depletion of tropospheric ozone in the marine boundary layer.

2.1. How atmospheric water chemistry is influenced by pollutants

Clouds alter the concentrations of pollutants through aqueous-phase chemical reactions and by altering radiation transfer and mixing of air masses. The presence of liquid water, for instance, can lead to the redistribution of soluble and insoluble pollutants in the atmosphere. Those soluble pollutants having large Henry law coefficients go preferentially in the droplet phase thus favoring aqueous-phase chemical reactions. Liquid/solid water can also alter concentrations of active species, primarily OH and HO₂ radicals, both in gas and liquid phases. The effect is caused by reactive uptake of the species from the gas. These OH and HO₂ radicals are produced in the gas in a sequence of processes initiated by sunlight absorption. Even with relatively inert and soluble HO₂ radicals their concentration in the gas in clouds falls not only as a result of transferring into condensed matter but also through rapid aqueous-phase reaction, HO₂ + HO₂.

2.2. Atmospheric water as a reaction medium

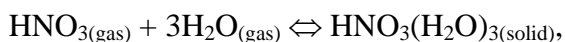
Water in the atmosphere can exist as gas, liquid and solid. Neither liquid nor solid water are free of impurities. The droplets/ice particles suspended in the gas represent a multi-component system with dissolved (captured) impurities present in molecular, ionic or radical forms. Ice particles can incorporate the gas as a clathrate—solid hydrates of H₂SO₄, HNO₃, HCl (i.e. H₂SO₄·H₂O, H₂SO₄(H₂O)₄, etc). All water-based particles in the atmosphere can be considered as mini-chemical reactors (surface and bulk). These are interchanging with surrounding gas, being involved in the processes of absorption or adsorption of stable and reactive constituents. Thermodynamic and kinetic approaches are needed therefore to describe in detail the basic properties and behavior of atmospheric water and the global modification of water chemistry caused by emission of man-made pollutants.

In the troposphere several types of liquid water must be distinguished. Clouds, fogs and mists represent examples of atmospheric water in a liquid form. They differ in water volume content in the gas ($L = V_{\text{liq}}/V_{\text{gas}}$) and droplet size (r). Typically for tropospheric clouds, $L \leq 10^{-6}$ and $r \approx 10 \mu$ (10^{-3} cm). Under meteorological conditions with cooling of humid air mass, water vapor may reach super-saturation of up to several tenths of 1%. At these super-saturations, with temperature not far below 0 °C, hygroscopic fine particles act as nuclei for condensation and growth of cloud droplets.

How frequently do clouds occur in the lower troposphere? On a global (area) basis 50% of the troposphere is filled with clouds. On a reasonable assumption of average cloud depth of 3 km, cloud water content (L) of 0.5 g m⁻³ and a fractional global coverage of 0.5 (50%), the total cloud water would represent about 1/30 of the total atmospheric water vapor pressure. With an assumed annual precipitation rate in the range of 70 to 100 cm, liquid water must therefore have an average residence time in the troposphere in the range of 7 to 11 hours, which is longer than the average lifetime of most clouds, which ranges usually from 30 min to 1 hour. Consequently the number of cloud evaporation-condensation cycles is of the order of 10. The condensation phase of the cloud cycle permits chemical reactions to occur in the liquid water; the evaporation phase delivers back to the troposphere a supply of aqueous solution aerosol of fine

particle size, which may provide the nuclei for the next condensation phase. For reasons given below, it would appear that the time for mass transfer and reaction to occur in cloud droplets has an average an upper bound of 30 min to 1 hour. Precipitation events may be somewhat shorter, with one estimate for average duration given as about 20 minutes. Of course, these represent very approximate estimates of the average and the variation about these figures may be considerable.

