Transition Metal-Catalyzed Oxidation of Sulfur(IV) Oxides. Atmospheric-Relevant Processes and Mechanisms

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Received March 29, 1994 (Revised Manuscript Received August 15, 1994)

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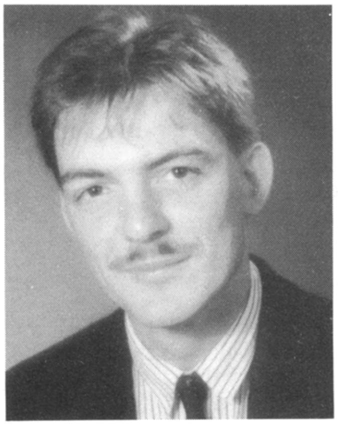
Introduction

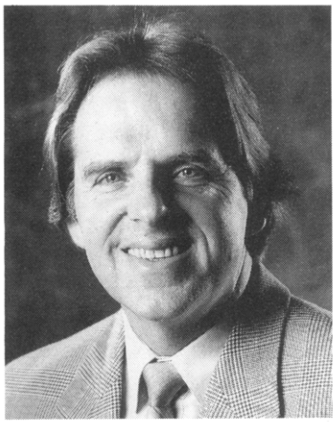
The transition metal-catalyzed oxidation of sulfur(IV) oxides has been known for more than 100 years (literature bibliographies: 1882–1951 see ref 1; 1897–1981 see ref 2). It has resulted in numerous and sometimes contradictory reports. There is a significant lack of information on the actual role of the transition metal-catalyzed reactions, and much of the earlier work was performed without a detailed knowledge of the chemical system. For this reason it is our goal to focus on the role of transition metal ions in the oxidation of sulfur(IV) oxides in terms of the coordination chemistry involved, as well as the stability and chemical behavior of the various participating species.

The oxidation process of sulfur(IV) oxides plays an important role in atmospheric chemistry (e.g. acid rain formation) as well as in industrial processes (e.g. desulfurization of plume gases and ore). The present report deals with the mechanism of the transition metal-catalyzed oxidation of sulfur(IV) oxides with the aim to discuss this in terms of atmospheric and chemical processes. In addition, we would like to emphasize the key role of oxygen in these processes.

Section 1 presents basic information on emission, distribution, and deposition of trace compounds and



Christian Brandt was born in 1962 in Dortmund, Germany. He studied chemistry at the University of Dortmund, where he received his Chemistry Diploma in 1990. In 1991 he started his graduate studies at the private University of Witten/Herdecke, working under Professor Rudi van Eldik. His research project concerned mechanistic studies on the metal-catalyzed autoxidation reactions of sulfur(IV) oxides in aqueous solution. He received his Ph.D. in 1994. He is the co-author of four papers in scientific journals. At present he is working at the Institute for Tropospheric Research, Leipzig (Germany). Areas of interest to him are biotechnology and analytical and environmental chemistry.



Rudi van Eldik was born in 1945 in Amsterdam, The Netherlands, and grew up in South Africa, where he received his B.Sc., M.Sc., and Ph.D. (1971) degrees from Potchefstroom University. He spent two years (1972 and 1978) with Gordon M. Harris at SUNY at Buffalo and one year as Alexander von Humboldt Fellow with Hartwig Kelm at the University of Frankfurt. He was appointed as Professor of Chemistry at Potchefstroom University (1979) and was awarded the Raikes Medal by the SA Chemical Institute in the same year. He moved to the University of Frankfurt in 1980, where he completed his Habilitation in Physical Chemistry (1982). He was appointed as Professor for Inorganic Chemistry at the University of Witten/Herdecke in 1987. In 1994 he accepted a Chair for Inorganic and Analytical Chemistry at the University of Erlangen-Nürnberg. His research interests are in mechanistic studies of inorganic, organometallic, and bioinorganic reactions, with special emphasis on the application of high-pressure techniques.

0009-2665/95/0795-0119$15.50/0

Table 1.1. Anthropogenic Sulfur and Nitrogen Emissions

country	industry (10^9 g a^{-1})	domestic (10^9 g a^{-1})	traffic (10^9 g a^{-1})	ref	country	industry (10^9 g a^{-1})	domestic (10^9 g a^{-1})	traffic (10^9 g a^{-1})	ref
				SO_2					
global			3000^{a}	7	England 1980	1321		106^{d}	24
Germany[b]	3.25	0.26	0.03	26	W-Europe 1980	7014.1		1219.2^{d}	24
Germany[c]	493.8	18.26	5.2	27	Asia 1987	5330^{e}	140^{e}	110^{e}	29
Germany 1960	1095.4	348.4	107.9	28	USSR 1989	16800			32
Germany 1970	1369.6	367.3	62.1	28	USA 1970	3200^{a}		500^{a}	33
Germany 1980	866.3		200.7^{c}	24	USA 1976	6500		646	34
Germany 1986		140	110	29	USA 1982	9195^{a}		902^{a}	13
Germany 1986	520.9^{a}	135.9^{a}	90.6^{a}	30	USA 1984	2040		900	35
Germany 1989	785	80	75	31	South Africa[f]	1006	32.3		36
Switzerland 1984			4.8	25	Saudi Arabia	121.1	15.8	7.1	37
France 1980	1947		261.8^{d}	24					
				NO_x					
global	1200^{g}		8000^{g}	3	England 1985	212^{h}	54^{h}	$777^{d,h}$	39
global			28000	7	Greece 1985	46		130.7	40
Germany[b]	0.29	0.17	0.49	26	W-Europe 1980	1661.3^{h}		$11712.9^{d,h}$	24
Germany[c]	329	10.6	92.7	27	Asia 1987	1430^{g}		1190^{g}	41
Germany 1980	406.3		$3385.5^{d,h}$	24	USSR	4500		2000	32
Germany 1986		90	1800^{i}	29	USA 1970	5800		1000	33
Germany 1989	760	70	1850	31	USA 1976	8990		9650	34
Switzerland 1984			149.5	25	USA 1982	5400		9336	13
Switzerland 1990	29.2^{j}	1.46^{j}	148.2^{j}	38	South Africa[f]	327.8	2.5	248	36
France 1980	396.3^{h}		$2335.3^{d,h}$	24	Saudi Arabia	121.9	3.1	94.9	37
England 1980	258^{h}		$1406^{d,h}$	24					

[a] SO_x. [b] Niedersachsen. [c] Nordrhein-Westfalen, 1987. [d] Value includes road traffic and all sorts of mobile sources. [e] Expressed as S. [f] Eastern Transvaal. [g] Expressed as N. [h] Expressed as NO_2. [i] NO_2. [j] Values are based on daily emission rates for a summer day.

their possible reaction products. From this section it follows that, for the present emission quantities in the Northern Hemisphere, SO_2 is the major precursor for acid rain formation.

The uncatalyzed and transition metal-catalyzed oxidation of sulfur(IV) oxides is controlled by the chemistry of these species. The main parameter is pH, since sulfur(IV) oxides and transition metal ions exhibit characteristic pH-dependent speciations in aqueous solution. Each species shows a different reactivity and the chemistry of these species is the basis for understanding the complex reaction mechanisms. Fundamental information concerning the behavior of sulfur(IV) oxides, transition metals, and oxygen in aqueous solution, is therefore given in section 2.

Fundamental considerations with respect to atmospheric relevant redox reactions and the individual atmospheric oxidation processes of sulfur(IV) oxides, are presented in section 3. Beside the uncatalyzed pathways, the main focus will be on the transition metal-catalyzed autoxidation of sulfur(IV) oxides. Possible reaction pathways for homogeneous catalysis are discussed, whereas heterogeneous catalysis is only briefly summarized. In addition, results on the role of oxygen and other reaction parameters on the overall processes are briefly reviewed.

In the case of the transition metal-catalyzed autoxidation of sulfur(IV) oxides there has been a contradictory discussion in the literature concerning which transition metal ion is the most important catalyst in the atmosphere (see section 4). On the basis of the information given in sections 1−3, we will discuss the possible role of the transition metal-catalyzed pathway in the overall atmospheric oxidation processes of sulfur(IV) oxides.

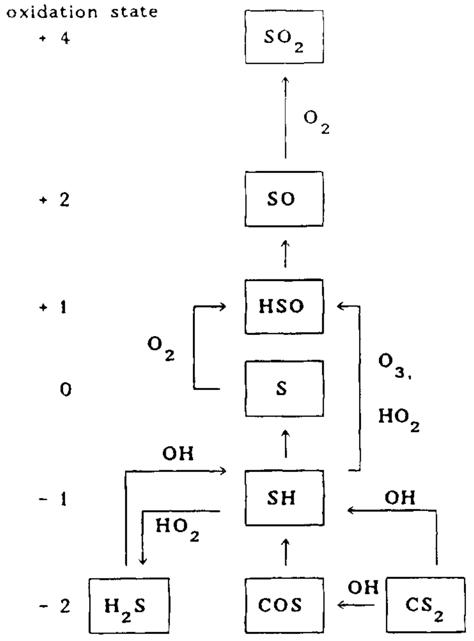


Figure 1.1. Transformation of sulfur species in the troposphere.[19]

1. Emissions and Atmospheric Processes

1.1. Emissions

SO_2 and NO_x [a] emissions are mainly responsible for the acid deposition in North America and Europe. These trace substances are emitted by both natural and anthropogenic sources. The global SO_2 and NO_x

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[a] It is convenient to refer to the family of oxidized nitrogen species as $NO_y = NO_x + HNO_2 + HNO_3 + N_2O_5$ + PAN + particulate nitrates, where $NO_x = NO + NO_2$.[3] The contributions of the individual daytime nitrogen species to the total NO_y in the troposphere are HNO_3 43%, NO_x 14%, particulate nitrates 5%, PAN < 5%.[4]

Table 1.2. Anthropogenic and Natural Sulfur and Nitrogen Emissions (see also ref 8)

anthropogenic (10^{12} g a^{-1})	natural (10^{12} g a^{-1})	remarks	ref
		Sulfur	
78.2	25.3	global	11
70[a]		global	43
70−80	17−64	global	44
79.2		global 1979	6
80[a]	50[b]	global	45
	50−100	global	5
104	147	global 1976	9
125.6[c]		global 1980	46
146[c]		global	47
0.8−2.5		global from biomass burning	44
2.5[a]		global from biomass burning	43
2.6		global from biomass burning	48
2.2		global from biomass burning	11
	4[c]	global from exploding volcanoes	49
	7−10	global from volcanoes	44
	8.5[a]	global from volcanoes	43
	9.3	global from volcanoes	11
	13[c]	global from volcanoes	49
	40−300	global from sea spray	50
69−90	16.6−112	Northern hemisphere	51
98	76	Northern hemisphere	52
70.5		Northern hemisphere	11
5−6	19.4−80	Southern hemisphere	51
7.7		Southern hemisphere	11
6	71	Southern hemisphere	52
4.0[c]		South America 1980	46
21.1[c]		USA 1988	53
3.8[c]		Canada 1987	53
34.8		Europe 1979	6
30.4[c]		Europe 1980	46
21.7[a]	0.5[a,d]	Europe 1985	54
40.64[c]		Europe 1988	55
17.9		Western Europe 1980	24
2.9	0.3−0.9	yearly average value in Southeastern Europe 1985	50
2.3[a]		Africa	6
4.15[c]		Africa 1980	46
1.3[c]		South Africa (Eastern Transvaal) 1984	36
18.2[a]		Asia	6
56.5[c]		Asia[e] 1980	46
29.1[c]		Asia 1987	56
16.49[c]		USSR 1980	57
3.83[c]		Poland 1988	55
4.7[c]		England 1980	24
1.8[a]		England 1985	54
3.5[c]		France 1980	24
0.7[a]		France 1985	54
1.55		Germany 1960	28
1.80		Germany 1970	28
3.2[c]		Germany 1980	24
1.2		Germany 1985	54
2.2[c]		Germany 1986	29
1.0[c]		Germany 1989	31
2.7		DDR[f] 1985	54
0.116[c]		Austria 1988	55
0.13[c]		Switzerland 1980	24
0.095[c]	2.0×10^{-5}	Switzerland 1984	58
2.22[c]		Italy 1988	55
0.47[c]		Greece 1985	40
1.54		India 1987	41
19.99[c]		China 1987	56
1.14[c]		Japan 1987	56
		NO_x	
16−48[h]	9−70	global	3
24.6[h]	7−40	global	44
52.9[i]		global	22
53	658[i]	global	47
	430[j]	global	47
30[k]	150[k]	global	45
72.9[i]		global 1980	46
90	1200	global	52
100	22	global	7
2.5−13[h]		global from biomass burning	44
3[g]		global from biomass burning	59
1[l]		global from biomass burning	60
4−24		global from biomass burning	3
18		global from biomass burning	7
56		global from biomass burning	59
	592[g]	global from biological activity	22
	501[j]	global from biological activity	22
13.2−57.4	5.0−23	Northern Hemisphere	51
6.5−19	1.5−9.4	Southern Hemisphere	51
3.53−7.94	0.26−0.45	Europe	61
11.5[i]		Europe 1980	24
15.5[i]		Europe 1980	46
21		Europe 1985	54
20.54		Europe 1988	55
0.8		yearly average value in Southeastern Europe 1985	
15.5		Asia 1987	56
27.7[i]		Asia[e] 1980	46
6.7[i]		USSR 1990	57
7.1		USSR 1985	62
1.86[i]		Africa 1980	46
0.5[i]		South Africa (Eastern Transvaal) 1984	36
2.34[i]		South America 1980	46
19.8[i]		USA 1988	53
1.9[h]		Canada 1990	53
1.36		Poland 1988	55
1.9[i]		England 1980	24
1.8[i]		England 1985	39
2.3[i]		England 1985	54
2.8[i]		France 1980	24
1.6[i]		France 1985	54
3.1[i]		Germany 1980	24
2.95		Germany 1985	54
2.96[i]		Germany 1986	29
2.7		Germany 1989	31
0.95[i]		DDR[f] 1985	54
0.8		DDR[f] 1985	62
0.22		Austria 1988	55
0.20[i]		Switzerland 1980	24
0.21[i]	9.0×10^{-3}[i]	Switzerland 1984	58
1.98		Italy 1988	55
0.24		Greece 1985	40
0.78[h]		India 1987	41
7.37		China 1987	56
1.94		Japan 1987	56

