



Tropospheric Chemistry - Precipitation

Environmental Chemistry, vanLoon & Duffy – Chapter 5

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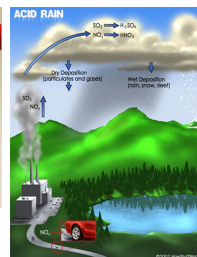
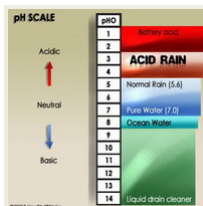


Introduction

One of the first environmental issues to generate widespread publicity and public attention was the problem of Acid Rain.

Emissions from energy and smelting industries were shown to be a source of sulphuric and nitric acid rain (pH sometimes <4)

When water condenses to form clouds, chemical species are incorporated in the cloud droplets. When chemicals are moved from the atmosphere during a precipitation event, it is referred to as **rainout**, while **washout** is the term used when chemicals are taken up by water droplets as they pass through air below the clouds.



Rain water is in equilibrium with gaseous species in air - it contains soluble forms of the atmospheric gases with concentrations determined by Henry's Law.

- CO₂ (378 ppm in 2004) is one of the major gases dissolved in water droplets.
- CO₂ is a weak acid, thus we suggest the unpolluted rain to have a pH of 5.7.

Other natural acid-producing species (organic acids, sulphur compounds, etc.) can also be a source of enhanced acidity in rain.

Other natural chemicals such as dust containing calcium carbonate can result in mildly alkaline solutions.

Depending on the setting, the pH of unpolluted rain might range from 4.5 to 8 or higher.

Table 5.1 The composition of rain from several locations^a.

	Concentration / $\mu\text{mol L}^{-1}$ in rain samples from				
	Urban Guiyang, Guizhou, PRC ^b	Birkenes, southern Norway ^c	Katherine, Northern Territories, Australia ^d	Pune, Maharashtra State, India ^e	St. Georges, Bermuda ^d
H ⁺	112 (pH = 3.95)	57 (pH = 4.2)	16.6 (pH = 4.8)	0.04 (pH = 7.4)	16.2 (pH = 4.8)
Cl ⁻		58	11.8	155	175
NO ₃ ⁻	10.3	38	4.3	18	5.5
SO ₄ ²⁻	222	68	6.3	11	36.3
Ca ²⁺	128	9	2.5	55	9.7
Mg ²⁺		13	2.0	35	34.5
Na ⁺		56	70	150	147
K ⁺		4	0.9	36	4.3
NH ₄ ⁺	57	38	2.4	28	3.8

^a The sites in China and Norway are considered to contain anthropogenic-source chemical species. The others are influenced to a smaller or negligible extent by human activity.

^b Dianwu, Z. and X. Jiling, Acidification in southwestern China, In *Acidification in tropical countries* (ed. Rodhe, H. and R. Herrera), John Wiley and Sons, Chichester; 1988. No data are provided for Cl, Mg, Na, and K.

^c Overreim, L.N., H.M. Seip, and A. Tollan, *Acid precipitation—effects on forest and fish*, Final report of the SNSF project 1972–1980, Oslo; 1980.

^d Legge, A.H. and S.V. Krupa, *Acid deposition, sulfur and nitrogen oxides*. Lewis Publishers, Chelsea, Michigan; 1990.

^e Khemani, L.T., G.A. Momin, M.S. Naik, P.W. Prakasa Rao, P.D. Safai, and A.S.R. Murty, Influence of alkaline particulates on pH of cloud and rain water in India, *Atmos. Environ.*, **24** (1987), 1137–45.

Table 5.2 Nitrogen and sulfur species present in the atmosphere.

	Approximate atmospheric mixing ratio / ppbv ^a	Approximate residence time / days	Source
Nitrogen species			
Nitrogen oxides, NO _x	1->10 (urban) 0.1-1 (remote)	0.2 (urban, summer) to 10 (remote, winter)	Fossil fuel, biomass, combustion; lightning; microbiological release
Ammonia, NH ₃	0.1-1	2-70	Animal excreta, fertilizers, microbiological release
Sulfur species			
Sulfur dioxide, SO ₂	0.01-0.3	3-5	Fossil fuel, biomass combustion; sulfide ore smelting
Hydrogen sulfide, H ₂ S	0.05-0.3	1-2	Submerged soils, wetlands
Carbon disulfide, CS ₂	0.02-0.5	≈50	Submerged soils, wetlands
Dimethyl sulfide, (CH ₃) ₂ S	0.01-0.07	≈1	Oceans
Carbonyl sulfide, COS	0.3-0.5	200-2500	Oceans, soils
Methyl mercaptan, CH ₃ SH			Oceans, soils
Dimethyl disulfide, CH ₃ SSCH ₃			Oceans, soils

The principal reaction sequence contributing to production of nitric acid begins with nitric oxide emissions occurring primarily during combustion processes.