Between the troposphere and stratosphere, liquid water also exists as extremely small droplets suspended in the gas, made up from concentrated sulfuric acid solutions, so called sulfate background aerosol (The Junge Layer). In addition, in Polar Regions where winter temperature drops to extremely low levels (e.g. to 190 K), ice particles of nitric acid trihydrate (NAT) ($r = 10\text{-}100 \mu$) are formed during co-deposition of nitric acid and water vapor on the cold surface of the nuclei. The formation of these ice particles appears possible at a temperature of 5 to 7 degrees above the frost point, when the vapor pressure product, $p_{\text{HNO}_3}(p_{\text{H}_2\text{O}})^3$ exceeds the equilibrium constant for the reaction:



The co-deposition of NAT increases the surface area of aerosol particles flying in the gas, making possible the occurrence of surface chemical reactions in the atmosphere at higher temperatures than the frost point of water ice (below 190 K). The volume of typical background aerosols in the stratosphere and droplet radius are several orders lower than those in the troposphere, namely $L \leq 10^{-13}$ and $r \approx 0.1 \mu$ (10^{-5} cm). Note that current knowledge of the processes of formation of water-based aerosols in Polar Regions is rather qualitative and requires further study.

Several factors favoring aqueous-phase/surface chemical reactions can be outlined. Despite seemingly low $L = V_{\text{liq}}/V_{\text{gas}}$, the liquid represents an ideal reaction medium for occurrence of chemical transformations because of the large specific surface (per unit of volume of the gas). As stated above, the water volume content varies over a wide range, from 10^{-13} in the stratosphere (in the absence of volcanic eruptions—when such events take place the aerosol volume content increases by a factor of 10^2) to approximately 10^{-6} in the troposphere. Hence the total surface of aerosol particles (S_{liq}) in unit volume of gas ($S_{\text{liq}}/V_{\text{liq}}$) varies from $\approx 10^{-8}$ to 10^{-3} cm^{-1} . Water molecules present on the surface of ice particles or NAT are capable of polarizing HCl and ClONO₂ molecules coming from the gas, thus facilitating the occurrence of surface chemical reactions. Typical solute concentrations in the droplets vary over a wide range approaching $\leq 40 \text{ mol/kg}$ (stratospheric water-based aerosol). High concentrations of reagents in condensed media, coupled with rapidity of liquid-phase/surface chemical kinetics (high k_i) and strong thermodynamic driving force (high K_i), enhances the potential importance of heterogeneous chemical reactions involving water-based aerosol.

The course of heterogeneous chemical reactions (surface or bulk) in the atmosphere proceeds, however, in several stages:

1. Gas-phase transport of reagents to the gas-liquid interface

2. Establishing of local solubility/saturation equilibria at the interface
3. Hydrolysis or ionization of the dissolved/adsorbed constituents
4. Diffusion in/onto the condensed phase
5. Chemical reaction

The rapidity of these processes as applied to gas-liquid interaction are given in Table 1.

Characteristic times	τ_i
<i>Gaseous diffusion</i>	$\tau_{gas} = r^2/\pi^2 D_{gas}$
<i>Phase equilibrium</i>	$\tau_{ph} = D_{aq}(4\eta HRT/\gamma \bar{\omega})^2$
<i>Hydrolysis/ionization</i>	$k_h[\text{H}_2\text{O}]$ or k_{ion}
<i>Aqueous diffusion</i>	$\tau_{aq} = r^2/\pi^2 D_{aq}$

Table 1. Summary of characteristic times (Schwartz, 1981)

Here D_{gas} and D_{aq} are the diffusivity in gaseous and aqueous phases, $\text{cm}^2 \text{s}^{-1}$; η is a factor reflecting the presence of the dissolved component in other than molecular form (hydrolyzed or ionized species), indicating an increase in solubility of the given constituent; R is a universal gas constant expressed as a unit of $\text{M}^{-1} \text{atm K}^{-1}$; T is absolute temperature, K ; γ is the uptake coefficient (dimensionless); $\bar{\omega}$ is the meaning of average thermal velocity of the impinged gaseous species, cm s^{-1} . The appeared figures $k_h[\text{H}_2\text{O}]$ and k_{ion} are respectively the rate constants of the hydrolysis or ionizing of the dissolved component, having a dimension of s^{-1} .