[a] SO_2, calculated as S. [b] SO_4^{2-}, calculated as S. [c] SO_2. [d] From oceans. [e] Includes all of the USSR. [f] Former German Democratic Republic. [g] N_2O. [h] NO_x, expressed as N. [i] NO_x, expressed as NO_2. [j] NO. [k] NO_2, calculated as N. [l] N_2O, calculated as N.

emissions are estimated to be in the range of (130−180) × 10^{12} g of S a^{-1} and (50−120) × 10^{12} g of N a^{-1}, respectively.[3,5-7] In general, there is a strong decrease in emission observed from north to south. The anthropogenic emission of pollutants in the Northern Hemisphere is much higher than in the Southern Hemisphere (see e.g. ref 8). Whereas ca. 90% of the emitted sulfur compounds come from anthropogenic sources in the Northern Hemisphere, this figure is down to 7% for the Southern Hemisphere.[9-11] In the case of NO_x species, 40% is emitted by natural sources.[12] A detailed literature evaluation of the contribution of natural and anthropogenic sources on the global SO_2 and NO_x emissions is given by Bubenick.[13] The north to south decrease has also been observed for trace gases like CO_2, CO, and

CH_4.[14] The concentration of carbon containing particles (continental origin) in the Northern Hemisphere, viz. 0.45 μg of C m^{-3}, is much higher than in the Southern Hemisphere, viz. 0.06 μg of C m^{-3}.[15]

The most important sulfur species in the atmosphere are COS, CS_2, $(CH_3)_2S$, H_2S, SO_2, and SO_4^{2-}.[16-18] The transformation of these compounds in the troposphere exhibits a clear tendency toward the higher oxidation state (Figure 1.1). An overview of atmospheric relevant oxidation processes for sulfidic sulfur species to SO_2 is given by Tyndall and Ravishankara.[20] For the atmospheric cycle of $(CH_3)_2S$, see for example ref 21. The most important nitrogen compounds in the environment are N_2O, NO, NO_2, and NH_4^+ and NO_3^- aerosols.[22,23]

Anthropogenic sources of SO_2 are normally combustion processes. For Western Europe the major source is the generation of electricity ($\approx$45%), followed by the industrial sector ($\approx$40%, there of ca. 75% from fuel combustion).[24] Traffic is the main anthropogenic source of NO and NO_2 ($\approx$44%) followed by processes for energy production ($\approx$22%) and industrial combustion ($\approx$10%).[24] In the case of traffic, it should be mentioned that passenger cars emit around 72% of the total emitted NO_x, whereas the emission from trucks contributes 65–70% to the total SO_2 emissions.[25] Further information is given in Table 1.1.

SO_2 plays a minor role in the case of natural sulfur emissions (see ref 42). The most important natural SO_2 sources are volcanoes with $(2-5) \times 10^{12}$ g of S a^{-1}.[5,9] Other important sulfur sources are sea spray (SO_4^{2-}, $175(\pm 50\%) \times 10^{12}$ g of S a^{-1}), and biogenic sulfur sources, e.g. from bacterial activity (H_2S, $(100-280) \times 10^{12}$ g of S a^{-1}, $(CH_3)_2S$, $(3-32) \times 10^{12}$ g of S a^{-1}; COS, $(0.1-2.5) \times 10^{12}$ g of S a^{-1}; CS_2, $(0.2-5) \times 10^{12}$ g of S a^{-1}).[5] A summary of anthropogenic and natural emitted sulfur and nitrogen compounds is given in Table 1.2. Biomass burning, e.g. forest or grassland fires, has to be considered as a major source of atmospheric sulfur in remote continental regions, especially the tropics.[48] In the case of NO_x emissions biomass burning contributes up to 40% to the total global emission.[59]

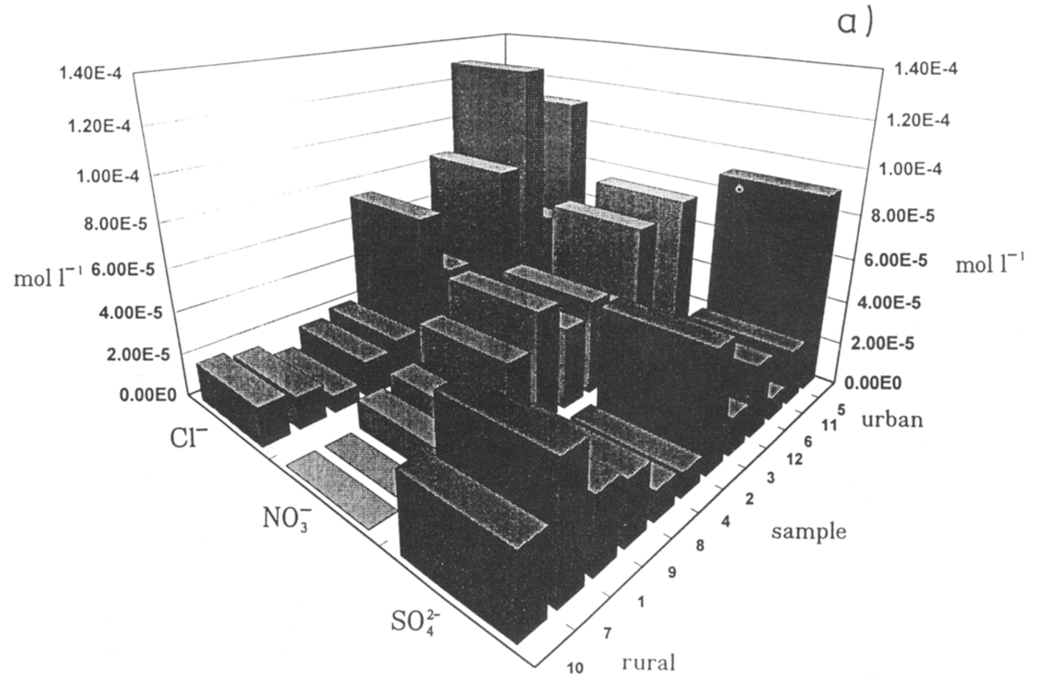
When comparing anthropogenic and natural sources it should be mentioned that natural sources are globally distributed, whereas anthropogenic sources are concentrated in populated areas. Thus, the concentration of the individual pollutants depends on the area over which they are measured (Figure 1.2). (See Table 1.3 for atmospheric SO_2 and NO_x concentrations.) The anthropogenic sulfur emission in the northwest of the USA is for example with a 90% contribution to the overall emitted amount of sulfur much higher than average.[79] An important anthropogenic source of SO_2 has recently been the burning oil fields in Kuwait following the Gulf War. The daily SO_2 emission was estimated to be 4×10^{10} g.[80]

Table 1.3. Atmospheric SO_2 and NO_y Concentrations

area	concentration (μg m^{-3})	ref
	SO_2	
NW of USA	0.83–1.64	64
Mid-W of USA	10.15	65
Amsterdam Island	0.11[a]	66
Amsterdam Island	0.013–0.019[b]	66
Antarctica	0.13[c]	67
Mediteranian Sea	2.27[c]	67
Europe	2.7[a,c]	68
Europe	7.0[b,c]	68
Northern Michigan	7.55[b]	69
Dübendorf (CH)	6–60	70
London	44–49[a]	39
London	71–77[b]	39
Rome	60–75[c]	71
New York	64	35
	NO_y	
Atlantic ocean	0.1–5.6[d]	72
Antarctica	0.03[e,f]	73
Northern Michigan	0.69[b,g]	69
Northern hemisphere	1–2.5[h]	12
Northern Michigan	1.19[b,e]	69
Northern Michigan	3.76[b,i]	69
SW of USA	63[i]	74
New York	78[i]	35
Germany	1.1[g]	75
Germany	3.0[h]	61
Germany	7.68[b,d,j]	75
Frankfurt	155.4[i,m]	76
Berlin	296.1[i,m]	76
London	81.9–94.5[a,i]	39
London	84.0–90.3[b,i]	39
London	17.6–25.7[a,k]	39
London	44.9–47.3[b,k]	39
London	264	77
London	90.3[i,l]	78
London	888.3[i,m]	76
Glasgow	54.6[i,l]	78
Manchaster	56.7[i,l]	78
Amsterdam	109.2[i,m]	76
Paris	296.1[i,m]	76

[a] Summer. [b] Winter. [c] SO_2, calculated as S. [d] NO_3^- aerosols. [e] NO_3^-. [f] Mean concentration 1987–1991. [g] HNO_3. [h] NO_2, calculated as N. [i] NO_2. [j] Average value 1982–1983. [k] NO. [l] Mean concentration 1991. [m] Maximum concentration, Dec 1991.