For high-temperature combustion, most of the nitrogen originates from the atmosphere, but some can also be derived from organic nitrogen compounds in fuels such as wood.

Smaller amounts of NO are released as a byproduct of microbial nitrification in soil, a process that is enhanced in the high-temperature tropical environment.

Lightning, which is also most frequent in the tropics, adds a further small input to the global nitric oxide budget.

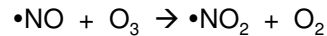




Atmospheric Production of Nitric Acid

Daytime Nitrogen Oxide Chemistry

Nitric oxide is oxidized by O_2 , O_3 , or $ROO\bullet$



Unfortunately, the principal mechanism for the removal of NO_x from the atmosphere is



Because this reaction involves starting materials formed in part through photochemical processes, it is largely a daytime reaction.



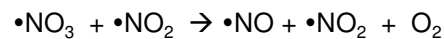
Atmospheric Production of Nitric Acid

Night-time Chemistry

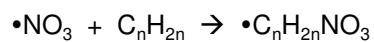
After sunset, an alternative sequence becomes more important for producing nitric acid. It involves nitrate radicals that are produced during both day and night by accumulates at night-time because it is destroyed by photolysis.



This radical can take part in a number of reactions:



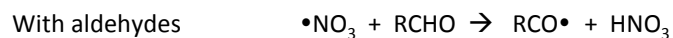
Nitrate radical is able to add to the double bond of olefins:



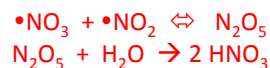
Susceptible to further reactions



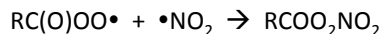
Nitrate radical (like hydroxyl radical) initiates reaction sequences by first abstracting hydrogen. Nitric acid is formed.



A kinetically rapid pair of reactions involving the nitrate radical and nitrogen dioxide results in the formation of dinitrogen pentoxide and then nitric acid

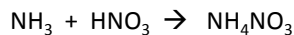


The majority of NO_x are removed according to the reactions in RED. A smaller fraction is converted to PAN



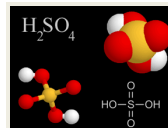
Nitric acid is removed from the atmosphere by either wet or dry deposition, and is one of the main contributors to precipitation acidity.

Nitric acid also reacts with ammonia, whose principal source is volatilization from nitrogen fertilizers, urea in animal urine, and other organic reduced nitrogen sources.



Ammonium nitrate (NH_4NO_3) can act as a condensation nucleus for the formation of a water droplet or it is deposited as part of the solid aerosol.

The production of sulphuric acid is a more complex process than that of nitric acid. The reaction sequence can begin with a wide range of reduced or partially oxidized sulphur compounds, mostly of natural origin.



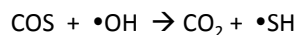
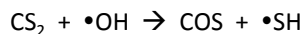
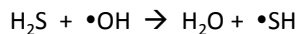
Hydrogen sulfide (H_2S), Carbonyl disulfide (CS_2), methyl mercaptan, dimethyl sulfide, and dimethyl disulfide all contain sulphur in the lowest (-2) oxidation state.

These compounds are released from oceans and soils under reducing conditions due to microbiological processes.

High temperatures favor microbial activity and so the release of reduced sulphur compounds is especially significant in the tropics.

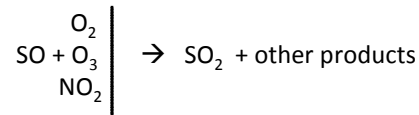
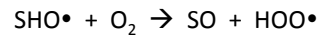
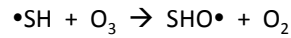
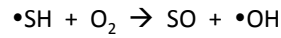
Once in the atmosphere, a sequence of reactions begins.