Both in the troposphere and stratosphere, the chemical reactions are the rate-determining step (Schwartz, 1981). Their occurrence within a volume/surface of the particles droplets in most important cases does not perturb the rates of the above-listed steps, thus not producing significant concentration gradients in the gas and liquid phase (except probably concentration gradients of OH_{aq} $\text{O}_{3(aq)}$ within the tropospheric droplets). The duration of chemical reactions in the droplet phase varies over a wide range. In the case of SO_2 removal from the gas the time can approach the lifetime of the droplet (precipitation events).

As most of aqueous-phase chemical reactions in the droplet are bimolecular, their rate (w , M s^{-1}) involving say A and B components, is expressed as $w = k_{A+B}[A][B]$. Typical rate constants of most important radical-driven aqueous-phase chemical reactions following atmospheric oxidation of SO_2 are given in Table 2. Some of these rate constants approach diffusion-controlled limit ($\approx 10^{10} \text{M}^{-1} \text{s}^{-1}$). The aqueous-phase rate of $A + B$ recalculated in moles per liter of air per second (w') is given by $w' = k_{A+B}[A][B]L$. In contrast, in the stratosphere the usage of the so-called reactive dimensionless uptake coefficient (γ_i) is widely accepted (see above). Consider, for instance, the rate of species A to be removed from the gas via reactive uptake expressed in moles per liter of air per second: one would have $w' = 3L\gamma_A [A]_{gas} \bar{\omega} 10^3/4rN_a$, where $[A]_{gas}$ is concentration in cm^{-3} , N_a is Avogadro number. As γ_i are sensitive to temperature, sulfuric acid content in the droplet phase and presence of other dissolved constituents, the use of parameterization is widely accepted. Typical example of such

parameterization of γ_i' for a number of liquid-phase reactions proceeding in sulfuric acid solution is given in Table 3. Accordingly to Zhang, the reaction probability for ClONO_2 hydrolysis approaches 0.01 at temperatures below 200 K, whereas the values for $\gamma'(\text{ClONO}_2 + \text{HCl})$ and $\gamma'(\text{HOCl} + \text{HCl})$ are of the order of a few tenths at 200 K, thus stressing the importance of these reactions in the stratosphere.

Reaction	Rate constant
* $\text{Fe}(\text{OH})\text{SO}_3\text{H}_{(\text{aq})}^+ \Rightarrow \text{Fe}_{\text{aq}}^{2+} + \text{SO}_{3(\text{aq})}^- + \text{H}_2\text{O}_l$ *The subscript (aq) hereinafter denotes aqueous-phase species	0.2 c^{-1}
$\text{SO}_{3(\text{aq})}^- + \text{O}_{2(\text{aq})} \Rightarrow \text{SO}_{5(\text{aq})}^-$	$2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
$\text{SO}_{5(\text{aq})}^- + \text{HSO}_{3(\text{aq})}^- \Rightarrow \text{HSO}_{5(\text{aq})}^- + \text{SO}_{3(\text{aq})}^-$	$3.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$
$\text{SO}_{4(\text{aq})}^- + \text{HSO}_{3(\text{aq})}^- \Rightarrow \text{SO}_{4(\text{aq})}^{2-} + \text{SO}_{3(\text{aq})}^- + \text{H}_{\text{aq}}^+$	$7.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$
$\text{SO}_{5(\text{aq})}^- + \text{SO}_{5(\text{aq})}^- \Rightarrow \text{SO}_{4(\text{aq})}^- + \text{SO}_{4(\text{aq})}^- + \text{O}_{2(\text{aq})}$	$8.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$
$\text{SO}_{5(\text{aq})}^- + \text{SO}_{5(\text{aq})}^- \Rightarrow \text{S}_2\text{O}_{8(\text{aq})}^{2-} + \text{O}_{2(\text{aq})}$	$1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$
$\text{HSO}_{5(\text{aq})}^- + \text{HSO}_{3(\text{aq})}^- + \text{H}_{\text{aq}}^+ \Rightarrow 2\text{SO}_{4(\text{aq})}^{2-} + 3\text{H}_{\text{aq}}^+$	$\approx 10^7 \text{ M}^{-2} \text{ s}^{-1}$
$\text{Fe}_{(\text{aq})}^{2+} + \text{SO}_{5(\text{aq})}^- \xrightarrow{\text{H}^+} \text{Fe}_{\text{aq}}^{3+} + \text{HSO}_{5(\text{aq})}^-$	$3.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
$\text{Mn}_{\text{aq}}^{2+} + \text{SO}_{5(\text{aq})}^- \xrightarrow{\text{H}^+} \text{Mn(III)}_{\text{aq}} + \text{HSO}_{5(\text{aq})}^-$	$> 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$
$\text{Mn(III)}_{(\text{aq})} + \text{HSO}_{3(\text{aq})}^- \Rightarrow \text{Mn}_{\text{aq}}^{2+} + \text{SO}_{3(\text{aq})}^- + \text{H}_{\text{aq}}^+$	$1.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$