The time-dependent development of the emission of pollutants (Table 1.4) can be clearly followed in snow samples, e.g. from Greenland and other polar regions, because these ice sheets allow us to trace the evolution of the acid precipitation in a remote location that is free from local effects.[51,92] In addition, sediments have also been used in order to follow the time-dependent development of the emission of pollutants (see e.g. refs 93–95). Snow deposited in Greenland since 1955 contains more than 10 times as much lead than snow that fell prior to 1840.[96] In sediments of Tokyo Bay, Japan, Hirao et al.[94] found an increase in lead concentration since 1900 due to anthropogenic activities. Since 1970 there is a clear decrease observable in the lead concentration. The SO_4^{2-} and NO_3^- concentrations in Greenland snow of 1788–1800 (42 μg of SO_4^{2-} g^{-1} and 65 μg of NO_3^- g^{-1}, respectively) compared to present Greenland snow samples (1976–1977: 120 μg of SO_4^{2-} g^{-1} and 120 μg of NO_3^- g^{-1}, respectively) has strongly increased[97] (see also refs 51 and 92). When averaged globally over the 1860 and 1980 period, sulfur emissions increased at the rate of 2.9% a^{-1} and the nitrogen emissions at the rate of 3.4% a^{-1}.[46] After the second World War, the most rapid increases in emissions have been registered in Asia, Africa, and South America.[46] As a result of special programs to reduce the amount of emissions during the last years (see e.g. refs 98–102), it is reasonable to expect a change in the composition of acid deposition (see section 1.5). It is clear from Table 1.4 that in many



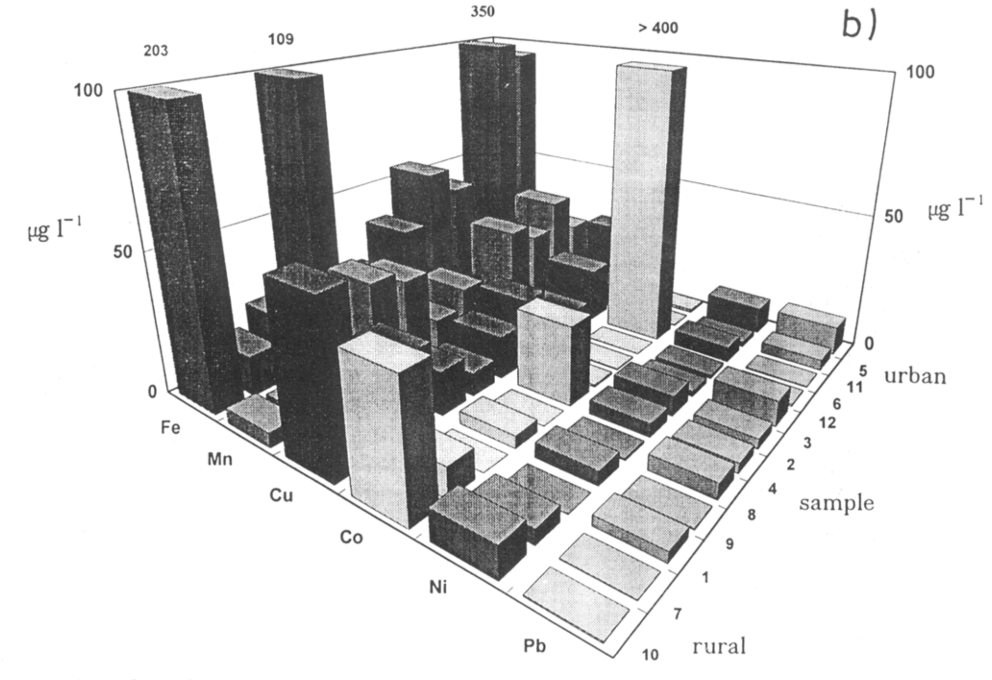


Figure 1.2. Concentration of (a) chloride, nitrate, and sulfate and (b) of transition metals in European rain (r) and snow (s) water and bulk deposition (bd) samples for various sample locations; all samples collected between Sept 1993 and Feb 1994.[63] Locations were as follows: 1(r), 8(s), 9(s) Dortmund (semirural site, Germany); 2(r), 3(r), 5(bd), 12(s) Witten (urban area, Germany); 4(s) Goslar/Harz (semirural site, Germany); 6(r) Krakow (urban area, Poland); 7(s) Hajnowka (rural area, Poland); 10(s) Spåtind (rural area, Norway); 11(r) Katowice (urban area, Poland).

countries there is a general trend to reduce air pollution (see also refs 9, 103, 104), except for nitrogen oxides. The emission of nitrogen oxides increases in the Northern Hemisphere by approximately 1% a^{-1} (1986).[14]

Besides gaseous compounds, particles are also emitted from anthropogenic and natural sources (see Table 1.5 and section 1.2). The fraction of aerosols emitted from anthropogenic sources is about 10% of the overall anthropogenic air pollution[45] (see also ref 116). Some of these atmospheric particles have an influence on atmospheric redox processes (see section 3.4). Aerosols emitted from anthropogenic sources are mainly metal oxide containing fly ashes. Sea salt particles are the main source for natural emitted aerosols.[105] The anthropogenic part of the overall aerosol emission is in the range of 5−30%.[117]

In view of atmospheric transition metal-catalyzed oxidation processes, the amount of emitted metals is an important parameter. For most of the heavy metals the dust bound emissions dominate. The anthropogenic emission of metals exhibited a drastic

Table 1.4. Time-Dependent Development of Emissions of Pollutants

country	time	industry	domestic	traffic	SO_2	NO_x	dust	ref
global	1880–1976				+94.0%			9
global	1929/30–1980				+153.2%	+350.0%		46
global	1965–1976					+41.2%		52
Europe	1929/30–1980				+42.1%	+152.4%		46
Germany	1960–1970	+25.0%	+5.4%	−42.0%	+15.9%			28
Germany[a]	1963/64–1991						−71.8%	81
Germany	1966–1982	−34.8%	−67.0%	+39.5%	−6.0%	+55.0%	−61.0%	82
Germany	1970–1989	−55.6%	−45.4%	−18.1%	−73.3%	+11.1%[b]	−64.6%	31
Germany[c]	1975[d]–1987		−76.0%	−12.5%	−39.2%	−7.8%	−73.1%	27
Germany	1975–1990				−71.9%	+8.6%[e]	−31.5%	83
Germany[f]	1975–1990				+15.8%[g]	+8.6%	−31.5%	83
GB[h]	1962–1975/76	−63.3%[i]	−86.4%[i]	−16.7%	−66.2%			84
GB	1970–1983				−38.2%	±0%[k]		84
GB[h]	1975/76–1988	−75.8%[i]	−59.0%[i]	−40.4%[i]	−73.8%			84
GB[h]	1975/76–1988	−59.3%[k]	+52.0%[k]	−41.7%[k]		+7.4%		84
France	1980–1990				−63.8%	−5.0%	−34.9%	85
Africa	1929/30–1980				+746.9%	+1062.5%		46
KSA[l]	1980–1990	+62.5%[i]	+57.0%[i,m]		+66.7%			37
KSA[l]	1980–1990	+65.0%[i]		+63.6%[k]		+22.2%		37
Asia[n]	1929/30–1980				+1030%	+1850.7%		46
Asia	1975–1987				+59.0%[o]	+64.9%		56
China	1975–1987				+96.4%	+97.8%[o]		56
Japan	1975–1987			−37.1%[k]	−149.7%[o]	−16.7%		56
India	1975–1987				+86.0%	+85.5%		56
India[p]	1971/73–1990				−76.9%	−40.8%[q]		86
USSR	1980–1990				−18.0%	+23.0%[q]		57
USSR	1981–1989	−13.8%[i]						32
USSR	1981–1989	+21.6%[k]		+20.0%[k]			−12.7%[r]	32
USSR	1925–1983				+12400%	+4700%		46
South-America	1929/30–1980				+852.4%	+1276.5%		46
USA	1900–1980	+629.4%[i]			+486.2%	+2022.5%		87
USA	1900–1980	+1328.6%[k]						87
USA	1940–1976				+26.8%	+74.8%	−45.8%	88
USA	1950–1980				+28.0%	+116.0%		87
USA	1975–1984	−34.0%[i]		−14.8%[i]	−16.4%		−32.7%	35
USA	1975–1984	−14.3%[g]		+7.5%[g]		+2.6%		35
USA[s]	1975–1987				−19.0%	−16.0%		89
USA	1977–1982				−7.6%	+10.6%		13
USA	1980–1990				−10.0%	−3.0%[q]		53
USA	1980–1985				−9.8%			90
Canada[t]	1970–1984				−55.0%			91
Canada[u]	1970–1985				−19.6%			90
Canada	1980–1985				−45.0%	+57.0%[v]		91
Canada	1980–1990				−18.0%	−1.0%[q]		53

[a] Ruhr District. [b] During 1970–1986, +20%; 1986–1989, −10%. [c] Nordrhein-Westfalen. [d] Beginning of the statistical inquiries during 1975–1979. [e] During 1985–1990, −12.0%. [f] Area of the former German Democratic Republic (DDR). [g] During 1985–1990, −11.9%. [h] London. [i] SO_2. [j] During 1970–1983 nearly constant. [k] NO_x. [l] Kingdom of Saudi Arabia. [m] During 1986–1990; −12.5%. [n] Includes all of the USSR. [o] Values from Corrigendum, *Atmos. Environ.* **1993**, *27A* (7), 1163–1164. [p] At Chembar (Bombay region); calculated from concentration values. [q] NO_2. [r] Particulate matter from industrial emissions; 1981–1985, +5.7%; 1985–1989, −17.5%. [s] Eastern parts of the USA. [t] Eastern Canada. [u] Dorset, central Ontario. [v] During 1980–1984 nearly constant.

Table 1.5. Anthropogenic and Natural Aerosol Emissions

natural (10^{12} g a^{-1})	anthropogenic (10^{12} g a^{-1})	remarks	ref	natural (10^{12} g a^{-1})	anthropogenic (10^{12} g a^{-1})	remarks	ref
1100	200	global	45		1	Germany 1970, $d < 10$ μm	110
1330	101	global	105		2	Germany 1970, $d < 30$ μm	110
683–1960	181–379	global	106		0.58	France 1975	110
2312	296	global	107		0.04	Austria 1988	55
1200		global	108		0.49	Italy 1988	55
2115	410	global 1968	109		1.1	USA 1968, $d = 0–1$ μm	112
1250	280	global 1968, $d < 5$ μm	109		3.6	USA 1968, $d = 0–3$ μm	112
421–1850	237–755	global, $d < 20$ μm	110		13.1	USA 1970	33
2000	300	global, $d < 20$ μm	111	122	15.4	USA 1973	113
1300		global from sea spray	108		1.25–3.85	USA	114
8000		global from weathering of soils and rocks	108		13.7	USSR 1989, from industry	32
					2.75[a]	Nigeria	115
	2.15	Poland 1988	55				

[a] 31.7% from bush burning, 29.1% from fugitive dust from roads.

increase since the beginning of this century.[95,118] For example, the globally emitted amount of copper, lead, and nickel increased from 1901–1910 to 1971–1980 by 1103%, 905% and 5060%, respectively (according to data from ref 118). In the case of lead emissions, traffic is the major source.[119,120] In Germany the

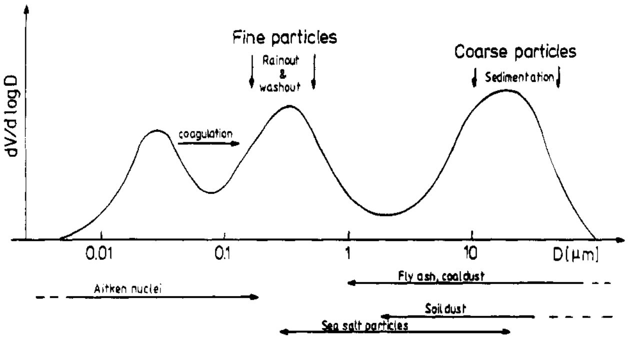


Figure 1.3. Characteristic distribution of fine and coarse particles in the atmosphere (according to refs 189 and 190).

contribution of traffic to the overall lead emission in 1986 (4089 × 10^9 g) was 78%.[29] As in the case of other pollutants in general the emission quantities of heavy metals have been reduced in the last years (see e.g. refs 95, 103, 120, 121). For instance, in Chilton, a semirural site in Southern England, the concentrations of cobalt, iron and manganese in atmospheric aerosols decreased from 1957 to 1974 by 10.7%, 8.2% and 7.2%, respectively, while lead concentration exhibited no significant trend.[103] In Canada, since 1976 methylcyclopentadienylmanganese tricarbonyl (MMT) has been used instead of lead as an antiknocking compound in gasoline. While the overall emitted amount of lead decreased by 28% during the period 1981–1990 in Canada, the overall emitted amount of manganese increased by 10% during the same period.[121] An overview on the emitted amounts of metals into the atmosphere is given in Table 1.6. Although not much data are available for iron, it is evident that iron is the metal with the highest emission quantity. According to data of Gatz[150] the range of compositions of emissions for pollution sources in Chicago can be given as Fe $\gg$ Ni > Mn > Cu > Co. In view of the transition metal-catalyzed oxidation in aqueous solution, iron and manganese are the most important catalysts (see section 3 and e.g. refs 151–153). The atmospheric concentrations of iron and manganese are given in Table 1.7 (see also Figure 1.2).