Hydrogen sulfide, carbon disulfide, and carbonyl sulfide are oxidized via hydroxyl radical giving the thionyl radical ($\bullet\text{SH}$) as initial product.

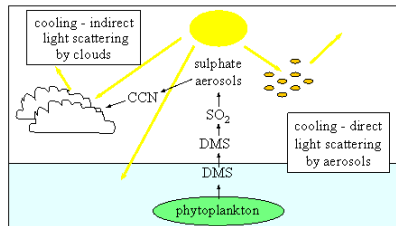
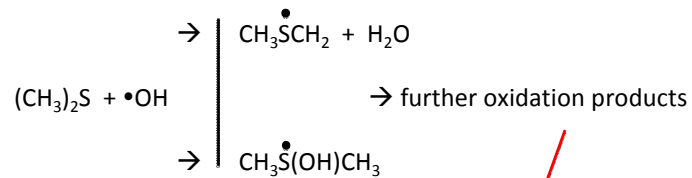


Of the three sulfide compounds, H_2S and CS_2 react quickly, however COS released from oceans or produced by oxidation of carbon disulfide is kinetically relatively stable.

Further oxidation of thionyl leads to production of sulphur dioxide



Phytoplankton living in surface waters of the oceans produce a large amount of dimethyl sulfide (one of the most important reduced sulphur compounds released in the atmosphere).

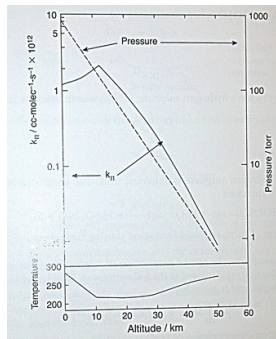
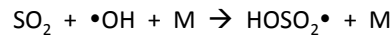


Dimethylsulfoxide and methane sulfonic acid
(both found in marine atmospheric aerosol)

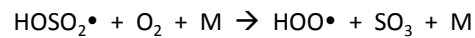
Sulphur dioxide (SO₂) is also released

Sulphuric acid production from sulphur dioxide takes place by at least two distinct sets of processes.

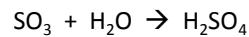
The first sequence occurs homogeneously in the gas phase and most frequently begins by a rate-determining step:



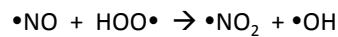
$HOSO_2\bullet$ can then undergo a number of relatively rapid reactions, some of which result in sulphuric acid production. The simplest and most important acid-producing process is:



Followed by dissolution in water to form sulphuric acid



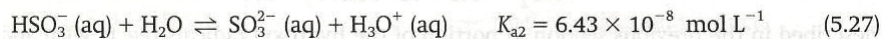
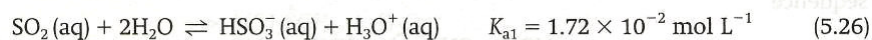
In addition



In Chapter 3, we encountered a sequence of heterogeneous reactions that leads to large-scale losses of stratospheric ozone during the polar spring.

Sulphuric acid can also be produced in a heterogeneous process when the required reactants are available in cloud droplets.

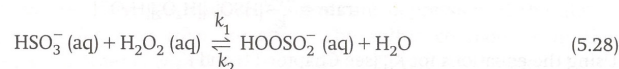
Beginning again with sulphur dioxide, the following reactions occur:



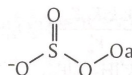
Like that of CO₂, the aqueous solubility of SO₂ is pH dependent, but it is much larger throughout the pH range.

The solubility is one of the factors affecting the rate of the heterogeneous reaction. Oxidation of sulphur species take place within the water droplets.

The most important oxidant is hydrogen peroxide, a chemical whose atmospheric mixing ratio is around 1 or 2 ppbv and which is readily soluble in water ($K_{\text{H}} = 7.0 \times 10^{-1} \text{ mol L}^{-1} \text{ Pa}^{-1}$).