Table 2. Condensed radical-driven mechanism for transition metal ions catalyzed aqueous phase oxidation of SO_2 (Warnek, 1996)

Reaction	Coefficients			Experimental Conditions
	a_1	a_2	a_3	
$\text{ClONO}_2 + \text{H}_2\text{O}$	114.4	-1.04	0.0023	$T = 195\text{-}220\text{K}$, $P_{\text{H}_2\text{O}} = 5 \times 10^{-7}$, $P_{\text{ClONO}_2} = (1\text{-}2.6) \times 10^{-9} \text{ atm}$
$\text{ClONO}_2 + \text{HCl}$	75.06	-0.616	0.00117	$T = 195\text{-}212 \text{ K}$, $P_{\text{H}_2\text{O}} = 3.8 \times 10^{-4}$, $P_{\text{ClONO}_2} = (1\text{-}2.6) \times 10^{-9}$, $P_{\text{HCl}} = (4\text{-}5.3) \times 10^{-10} \text{ atm}$
$\text{HOCl} + \text{HCl}$	-42.54	0.52	-0.00157	$T = 195\text{-}212 \text{ K}$, $P_{\text{H}_2\text{O}} = 5 \times 10^{-7}$, $P_{\text{HOCl}} = (0.9\text{-}1.0) \times 10^{-7}$, $P_{\text{HCl}} = (3\text{-}4) \times 10^{-7} \text{ torr}$

$$* \lg \gamma' = a_1 + a_2 T + a_3 T^2$$

Table 3. Summary and parameterization* of the reactive dimensionless uptake coefficient measurements (Zhang, 1994)

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Biographical Sketch

Anatoly P. Purmal is a Doctor of Science (Chemistry), Professor, a senior scientist of the Semenov Institute of Chemical Physics of the Russian Academy of Sciences, and Professor of Moscow State Institute of Physics and Technology ("Phystech"). He is the author of several textbooks on chemical thermodynamics and chemical kinetics. His most recent textbook is "ABC of Chemical Kinetics" (Rus), Publ. IKC Akademkniga, 2004, 277. His field of scientific interest is mainly Solution Chemistry including the Chemistry of Atmospheric Water. *Recent publications*: Yermakov A.N., Purmal' A.P., *Iron-catalyzed oxidation of sulfite: From established results to a new understanding*, Progress in Reaction Kinetics and Mechanisms, 2003, V.28, № 3, 189-255. Yermakov A.N., Larin I.K., Ugarov A.A., Purmal' A.P. *On iron catalysis of SO₂ oxidation in the atmosphere*. Kinetics and Catalysis, 2003, V.44 (4) 524-537 (in Russian). Purmal' A.P. "ABC of Chemical kinetics", Publ. IKC Akademkniga, 2004, 277 (in Russian).