For an analysis of sources of air pollutants see e.g. refs 110, 123, 147, 150, 185, and 186.

1.2. Aerosols

For a detailed treatment of atmospheric aerosol chemistry see ref 187. For problems of the global aerosol distribution see ref 188.

Aerosols can be separated in small (0.1–1 μm) and coarse (1–100 μm) particles and exhibit a characteristic distribution (Figure 1.3). The fine particles mainly originate from chemical processes and are usually acidic. The coarse particles are mainly nonacidic and caused by wind soil erosion and sea spray.[108,190] This acid–alkaline properties of aerosols depending on their size have been observed very often.[191–193] While fine particles contain a higher fraction of acidic anions like SO_4^{2-}, NO_3^-, or Cl^-, coarse particles contain a higher amount of metals.[74] The coarse aerosols are mainly concentrated in the lowest atmospheric layer (0–250 m).[108] 20% of the total aerosol particles are in the layer of 0–250 m, whereas 50% are in the layer of 0–1000 m.[108] Particle concentrations for different atmospheric conditions are given in Table 1.8, which clearly indicates an increase in trace substances under smog conditions. During winter smog, SO_2, NO_x, and their oxidation products are the main species, whereas during summer smog, O_3 is the main compound.[197]

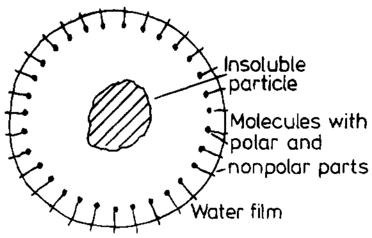


Figure 1.4. Schematic diagram of the possible structure of aged atmospheric aerosols (according to refs 187 and 229).

The deposition velocity (see section 1.4) of aerosols depends on their size[187,198,199] and therefore influences the lifetime of the aerosols in the atmosphere (see section 1.3), which can be a limiting factor in chemical transformation processes (see refs 171, 175, and 200). Table 1.9a summarizes the lifetime of aerosols as a function of their size. Sulfate aerosols collected during the summer have the size of Aitken nuclei (radius < 0.1 μm) and are smaller than sulfate aerosols collected during the winter.[203] The size of the aerosols depends on the relative humidity[204–207] as well as on the acid content (see further Discussion).[207] Chloride and nitrate aerosols are in general bigger than other aerosols.[203] The lifetime of metals in the atmosphere is summarized in Table 1.9b.

The atmospheric lifetime of water-soluble aerosols and gases depends not only on the amount of precipitation but also on the characteristics of the precipitation regime, such as duration and frequency of the precipitation events.[208] Aerosols can contain water-soluble (e.g. salts) and insoluble particles (e.g. metal oxides). Aerosols of continental origin contain about 40% water soluble substances. Over 80% of the latter substances dissolve within the first 20 s after contact with water.[201] The chemical composition of aerosols in the troposphere (Table 1.10; see also e.g. refs 223 and 224) depends on the production mechanism and the chemical environment. Chloride and sulfate are the most important water-soluble compounds of atmospheric aerosols (refs 180 and 216; see also Table 1.10b). For a general review on the chemical composition of aerosols see refs 17, 225, and 226, and for the chemical characterization see refs 225 and 227.

Insoluble particles function as condensation nuclei since they reduce the required supersaturation for the condensation of water droplets.[228] Depending on the humidity, many insoluble particles are surrounded by a water film (Figure 1.4), which may contain many different substances. The water content of tropospheric aerosols has been estimated to be in the range of 30–50% of their weight,[187] whereas no water has been detected on the surface of desert aerosols.[230] For a review on the water content of atmospheric aerosols see ref 206.

Table 1.6. Emissions of Metals into the Atmosphere

	emitted amount (10^{-9}/g a^{-1})						
area, source	Co	Cu	Fe	Mn	Ni	Pb	ref
Natural							
global, sea salt spray	0.07	3.6		0.86	1.3	1.4	122
global, sea salt spray		100				100	123
global, continental dust	4.0	10.0	19000	425	20.0	5.0	124
global, windblown dust	4.0	12.0		425	20.0	16	125
global, volcanoes, dust	3.0	9.3	8.77	0.18	8.3	0.87	124
global, volcanoes	1.4	3.6		82.5	3.8	6.4	125
global, volcanoes, gas	4.0×10^{-3}	1.2×10^{-3}	0.37	0.21	9.0×10^{-5}	1.2×10^{-3}	124
global, volcanoes	0.96	9.4		42.0	14.0	3.3	122
global, weathering (river flow + sediments)	15.2	330	124000	2250	171	131	126
global, biomass burning	1.3	35.0	350	1580	7.5	6.8	124
global, forest wildfires		0.3			0.6	0.5	125
global, vegetation		2.5			1.6	1.6	125
global	7.0	19.0		610	28.0	5.9	127
global	6.1	28.0			30.0	12.0	122
Mount Etna (volcano), Italy	4.9×10^{-3}	0.57	2.4	4.2×10^{-2}			128
Anthropogenic							
global[a]	4.4	263	10700	316	98.0	2030	124
global[b]	2.4	0.22	7500	300	60.0	1600	124
global[c]	0.7	2.1	1400	7	2.1	3.5	126
global[d]	0.03	0.02	0.41	0.02	1.6	0.05	126
global	4.4	260		320	98.0	2000	127
global 1975		56.0			47.0	449	118
global 1983		35.4		38.3	55.7	332.4	129
Antarctica, waste burning[e]		$(1.4-13) \times 10^{-5}$				$(0.5-9) \times 10^{-5}$	130
Antarctica, fuel burning (excluding ships)[e]		2.4×10^{-5}				1.8×10^{-3}	130
Europe 1979	2.0	15.5		17.7	16.0	123	131
European Community, coal-fired power plants		5.6			9.7	10.6	132,133
Europe, hard coal-fired power plants, 1979	0.17	0.39		0.43	0.62	0.31	134
Europe, lignite-fired power plants, 1979	0.19	0.426		0.45	0.676	0.38	134
Europe, oil-fired power plants, 1979	0.416	0.56		0.13	3.29	0.405	134
Denmark, thermal power plants, 1979	1.04×10^{-2}	1.59×10^{-2}		7.64×10^{-3}	7.48×10^{-2}	1.22×10^{-2}	135
Germany 1979	0.14	1.6		2.1	1.0	9.3	131
Germany 1990		2.0[f]			2.8[f]	4.2[f]	133
Germany, coal-fired power plants, 1980					0.08	0.65	136
Germany, coal burning		4.9×10^{-2}				0.17	137
West-Germany, iron and steel industry, 1985	7.5×10^{-2}	6.5×10^{-2}		0.3	2.7×10^{-2}	0.33	138
West-Germany, cement industry, 1985					3.0×10^{-3}	5.7×10^{-3}	138
Germany, waste burning 1975		2.8×10^{-3}				5.1×10^{-2}	137
West Germany, refuse incinerators, 1985	2.0×10^{-4}	5.3×10^{-3}		5.0×10^{-3}	7.6×10^{-3}	9.0×10^{-2}	138
West Germany, refuse incinerators, 1990						0.01	139
West Germany, traffic, 1990						1.5	139
East Germany, refuse incinerator, 1990						0.008	139
Germany[g]	0.01	7.0×10^{-4}		7.0×10^{-3}	1.3×10^{-4}	0.08	140
Germany[h]	0.11	3.0×10^{-3}		0.3	1.0×10^{-3}	0.87	140
DDR[i] 1979	0.10	0.4		0.4	0.6	2.1	131
Switzerland, refuse incinerators			6.3×10^{-2}				141
France	0.10	0.45[j]		1.2[j]	0.91[j]	10.5[j]	142
France 1979	0.10	0.5		1.2	0.9	10.5	131
France 1990		0.1[f]			0.3[f]	0.35[f]	133
France[k]		0.02[j]		0.03[j]	0.04[j]	0.09[j]	142
United Kingdom 1979	0.13	0.6		1.0	0.9	10.1	131
Poland, power plant		0.02[l]	1.4[l]			0.02[l]	143
USA		12.25		17.28	5.45	8.45	144
USA[m]	5.0×10^{-2}[e]	3.2[e]	86.2[e]	4.6[e]	1.0[e]	2.2	145
USA 1970				8.95	3.65	11.5	33
USA, coal combustion[m]	2.3×10^{-2}[e]	9.9×10^{-2}[e]	17.7[e]	6.1×10^{-2}[e]	9.9×10^{-2}[e]	0.3[e]	145
USA, fuel oil combustion[m]	2.5×10^{-2}[e]	2.5×10^{-2}[e]	0.4[e]	5.4×10^{-3}[e]	9.3×10^{-2}[e]	3.0×10^{-2}[e]	145
USA, iron and steel industry[m]		3.1[e]	66.2[e]	4.5[e]			145
USA, stationary sources, 1969–1971		13.5	unknown[n]	19.0	6.0	9.3	146
USA, stationary sources, 1970				1.0	3.1	1.1	33
USA, industrial processes, 1970				7.85	0.52	5.35	33
USA, waste burning, 1973/74		8.4×10^{-2}				2.3	137
USA, coal burning, 1973/74	0.49					1.03	137
USA, Los Angeles area 1976	0.04[o]	0.1[o]	7.7[o]	0.2[o]	0.2[o]	3.2[p]	147
Canada 1990				0.48		1.49	121
Canada,[p] ore smelters, 1973–76		0.14[q]	0.47[q]	2.7×10^{-3}[q]		0.08[q]	148
oil-fired 100 MWe power plant	4.0×10^{-4}[j]	5.5×10^{-4}[j]		1.3×10^{-4}[j]	3.2×10^{-3}[j]	4.0×10^{-4}[j]	149

[a] Emissions from industrial processes and fossil fuel combustion. [b] Industrial particulate emissions. [c] Coal combustion. [d] Oil combustion. [e] Emissions from human activities south of 60 °S. [f] Estimated value. [g] Area of Cologne. [h] Area of Duisburg. [i] Former German Democratic Republic. [j] Value based on daily emission rates; oil contains 1% sulfur. [k] Fos area; industrial area at the Mediterranean coast with refineries, power stations, cement works, iron and steel mills. [l] Value based on daily emission rates by a 2000 MW lignite-fired power plant. [m] Metropolitan areas of Chicago, Milwaukee, and northwestern Indiana. [n] Iron could be expected to exceed the highest levels given for this source. [o] Values based on daily fine particles (d < 10 μm) emissions in the South Coast Air Basin. [p] Sudbury area, Ontario, Canada. [q] Average value of three ore smelters (Copper Cliff, Falconbridge, Inco Iron Ore Recovery); based on daily emission rates.

Table 1.7. Atmospheric Iron and Manganese Concentrations (see also Figure 1.2.b; for further information see e.g. refs 154–161)

Fe (μg L^{-1})	Mn (μg L^{-1})	remarks	ref
$(0.9-1.2) \times 10^{-3}$ [a]		atmosphere	162
6.6	0.26	atmosphere[b]	163
100	1.8	atmosphere[c]	164
$(0.6-1.8) \times 10^{-3}$	$(0.2-1.7) \times 10^{-4}$	urban air	165
	$(0.01-10) \times 10^{-3}$	urban air[d]	166
1.6×10^{-3}	7.0×10^{-5}	urban air[d,e]	145
1.9×10^{-3}	1.2×10^{-4}	urban air[d,f]	145
$(1.1-2.1) \times 10^{-3}$		urban air	167
$(0.2-0.5) \times 10^{-3}$		rural air	167
	0.2×10^{-3}	rural air[d]	166
15–131	3–20	rain water[g]	168
35.4	2.9	rain water[g]	169
22–55	5.5–11.5	rain water[g]	63
50–100		rain water[h]	170
20–66		rain water[h]	171
		rain water[h,i]	172
88	3.8	rain water[h,j]	173
200	8.1	rain water[h,k]	174
212	14.3	rain water[g]	175
230	12	rain water[g]	176
1300	28	rain water[l]	177
24	27.5	rain water[m]	63
12–109	13–37.5	snow water[g]	63
140	6.4	snow water[g]	176
203	5.3	snow water[n]	63
14.3	3.2	snow water[m]	63
0.08–10.7	0.003–0.52	fog water[d]	178
0.02–1.4	0.003–1.3	fog water[d]	156
90–2100	18–160	fog water[d]	179
17–5100	0–420	fog water[o]	180
547–12900	17–170	fog water[o]	181
4820	2320	fog water[p]	182
0.02–6.8		cloud water[d]	183
99	35.1	cloud water[h,q]	184

[a] As particulate ferric oxide. [b] Greenland. [c] Bermudas, 1974. [d] USA. [e] Chicago, 1964. [f] Milwaukee, 1964. [g] Germany. [h] Great Britain. [i] Mean value of samples collected in both urban and rural areas of South Wales and northern England. [j] Great Britain, North Sea coastal site, average value 1987–1988. [k] Rural area. [l] Nigeria (Africa; May–October). [m] Poland. [n] Norway. [o] Switzerland. [p] Japan, maximum value 1991/92. [q] Great Dun Fell, May 1993.