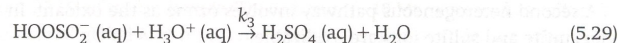
Peroxymonosulfite, HOOSO₂⁻, has a structure



and rapidly rearranges to form hydrogen sulfate, HSO₄⁻, whose structure is



In protonated form, hydrogen sulfate is sulfuric acid. The combined rearrangement and protonation reaction is therefore



Oxidation of SO_2 by Heterogeneous Reactions

In the steady-state condition, the rate of production of sulfuric acid by hydrogen peroxide oxidation of sulfur dioxide is calculated in the following way. Based on reaction 5.29, the rate of production of sulfuric acid is given by

$$\frac{d[H_2SO_4]}{dt} = k_3[HOOSO_2^-][H_3O^+] \quad (5.30)$$

Assuming a steady-state concentration of HSO_4^- ,

$$\frac{d[HOOSO_2^-]}{dt} = 0 = k_1[HSO_3^-][H_2O_2] - k_2' [HOOSO_2^-] - k_3[HOOSO_2^-][H_3O^+] \quad (5.31)$$

In eqn 5.31, $k_2' = k_2[H_2O]$ is a pseudo first-order rate constant since $[H_2O] \gg [HOOSO_2^-]$.

$$k_1[HSO_3^-][H_2O_2] = [HOOSO_2^-](k_2' + k_3[H_3O^+]) \quad (5.32)$$

$$[HOOSO_2^-] = \frac{k_1[HSO_3^-][H_2O_2]}{k_2' + k_3[H_3O^+]} \quad (5.33)$$

Substituting eqn 5.33 in 5.30,

$$\text{rate} = \frac{d[H_2SO_4]}{dt} = \frac{k_1 k_3 [HSO_3^-][H_2O_2][H_3O^+]}{k_2' + k_3[H_3O^+]} \quad (5.34)$$

The values of the rate constants are¹

$$k_1 = 5.2 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$$

$$k_2' / k_3 = 10^{-1}$$

 Oxidation of SO_2 by Heterogeneous Reactions

When the pH is greater than 2, $k_3[H_3O^+] \ll k_2'$ and the rate is given by

$$\text{rate} = \frac{k_1 k_3}{k_2'} [HSO_3^-][H_2O_2][H_3O^+] \quad (5.35)$$

Using the equations for K_{a1} (see Chapter 11) and K_{a1} ,

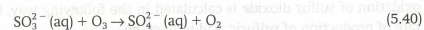
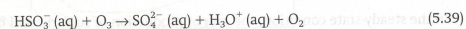
$$[H_3O^+][HSO_3^-] = K_{a1}K_{a1}P_{SO_2} \quad (5.36)$$

$$\text{rate} = \frac{k_1 k_3 K_{a1} K_{a1}}{k_2'} [H_2O_2] P_{SO_2} \quad (5.37)$$

$$= k' [H_2O_2] P_{SO_2} \quad (5.38)$$

This rate law applies between pH approximately 2 and 5 where hydrogen sulfite (HSO_3^-) is the principal aqueous sulfur (IV) species. Within this range, the oxidation of sulfur dioxide by hydrogen peroxide is the dominant mechanism and the reaction rate is approximately independent of pH. Below pH ~2 the rate decreases as reflected by an increase in the denominator of eqn 5.34. At higher pH values, sulfite (SO_3^{2-}) becomes the dominant sulfur species and, because it does not react with hydrogen peroxide, the rate of oxidation via this oxidant again decreases.

A second heterogeneous pathway involves ozone as the oxidant. In this case both hydrogen sulfite and sulfite ions are oxidizable.



The rates of the ozone-based reactions are such that, taken together with the previous processes, below pH 5.5, hydrogen peroxide is the primary oxidant while, above that value, ozone becomes more important. Depending on availability of oxidants, the heterogeneous reactions can make a greater contribution to sulfur dioxide oxidation than do the gas-phase processes.

Metals like iron (II) and (III), manganese (II), copper (II) and Cobalt (III) increase the oxidation rate of sulphur dioxide into sulphuric acid.

In acidified water, small concentrations of these metals are soluble and the soluble species are the catalytic agents.

Furthermore, even in higher pH situations where metals such as iron (III) are very insoluble, surface-based catalysis still occurs.

Metal ions may also enhance the rate of heterogeneous reaction of sulphur dioxide by hydrogen peroxide and ozone.

The acid is dissolved in cloud water droplets and rained out or washed out of the atmosphere.

Like its nitric acid counterpart, some sulphuric acid reacts with ammonia and forms two compounds that then become part of the atmospheric aerosol where they act as sites for the condensation of water vapor.