Table 1.8

(a) Particle Concentration in Los Angeles (Temperature and Relative Humidity: 22.0 °C and 23.6% on April 7, 1983, 29.8 °C and 50.5% on Aug 25, 1983)[194]

compound	clean day April 7, 1983 (μg m^{-3})	smog Aug 25, 1983 (μg m^{-3})
$(NH_4)_2SO_2$	3.54	14.90
NH_4NO_3	1.23	1.79
$NaNO_3$		12.80
Al_2O_3	2.82	9.34
SiO_2	4.53	15.54
Fe_2O_3	0.91	4.58
PbO	0.06	0.72

(b) Trace Species Concentrations in the Clean Troposphere and in Polluted Urban Air (Taken from Ref 16)

compound	clean troposphere (μg m^{-3})	polluted air (μg m^{-3})
SO_2	2.6–26.6	53–532
NO	0.01–0.06	63–938
NO_2	0.2–0.95	96–478
HNO_3	0.05–0.8	8–131[a]
CO	140.4	1170–11700
O_3	40–159	199–995

[a] Data from refs 195 and 196.

Table 1.9

(a) Average Lifetime and Travel Distances of Atmospheric Aerosols[187] According to Data from Ref 201

radius (μm)	τ (days)	horizontal distance (km)
0.001	0.01	8
0.01	1	800
0.1	10	8000
1	10	8000
10	1	800
100	0.01	8

(b) Residence Time of Metals in the Atmosphere

	τ (days)		
metal	Osaka[a]	La Jolla[b]	Ensenada[c]
Co	0.2	1.2	0.2
Cu	0.3	0.5	1
Fe	0.09	1	0.4
Mn	0.3	0.8	0.2
Ni	0.5	3	0.8
Pb	1.4	7	8

[a] Japan.[93] [b] California.[202] [c] Baja California, Mexico.[202]

The acidity of aerosols depends on the amount of adsorbed water and lies supposedly in the pH range 1–3. In the case of low humidity the pH value can be below 1.[231] Atmospheric dusts collected during the summer, normally react neutral, whereas samples collected during the winter show acidic reactions.[232] The fine fraction ($d < 2.5$ μm) of aerosols collected in Houston, TX, exhibited an acidic reaction, whereas the coarse fraction ($d = 2.5-15$ μm) behaved basic.[222] This difference was attributed to the fact that in the fine particles SO_4^{2-} was the major compound, whereas crustal matter, e.g. $CaCO_3$, was the major component in the coarse fraction (see Table 1.10c).

With respect to the catalytic activity of aerosols in different redox processes (see section 3.4), the relative humidity and the water film around the aerosol play important roles. The amount of SO_2 adsorbed on particles increases with increasing humidity.[232,233] In the presence of sea salt aerosols an increase in the SO_2 oxidation rate by a factor of 10 has been observed when the relative humidity is increased from 40% to 80%.[216] Catalytic activity of manganese(II) sulfate aerosols has only been found at a relative humidity higher than 70%.[234] Matteson et al.[235] report a limiting value of 95% relative humidity for catalytic activity.

In the case of water-soluble particles the oxidation rate strongly increases as the catalyst particles change from the solid form into the droplet form (see Table 1.11) at high relative humidity.[238,239] When the relative humidity lies over the deliquescence point of these particles, they are covered by a saturated salt solution. This solution is characterized by a nonhomogeneous mixture of dissolved substances. Thus, the SO_2 oxidation process is distributed nonhomogeneously over the whole droplet volume.[239]

In view of the possible catalytic activity of aerosols, their surface is an important parameter. A comparison of the surfaces of atmospheric aerosols and rain drops indicates that the surface area of aerosols [$(0.2-2) \times 10^{-6}$ cm^2 (cm^3 of air)$^{-1}$] is smaller than the surface area of raindrops [$(1-10) \times 10^{-6}$ cm^2 (cm^3 of air)$^{-1}$].[187] The surface area of most of the fly ashes is in the range of 1–30 m^2 g^{-1},[240] which limits the

Table 1.10. Chemical Composition of Atmospheric Aerosols from Different Origins

(a) Insoluble Compounds

	fraction in percentage							
compound	volcano[a]	continental[b]	dust[c]	urban[d]	cupola dust[e]	dust from steel works[f]	fly ash (coal)[g]	fuel ash from coal burning power plants[h]
Al_2O_3	15–18	3.23	12.4 (7.4)	8.3 (8.5)	5.8 (5.6)	3.9 (1.1)	14.1 (27.5)	27.02
CaO	2.3–4.8	1.5	5.9 (10.4)		6.7 (6.4)	18.9 (6.0)	7.5 (1.8)	1.42
CoO			traces					
Cr_2O_3			0.03					
CuO			traces					
Fe_2O_3	2.5–4.6	2.1	3.0 (3.4)	12.2 (5.1)	30.9 (23.4)	34.2 (75.4)	11.6 (4.3)	9.32
K_2O			1.96 (1.7)				0.5 (0.6)	
MgO	0.5–1.5		1.9 (2.5)			9.2 (0.3)	12.9 (0.2)	1.64
MnO			0.1		2.9 (4.3)	4.2 (2.1)		0.05
SiO_2	65–70	9.6	63.7 (54.5)	13.6 (27.8)	27.9 (22.7)	0.21 (traces)	23.0 (52.5)	50.32
TiO_2	0.4–0.6		0.82				0.7 (1.4)	0.99

(b) Soluble Compounds

	fraction in percentage							
compound	continental[b]	ocean[i]	tropics[j]	arctic[k]	urban[d]	dust[l]	highway aerosol[m]	fly ash (fuel oil)[n]
SO_4^{2-}	45.6	23.1 (6.5)	47 (45)	78 (67)	31.7 (21.8)	5.2 (0.62)	1.4	31.9 (39.4)
NO_3^-	13.3	0.4 (0.03)	20 (16)	13 (13)	6.9 (12.8)	(0.42)	0.1	4.5 (0.01)
Cl^-	0.2	41.4 (47.9)	6 (31)	4 (8)	7.3 (0.9)	4.13		(0.04)
NH_4^+	18.8	1.4	56 (26)		11.1 (9.1)			(1.7)
Na^+	0.7	26.1 (31.0)	25 (39)		2.7 (4.1)			(1.4)
K^+	0.9	1.0 (0.5)	20 (7)		1.0 (1.2)			(0.1)
Ca^{2+}	2.2	1.5 (2.6)			3.6 (2.5)			(0.2)
Mg^{2+}		3.6 (3.6)			1.4 (1.8)			(2.7)
CO_2						5.75		

(c) Fine and Coarse Fraction

	fraction in percentage							
compound	fine[o] day (night)	coarse[o] day (night)	fine[q]	coarse[q]	fine[r]	coarse[r]	fine[s]	coarse[s]
Co					1.6×10^{-3}	2.2×10^{-3}	1.2×10^{-3}	9.1×10^{-4}
Cu	0.04 (0.04)	0.03[p]	0.05	0.05	4.4×10^{-2}	2.4×10^{-2}	1.7×10^{-2}	2.5×10^{-2}
Fe	0.4 (0.17)	1.7 (1.1)	0.31	2.2	1.5	4.6	0.33	1.6
Mn	0.03 (0.01)	0.05 (0.04)	0.08	0.12	0.15	0.27	2.2×10^{-2}	6.0×10^{-2}
Ni	7.1×10^{-3} [p]	0.01 (9.4×10^{-3})			1.1×10^{-2}	1.2×10^{-2}	3.1×10^{-3}	6.4×10^{-3}
Pb	1.1 (0.91)	0.3 (0.26)	1.6	0.29	0.43	0.11	0.11	4.0×10^{-2}
SO_4^{2-}	39.3 (25.6)	2.6 (1.6)	8.5	1.7				
NO_3^-	0.6 (1.3)	4.2 (3.1)	13.4	2.25				
Cl^-	0.04 (0.06)	0.8 (1.1)	1.5	0.4	1.7	1.0	0.12	0.4
NH_4^+	10.1 (8.1)	<0.4[p]	5.8	0.36				
Na^+	0.7 (0.8)	0.66[p]						
K^+	0.3 (0.2)	0.4 (0.3)	0.53	0.7	0.48	0.55	0.37	0.97
Ca^{2+}	0.35 (0.3)	7.3 (6.6)	0.6	3.6	0.37	5.5	0.32	3.5

[a] Mount St. Helen, WA.[209] [b] Mountain station near Garmisch, Germany; data taken from ref 17. [c] Jaipur, India.[210] Values in brackets: Mt. Carmel, Israel, dry fall dust, Spring 1990.[211] [d] Tees-side, northeast coastal area of England. Values in brackets: West Covina, greater Los Angeles Area, CA; data taken from ref 17. [e] Cupola dust from iron production in the United Kingdom; average values for particles with $d > 63$ μm ($d < 63$ μm); values for Fe_2O_3 are sum of Fe_2O_3 + FeO; data according to ref 212. [f] Dust from electric arc process. Values in brackets: dust from basic oxygen process.[213] [g] Fly ash from combustion of Victorian brown coals, Australia; average value of four samples. Data in brackets are from combustion of New South Wales bituminous coals, Australia; average values of four samples; data according to ref 214; compare also with ref 215. [h] Reference 213. [i] Central Atlantic; data taken from ref 17. Values in brackets: sea-salt particles, Red Sea, Eilat, Israel, data according to ref 216. [j] Central Amazon basin, South America; dry season. Values in brackets are for the wet season.[217] [k] Arctic summer troposphere (free troposphere). Values in brackets are for boundary layer.[218] [l] Mt. Carmel, Israel, dry fall dust, spring 1990.[211] Values in brackets: road dust.[219] [m] Composite of gasoline- and diesel-powered highway vehicle exhaust, plus tire and brake dust.[147] [n] Reference 220. Values in brackets: average value of five samples.[221] [o] Houston, TX.[222] [p] Same value for day and night samples. [q] Phoenix, AZ. Winter time haze, January 1983.[74] [r] Southeast Chicago, IL. Particles less than 10 μm diameter.[186] [s] Bondville, IL, rural area; particles less than 10 μm diameter.[186]

adsorption capacity of gases. Iron oxide, Fe_2O_3, for example has an adsorption capacity (see also Table 3.12) for SO_2 of 62.6 μg (mg of Fe_2O_3)$^{-1}$, whereby only 35% of the surface area is covered.[241] A possible explanation for this low value is the occupation of potentially active adsorption sites by organic molecules (see ref 242). Extraction of atmospheric dust with benzene resulted in a 2-fold increase in the amount of SO_2 adsorbed.[232] Rani et al.[210] reported no influence of the particle size on the catalytic activity of atmospheric dusts.

The adsorption of SO_2 on particles occurs in two steps. Only the first one, the fast adsorption until equilibrium is reached, is believed to be of environmental significance. The second step is a slower further uptake of SO_2.[239] For a detailed discussion on the uptake of atmospheric gases into water droplets (Table 1.12) see ref 244–246.

Table 1.11. Deliquescence Points of Some Salts as Function of the Relative Humidity

salt	deliquescence point at % relative humidity	ref
$CuCl_2$	72	236
$CuSO_4$	98	236
$FeCl_3$	77	237
$MgCl_2$	33	17
$MgSO_4$	88	17
$MnCl_2$	40	237
$MnCl_2$	57	236
$MnSO_4$	86	236
NaCl	76	229
$NaNO_3$	75	17
Na_2SO_3	85	229
Na_2SO_4	86	237
Na_2SO_4	91	229
NH_4Cl	77	237
NH_4Cl	80.5	229
$(NH_4)_2SO_4$	81	237

Table 1.12. Uptake of Some Gases by Fog Droplets[243]

	fraction scavenged from gas phase (%)		
gas	$t = 0$ min	$t = 30$ min	$t = 180$ min
(a) $T = 1$ °C, Liquid Water Content (LWC) = 0.1 g m^{-3}			
HNO_2	10.2	3.4	0.0
HNO_3	100	100	100
H_2O_2	58.0	100	100
NH_3	76.0	97.0	100
SO_2	10.7	13.0	18.2
O_3	0.0	4.2	4.2
(b) $T = 10$ °C, Liquid Water Content (LWC) = 0.1 g m^{-3}			
HNO_2	3.8	0.0	0.0
HNO_3	100	100	100
H_2O_2	32.1	100	100
NH_3	43.9	99.5	100
SO_2	2.7	11.8	17.5
O_3	0.0	1.5	1.5

1.3. Distribution and Lifetime of Trace Compounds

The spatial and time-dependent distribution of trace gases emitted into the atmosphere depend on transformation and transportation processes as well as atmospheric conditions (e.g. concentrations, humidity, cloud distribution, sun light, etc.). The atmospheric lifetime τ of a trace compound can be described by its chemical half-life τ_c (reactivity, see Table 1.13) and the deposition time τ_d (transportation processes, meteorological conditions). For the estimation of τ, several reactions of the studied compounds are usually compared with each other. In the case of SO_2 the estimated value of τ is 3 days (lower troposphere, day light conditions) if SO_2 reacts only with OH radicals; τ increases to a value of about 10^5 days (lower troposphere, day light conditions) if SO_2 reacts only with ozone.[248] For a summary concerning τ for SO_2 see ref 17, pp 512–513. For NO_x a value of $\tau = 3-4$ days in the troposphere is reported by Bónis et al.[61] Lammel[23] reported the following τ values for NO_y compounds in the surface near atmosphere: NO_2, 6–48 h; HNO_2, N_2O_5, and NO_3 < 1 night; HNO_3, 1–10 days; N_2O, 100 years. In the stratosphere τ is often several times higher than in the troposphere because of the absence of effective sinks.[45] The atmospheric lifetime τ is a main parameter for the atmospheric relevance of chemical processes. Reactions with a half-life $t_{1/2} > \tau$ are only of minor relevance in comparison to processes with $t_{1/2} < \tau$ or $t_{1/2} \ll \tau$.

The import or export of acid precipitation due to trace substances from or to foreign countries is a global problem (see e.g. refs 188 and 249). Approximately 10% of the overall deposited SO_2 in Europe comes from anthropogenic sources in North America.[250] The export of SO_2 from the United Kingdom in 1980 to e.g. France, Denmark, USSR, and the Netherlands was 6.3, 5.7, 3.5, and 2.3%, respectively.[101] In the Netherlands, the imported fraction of SO_2 and NO_x in acid deposition is 80 and 65%, respectively[251] (see also refs 101 and 252). Approximately 77% of the anthropogenic emitted sulfur in the atmosphere over Sweden (70%) has its origin in other countries.[253] For a detailed summary on the import and export of sulfur deposition in Europe see ref 85, p 358. For an overview concerning import and export of air pollution in Europe see ref 254.

1.4. Deposition

Substances emitted into the atmosphere return, maybe chemically transformed, to the earth surface via deposition processes.[47,255–258] These processes can be divided into dry and wet deposition.[257,258] Dry deposition is the transfer of trace substances from the atmosphere to the earth surface without participation of a liquid phase. Wet deposition occurs via rain, dew, fog, and snow. For a literature survey concerning the deposition of particles, SO_2, and O_3, see ref 255. For a review of deposition monitoring methods, see ref 259. The term acid rain (see section 1.5) is often used as an overall expression for the wet deposition process.

The fractions of dry and wet deposition vary with the trace substances, the water solubility, the air pollution and the source distance. The wet deposition dominates over the dry deposition for SO_4^{2-}, NO_3^-, and Cl^-, whereas the dry deposition dominates for particles with $d > 2$ μm.[168] The deposition of manganese and iron occur mainly in the closer surroundings of the sources, viz. the industrial areas[168,261–263] (Figure 1.5). From the emitted quantities of metals by a nickel–copper smelter in Canada, 40% of the copper, 42% of the nickel, and 52% of the iron were deposited within a radius of 60 km,[260] whereas 0.14% of the sulfur emitted by a source is deposited within a radius of 25 km[264] and less than 3% within a radius of 60 km.[260] Acidic wet deposition in India is only a local phenomenon and is restricted within a 2 km distance upwind and downwind of the industrial complexes, whereas the precipitation in other areas of India is somewhat between weakly and strongly alkaline[86] (compare also with ref 261). The mechanisms of dry deposition are in nonpolluted areas a factor of 3 (manganese) or 2 (iron) less effective than in polluted areas.[168] The contribution of the wet deposition increases with increasing distance from the source.[3,265] The wet deposition of trace substances occurs in agreement with rain events, in remote areas with respect to the sources. Model calculations[266] indicate that about 30% of the emitted NO_x undergoes wet deposition in the source regions, whereas dry deposition accounts for another 40–45%.

Table 1.13. Chemical Behavior of SO_2 and NO_x in Air[247]

	SO_2	NO_x
photochemical behavior	inactive; light absorption without chemical consequence	NO_2 is very active; photolysis reason for anthropogenic O_3 formation
behavior against radicals	passive; acts as weak scavenger for OH radicals (formation of H_2SO_4)	very reactive, especially through $HO_2 + NO \rightarrow OH^\bullet + NO_2$; NO_2 acts as radical sink, e.g. $OH^\bullet + NO_2 \rightarrow HNO_3$
behavior against O_3	no reaction	fast reaction with NO, slower with NO_2; formation of N_2O_5
uptake into droplet phase, transformation	very important sink	important, but not well investigated; occurs probably via N_2O_5
dry deposition	important sink	less important
products	H_2SO_4 and SO_4^{2-} in aerosols and rain	HNO_3(g), NO_3^- in aerosols and rain

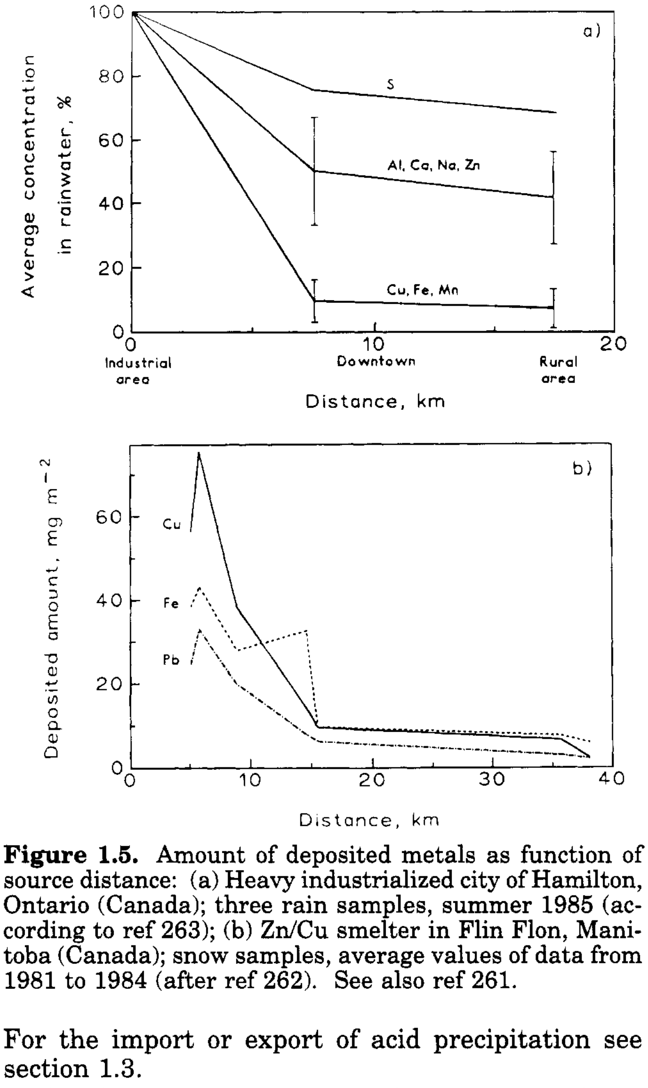


Figure 1.5. Amount of deposited metals as function of source distance: (a) Heavy industrialized city of Hamilton, Ontario (Canada); three rain samples, summer 1985 (according to ref 263); (b) Zn/Cu smelter in Flin Flon, Manitoba (Canada); snow samples, average values of data from 1981 to 1984 (after ref 262). See also ref 261.

For the import or export of acid precipitation see section 1.3.

The deposition quantities of some atmospheric trace substances are summarized in Table 1.14. Model calculations[199] indicate that fine particles ($d < 2.5$ μm; see section 1.2) are responsible for only a small fraction (0.06% for particle mass) of the total dry deposition flux.

The determination of the deposition velocity (see Table 1.15) as well as the amount deposited is subjected to large errors. The uncertainty (in each case for a monitor period of 14 days) for manganese has been determined to be ±6%, whereas the uncertainty for iron is ±61%.[168] The uncertainty for the wet deposition of NO_x has been determined to be ±50%.[61] For the deposition of NO_3^- over North America, an error of ±20% is cited.[3] The dry deposition of SO_2 is one of the most uncertain parameters in the atmospheric sulfur cycle[50,279] since the dry deposition is strongly influenced by atmospheric conditions. Whereas the wet deposition of SO_2 is nearly constant over the entire year, the amount of the dry deposited SO_2 is double in winter than in summer.[68] The fraction of the dry and wet depositions for the atmospheric SO_2 sinks is 45 and 11%, respectively.[280] In polluted areas the dry deposition of sulfur (SO_2 and SO_4^{2-}) is the dominant sink compared to the wet deposition.[168]

Chemical transformation of the trace substances also occurs during the deposition process. Thus, the deposition velocity (Table 1.15) is an important parameter for the chemical transformation during the deposition process. It should also be mentioned, that the deposition velocity depends on the surface over which it is measured.[278,281]

1.5. Acid Rain

The scientific interest in wet deposition has increased in terms of "acid rain" as a result of ecological and economical damages (e.g. damages to forests, fish populations, buildings).[13,282–290] Furthermore, atmospheric acidity can cause health problems (see ref 291 for an overview). The term "acid rain" was probably used for the first time in the scientific literature in 1842.[b,292] The actual meaning of acid rain is the washout[c] of trace substances by rain events, although fog, dew, and snow are also forms of wet deposition (see section 1.4) and also result in the acidification of waters and soils, and the damage of buildings. A comparison of the relative magnitude of frost, dew, and fogs as compared to rainfall, indicate that the daily moisture deposition of fog, dew, and frost is around 45%, 0.6% and 0.2%, respectively, compared to that of rain.[294] Acid rain is a global problem and has been recognized in all parts of the world.[295] For a detailed literature survey on acid rain problems and its effects on the environment from 1980 to 1984 see ref 296, from 1984 to 1988 see ref 297, and from 1988 to 1991 see ref 298. For a historical review see refs 299–301.

Dry acid deposition is generally not noticed very often in atmospheric studies, but it is also responsible for the effects caused by the overall acid rain phenomenon. For example, in the Netherlands 70% of the overall acid deposition is caused by dry acid

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[b] The text by Poggendorff[292] was based on a letter from Pilla[293] in which the acidification of rain by emissions of the volcano Vesuv was described.

[c] Washout represents all processes that include the absorption or incorporation of aerosols and gases beneath the cloud layer during the falling of water droplets. Rainout represents all processes within a cloud that result in the absorption or incorporation of trace compounds into the cloud water droplets.

Table 1.14. Deposited Amount of Some Trace Substances

substance	amount (mg m^2 d^{-1})	remarks	ref
Fe[a]	0.01	urban area; wet deposition	159
	0.03	urban area; dry deposition	159
	0.13	rural area in Great Britain 1971; dry deposition	174
	0.15	rural area; wet deposition	159
	0.2−0.5	in Germany according to data from Sept 1979 to Aug 1981	168
	0.361−4.027	Great Britain 1972/73	267
	0.52	Central Ontario, Canada; wet + dry deposition; Jan 1976 to June 1978	268
	0.77	rural area in Great Britain 1971; total deposition	174
	0.8−1.5	peak values in urban and industrial areas in Germany according to data from Sept 1979 to Aug 1981	168
	2.08	at Bagauda, Nigeria, 1976; dry deposition	177
	4.24	at Bagauda, Nigeria, 1976; total deposition	177
Mn[a]	0.0026	rural area in Great Britain 1971; dry deposition	174
	0.016−0.116	rural areas (England) 1972/1973	267
	0.02	central Ontario, Canada; wet + dry deposition; Jan 1976 to June 1978	268
	0.03	at Bagauda, Nigeria, 1976; dry deposition	177
	0.031	rural area in Great Britain 1971; total deposition	174
	<0.07	rural area; wet deposition	159
	<0.08	rural area; dry deposition	159
	0.09	at Bagauda, Nigeria, 1976; total deposition	177
	<0.22	urban area; dry deposition	159
	<0.27	urban area; wet deposition	159
	0.3−0.5	in Germany according to data from Sept 1979 to Aug 1981	168
	1.43	peak value in Essen (Germany, iron industry) according to data from Sept 1979 to Aug 1981	168
SO_2	<1.3−1.9	in Austria; dry deposition over grass; summer	269
	11.05	in the Netherlands 1986; dry deposition	251
	32.0−83.3	in Austria; dry deposition over grass; winter	269
SO_4^{2-}	1.0−1.9[b]	in Austria; dry deposition over grass; summer	269
	1.8	in the Netherlands 1986; dry deposition	251
	2.9−11.5[b]	in Austria; dry deposition over grass; winter	269
	3.7−7.4[c]	in Germany according to data from Sept 1979 to Aug 1981	168
	3.4−7.4[c]	in Southeastern Europe, yearly average 1983−1985	50
NO_2	1.8−6.4	in Austria; dry deposition over grass; summer	269
	16.1−96.6	in Austria; dry deposition over grass; winter	269
NO_3^-	0.25[d]	in Austria; dry deposition over grass; summer	269
	0.6−1.2[d]	in Austria; dry deposition over grass; winter	269
	0.46[e]	in Guizhou, China	270
	0.5−8.5	in Western Europe; wet deposition; calculated values	266
	1.02	in the Netherlands 1986; dry deposition	251
	1.3−2.7[e]	in Europe	61
	1.2−2.8	in Germany according to data from Sept 1979 to Aug 1981	168
	2.9−7.6	in North America; wet deposition; calculated values	266
	7.6−18.9[e]	in Austria; dry deposition over grass; summer	269
	6.3−18.9[e]	in Austria; dry deposition over grass; winter	269

[a] For a compilation of deposited amounts of other metals see ref 268. [b] Particulate SO_4^{2-}. [c] Calculated as S. [d] Particulate NO_3^-. [e] Calculated as N. [f] HNO_3.

deposition.[251] Thus, it would be more appropriate to substitute the term "acid rain" by "acid deposition". In the following we will focus only on wet deposition.

The pH value of rain is in the range of 4.5−5.6 when the natural CO_2 content and the sulfur cycle are taken into consideration.[86,302−306] According to Khemani[86] the term "acid rain" has come to mean rainfall with pH less than 5.65. Delmas and Gravenhorst[305] discussed in their review article that the pH value of 5.6 cannot be taken as natural reference pH of rain water because atmospheric acid and basic trace constituents can significantly change this value. In several areas in Europe and North America the pH is around 4−4.5,[10,176,307] and 49.5% of rain water samples collected in an urban area in Germany in 1974 had a pH between 4.1 and 4.4, whereas for 27.5% of the samples the pH was between 3.7 and 4.0.[176] The pH of 72% of the samples collected in a rural area in Germany during the same time was between 4.3 and 4.5.[176] Of rain and snow samples collected in 1993 in Germany, Norway, and Poland 30% had a pH lower than 5.6, with a lowest value of 4.6 (snow sample from Germany) and a highest value of 7.2 (snow sample from Poland).[62] In India the overall probability for the occurrence of acid rain (pH < 5.6) is about 2% (see further Discussion).[308] In Scandinavia and Northeastern America a strong increase in the acidity of precipitation was observed between 1955 and 1970.[302] Between 1974 and 1984 the pH of precipitation collected at several places in India exhibited a decreasing trend toward the acidic range.[308] The pH of precipitation water collected in Agra and Dehli, two cities in India that developed industrially to a great extend, during the summer monsoon season decreased from 9.1 and 7.0 (1963/65) to 6.3 and 6.1 (1984), respectively.[309] In cloud

Table 1.15. Deposition Velocity of Some Trace Substances (see also ref 271)

substance	deposition velocity (cm s^{-1})	remarks	ref
Fe	0.2	dry deposition; 0% relative humidity	163
	0.3–1.9	dry deposition	159
	0.46	dry deposition	177
	0.57	dry deposition	174
	1.44	dry deposition; 99% relative humidity	163
	1.5	dry deposition	168
	2.4–9.9	dry deposition; mean value during non dust storm periods	272
	4.1–62	dry deposition; during dust storms	272
	9.5	dry deposition; calculated value over the North Sea	273
Mn	0.15	dry deposition; 0% relative humidity	163
	0.24	dry deposition	174
	0.4–0.9	dry deposition	159
	0.57	dry deposition	177
	0.95	dru deposition	168
	1.08	dry deposition; 99% relative humidity	163
	8.4	dry deposition; calculated value over the North Sea	273
SO_2	0.06	above snow (dry deposition); temperature dependent: $T < -3$ °C	69
	<0.1	above snow (dry deposition); temperature dependent: $T < -3$ °C	274
	0.1	above snow (dry deposition)	275
	0.1	during the night	276
	0.15	above snow (dry deposition); temperature dependent: $T > -3$ °C	69
	0.2–0.3	average value over 24 h	277
	0.25	above snow (dry deposition)	264
	0.4	above water (dry deposition)	50
	0.6	during the day	276
	0.8	average value for one year (dry deposition) over heather vegetation	278
	0.9	average value 1980–1986 (dry deposition in the Netherlands)	251
	1.2	average value for one year (dry deposition) over grassland	278
SO_4^{2-}	0.08	dry deposition	279
	0.15	average value 1980–1986 (dry deposition in the Netherlands)	251
	0.4	above water (dry deposition)	50
NO	<0.03	above snow (dry deposition)	274
	0.15	average value (dry deposition)	251
NO_2	<0.03	above snow (dry deposition)	274
	0.005–0.5	average values for different surfaces	23
	0.33	average value (dry deposition)	251
NO_3^-	0.1–0.4	above land (dry deposition)	50
	0.1–0.4	above water (dry deposition)	50
	0.1–18	average values for different surfaces	23
	0.15	average value 1980–1986 (dry deposition in the Netherlands)	251
HNO_2	0.2–2	average values for different surfaces	23
HNO_3	0.02–26	average values for different surfaces	23
	1.4	above snow (dry deposition)	69
	3.4	average value 1980–1986 (dry deposition in the Netherlands)	251

water collected over Hawaii the pH was found to be between 4.2 and 4.7.[310] pH values of fog water collected in Los Angeles and in Switzerland were between 2.2–5.8 and 2.9–7.1, respectively.[154,180,311,312] Rain water with alkaline pH (pH > 6) has been observed for example in India.[86,313] A shift of pH toward the alkaline region can be due to the incorporation of alkaline soil particles released from crustal sources. Thus, precipitation acidity is a function of the contents of both acids and bases (Figure 1.6). Any attempt to understand the processes causing acid precipitation must deal with the acid neutralization capacity of alkaline materials.[86,314,315] On the basis of model calculations, Gatz et al.[314] reported that alkaline compounds (e.g. NH_4, Ca, Mg, K, Na) buffer between 25 and 50% of the potential acids in precipitation in the United States. According to Pilinis et al.,[206] the molar ratio of the sum of NH_3 and NaCl to H_2SO_4 is of fundamental importance in determining whether unneutralized

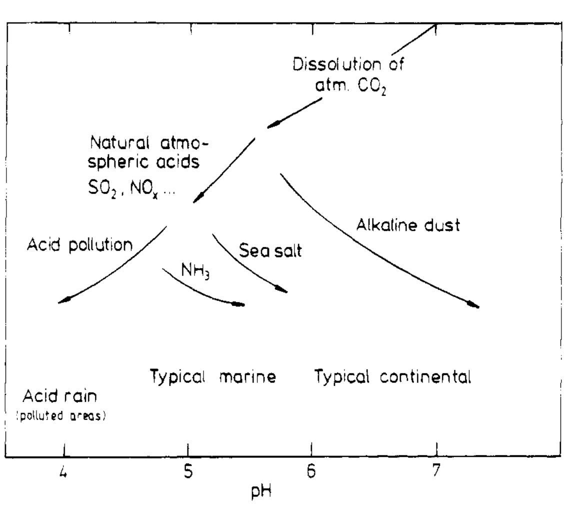

Figure 1.6. pH range predicted for background precipitation depending on the relative concentrations of various atmospheric trace constituents.[305]

Table 1.16. Concentrations of Sulfuric and Nitric Acid in Precipitation and Atmospheric Water Droplets (see also Figure 1.2.a)

area	sulfuric acid (μmol L^{-1})	nitric acid (μmol L^{-1})	pH	remarks	ref
subarctic tundra near Bethel, AK	4.3^a	3.7^b	4.69	precipitation events from July 11 to Aug 11, 1988	218
Central Amazon region (Brazil, South America)	4.5^a	5.5^b	4.6	rain water during July–Aug 1985; dry season	318
La Paragua, Venezuela	2.5^a	3.2^b	4.7	rain water during Oct–Nov 1985; remote area; nonburning period	319
Dimonika, Congo, Africa	5.3^a	8.6^b	4.74	precipitation events from Nov 1986 to Sept 1987	320
Dhahran, Saudi Arabia	116.5^a	143.7^b	5.48	rain water and bulk deposition (rain + dry fallout); March 1987 to March 1988	321
Mt. Carmel, Israel	48^a	37^b	4.33	precipitation water; Jan 5, 1992	211
Mt. Carmel, Israel	55^a	59^b	6.35	bulk precipitation; Jan 5, 1992	211
Mt. Carmel, Israel	101^a	150^b	7.32	precipitation water; March 4, 1992	211
Mt. Carmel, Israel	96^a	123	7.06	bulk precipitation; March 4, 1992	211
Everglades National Park, FL	8.0^a	10.5^b	5.17	precipitation events 1989	306
Ithaca, NY	57.1	44.4	3.84	rain water, July 1975	322
Long Island, NY	24.7^a	27.9^b	4.29	rain + snow water; Oct 1983 to June 1985	323
Clingmans Peak, NC	11^a	8.8^b	4.55	rain water; Aug–Sept 1986	324
Northeastern USA	45.8^a	38.7^b	4.08	precipitation water; June 1972 to Aug 1973	325
Minnesota USA	23.4^a	27^b	4.83	rain water; summer 1982	326
Warren, OH (Northeastern USA)	33^a	31^b		rain water (winter precipitation), Dec 1981 to April 1985	327
Warren, OH (Northeastern USA)	13^a	41^b		snow; Dec 1981 to Apr 1985	327
Detroit, MI (Northeastern USA)	121^a	166^b	6.5	dew water; June 1981 to July 1983	328
Westwood (Los Angeles), CA	10.7^a	16.6^b	4.81	rain water; Sept 1985 to Aug 1991	329
Westwood (Los Angeles), CA	16.4^a	34.0^b	4.97	rain water; Jan–March 1989	329
Pasadena, CA (Southeastern California)	31–190^a	130–930^b	4.74–5.25	fog water; Nov 11, 1981	154
Pasadena, CA (Southern California)	240–472^a	1220–3520^b	2.92–4.85	fog water; Nov 23, 1981	154
Pasadena, CA (Southern California)	2530	1200	2.25	fog water, Jan 17, 1982	154
Alberta, Canada	21.6^a	15.8^b	5.53	precipitation events 1980–1984	330
USSR	28.1^a	3.3^b	5.3	rain water	108
Kitakyushu City, Japan	42.1^a	28.1^b	4.93	bulk precipitation; Jan 1988 to Dec 1990	331
Mt. Oyama, Japan	5.5–698^a	7–3036^b	3.02–6.59	fog water; 1991–1992	182
Mt. Oyama, Japan	2.0–145.5^a	0–329^b	3.77–6.55	rain water; 1991–1992	182
Yokohama, Japan	9.5–225.5^a	8–438^b	3.49–5.56	rain water; 1991–1992	182
Yokohama, Japan	30.7^a	32.5^b	4.4	rain water; May–Nov 1985	332
Southern China	223.5^a	10.0^b		rain water; urban area, 1984	270
Southern China	114.3^a	10.1^b		rain water; rural area, 1984	270
Trivandrum, India	17.8^a	15.8^b	5.30	rain water; coastal area	86
Kalyan, India	54.1^a	31.0^b	5.70	rain water; industrial area	86
Dehli, India	28.4^a	41.0^b	6.10	rain water; urban area	86
Dehli, India	45.6^a	187.9^b	6.91	fog water; urban area	86
Dehli, India	69^a	80^b	7.2	fog water; 1986	309
Pune, India	18.5^a	7.7^b	6.30	rain water; urban area	86
Pune, India	15.6^a	29.0^b	6.90	cloud water	86
Netherlands	18–400^a	8–860^b	3.2–5.5	cloud water; June 1982	333
Darmstadt, Germany	30.5^a	23.4^b	4.43	rain water; Feb 1989	169
Great Dun Fell, UK	168.7^a	102.6^b		cloud water; April–May 1993	334
Lancaster, UK (NW England)	44.5^a	28^b		rain water; rural area, 1979–1981	335
Zürich, Switzerland	360^a	698^b	4.6	fog water; Sept 1986 to Dec 1987	180
Zürich, Switzerland	320–1340^a	310–2130^b	3.28–5.15	fog water; Nov 27–29, 1991	181
Zürich, Switzerland	40–190^a	60–80^b	3.78–5.36	fog water; Feb 12–13, 1992	181
Zürich, Switzerland	120–290^a	120–260^b	5.82–6.17	fog water; Nov 5–6, 1992	181
Hrádek u Pacova, Czechoslovakia	52.2^a	44.8^b	4.37	precipitation water; rural area, 1976–1984	336
Patros, Greece	38^a	57^b	4.12–8.76	precipitation water; Oct 1985 to April 1986	337

^{a} Sulfate. ^{b} Nitrate.

H_2SO_4 will exist in the particulate phase. If this ratio is less than 2, HSO_4^- and H_2SO_4 (l) may be present in the aerosol phase, whereas for values larger than 2, H_2SO_4 is completely neutralized. Long-term trends in base cations in precipitation have exhibited a steep decline over the past 10 to 26 years.[316] For analytical problems related to the determination of atmospheric acidity see ref 317.

The most important inorganic acidic substances in the atmosphere are H_2SO_4 and HNO_3 (Table 1.16).[d] As organic acids only formic and acetic acid are important (Table 1.17). Since the beginning of the 1980s an increase in the concentrations of the oxidation products SO_4^{2-} and NO_3^- has been observed (see also Table 1.4). In Harwell, England, for instance, the sulfate concentration in aerosols increased by 50% from 1957 to 1974.[103] From 1890 to 1970 the deposited amount of NO_3^- increased nearly by a factor of 10 in the eastern parts of the United

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[d] For historical values of the inorganic composition of precipitation water see, e.g. refs 338 and 339.

Table 1.17. Concentrations of Formic and Acetic Acid in Precipitation and Atmospheric Water Droplets (for a comparison of ion chromatographic methods for the determination of organic acids in precipitation see refs 340 and 341)

area	formic acid (μmol L^{-1})	acetic acid (μmol L^{-1})	pH	remarks	ref
Subarctic Tundra near Bethel, AK	7.9[a]	7.0[b]	4.69	precipitation events from July 11 to Aug 11, 1988	218
Dayalbagh, Agra, India	7.7[a]	5.62[b]	6.79	wet precipitation water (Aug–Sept 1991)	313
Hari Parvat, Agra, India	2.45[a]	11.62[b]	6.69	wet precipitation water (Aug–Sept 1991)	313
Taj Mahal, Agra, India	3.6[a]	4.91[b]	7.22	wet precipitation water (Aug–Sept 1991)	313
Udyog, Agra, India	1.78[a]	6.43[b]	7.15	wet precipitation water (Aug–Sept 1991)	313
Dimonika, Congo, Africa	6.6[a]	3.0[b]	4.74	wet precipitation from Nov. 1986 to Nov. 1987	320
Dimonika, Congo, Africa	6.3[a]	3.0[b]	4.75	wet precipitation during dry season	320
Dimonika, Congo, Africa	10.6[a]	3.3[b]	4.58	wet precipitation during wet season	320
Central Amazon region (Brazil, South America)	17.9[a]	11.4[b]	4.6	rain water during July–Aug 1985; dry season	342
La Paragua, Venezuela	8.4[a]	4.5[b]	4.7	rain water during Oct–Nov 1985; remote area; nonburning season	319
La Esperanza, Venezuela	4.4	5.5	4.1	rain water from Nov. 1988 to Nov. 1989; rural site	318
Minnesota	not determined	3.87[b]	4.83	rain water; summer 1982	326
Westwood (Los Angeles), CA	12.4[a]	4.1[b]	4.81	rain water; Sept 1985 to Aug 1991	329
Charlottesville, VA	13.5[a]	5.2[b]	4.17	precipitation events from April 16 to Oct 1, 1983	343
Charlottesville, VA	12.7[a]	6.0[b]	4.47	precipitation events from Nov 1983 to Dec 1984	344
Wilmington, NC	2.5	1.9	4.66	rain water; average value for nongrowing seasons 1987–1990	345
Wilmington, NC	9.4	4.3	4.44	rain water; average value for growing seasons	345
Ithaca, NY	0.4	2.1	3.84	rain water; July 1975	322
Darmstadt, Germany	5.9[a]	5.2[b]	4.43	rain water; Feb 1989	169
Central Germany	53.8	50.7	5.54[c]	cloud water; Sept 1988	346
Zürich, Switzerland	21.7–223.7[a]	56.2–831.0[b]	3.6–5.5	fog water; Nov 1987	347
Zürich, Switzerland	34.9–134.0[a]	69.1–414.6[b]	3.28–5.15	fog water; Nov 27–29, 1991	181
Zürich, Switzerland	7.7–16.8[a]	14.8–61.9[b]	3.78–5.36	fog water; Feb 12–13, 1992	181
Zürich, Switzerland	17.0–39.1[a]	30.8–42.9[b]	5.82–6.17	fog water; Nov 5–6, 1992	181
Po Valley, Italy	9.5–49	12.5–91.5	4.0–4.94	fog water; Nov 1985	348
Great Dun Fell, UK	14.65	7.67		cloud water; April, May 1991	334
Mace Head, Ireland	3.16	0.38	5.48[c]	dew water; Sept 1989	346

[a] Formate. [b] Acetate. [c] Calculated value.

States.[349] A direct correlation between the SO$_4^{2-}$ concentration in precipitation and anthropogenic SO$_2$ emissions has been found in Sweden. The increase in SO$_4^{2-}$ by 50% (1954–1970) and the decrease by 25% (1970–1980) can be correlated very well with the SO$_2$ emissions during the same time.[350] A similar correlation was observed in the United States between SO$_2$ and NO$_x$ emissions and the acidity of rain and the deposited amount of SO$_4^{2-}$ and NO$_3^-$, respectively.[89,91,351–353] In contrast, Shin and Carmichael[354] found that only the dry deposition of SO$_4^{2-}$ and NO$_3^-$ is proportional to the SO$_2$ and NO$_x$ emissions, respectively, whereas the liquid phase production of SO$_4^{2-}$ is not proportional to SO$_2$ and NO$_x$ emissions.

The oxidation products of the sulfidic sulfur species (see Figure 1.1) can also contribute to the acidity of rain. For example, the oxidation products of dimethyl sulfide have contributed around 40% to the rain acidity at Amsterdam Island (Indian Ocean).[21] Tanaka et al.[332] calculated that the contribution of sulfur(IV) oxidation to the decrease of pH in rain water is in the range of 6–67%. The relative contribution of acidic compounds to the acidity of precipitation[e] (Table 1.18) depends on location and

Table 1.18. Percentage of Acid Contributing to the Acidity of Rain Water

% H$_2$SO$_4$	% HNO$_3$	% HX	area	ref
65	17	18[a]	Alaska	303
43	18	52[b]	Bethel, AK	218
38.9	33.6	27.4[b]	Los Angeles, CA	329
58 (32)[c]	39 (22)[c]	2.4 (2.6)[b,c]	NE of USA[d]	302
73	31		NE of USA[e,f]	355
59	61		NE of USA[e,g]	355.
65	30	>5[h]	NE of USA	325
65	35		NE of USA	322
62	32	6[h]	NE of USA	356
		16[i]	North America	357
		23[i]	North Carolina	345
		36.2[b,j]	Minnesota	326
18	17	65[a]	Venezuela	303
23	16	16,[h] 43,[k] 23[l]	Venezuela[m]	319
19	12	63[i]	Brasil[n]	318
22.7	41.5	35.8[i]	Kongo[o]	320
70	30		England[p]	358
60	25–30		Germany	168
52	48		Patras, Greece	337
66	33		Northern Europe	359
73	14	13[a]	Amsterdam Island	303
33	26	41[a]	Northern Australia	303
18	21	64[i]	Northern Australia[q]	360
		48,[r] 55[s]	Jaribu, Australia	361

[a] HCl, H$_3$PO$_4$, or organic acids. [b] Organic acids. [c] See footnote e (text). [d] Ithaca, NY, Oct 1975. [e] Average value 1964–1979. [f] Summer. [g] Winter. [h] HCl. [i] HCOOH + CH$_3$COOH. [j] Mainly acetate; contribution of S(IV) to free acidity; 7.5%. [k] HCOOH. [l] H$_3$COOH. [m] Savannah region. [n] Dry season, July–Aug 1985. [o] Average value Nov 1986 to Sept 1987. [p] Yearly average value. [q] Average value 1980–1984. [r] HCOOH, in the overall wet season. [s] HCOOH, in the monsoonal periods.

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[e] Likens[302] points out that by the determination of the contribution of acidic compounds to the acidity of precipitation the contribution of carbonic acid has sometimes not taken into account, since carbonic acid dissociates at pH > 5, and influences than the H$^+$ concentration. If the contribution of carbonic acid is taken into account, the percentage contribution of the other compounds decreases (values in brackets in Table 1.18).

time, but is nearly similar in the eastern parts of the United States and in Europe.[362] The contribution of organic acids can dominate over sulfuric and nitric acid in tropical and equatorial areas (Table 1.18). Formic and acetic acid have also been found in the atmosphere and in the precipitation of industrialized countries[313,345,357,363–368] (Table 1.17; for a general review on organic compounds in rain water see ref 369). Natural sources for these organic acids or their precursors are primarily plants,[320,370,371] but also anthropogenic activities including emission by traffic should be taken into account.[313,363,364,368,372] The concentration of these two organic acids in precipitation (Table 1.17) varies with the season and the geographical origin. During the growing season of plants (spring, summer) a higher concentration in rain water has sometimes been observed compared to the nongrowing season (autumn, winter).[344,345] In rain water collected in the Venezuelean savannah region higher formic and acetic acid concentrations were observed during the burnig periods.[319,373] Rain water from continential storm systems contains higher concentrations of formic and acetic acid than from maritime storms.[345] For the influence of meteorological conditions on sulfate and nitrate concentrations in rain water see e.g. ref 374.

As a result of the change in the emitted quantities of pollutants (see Table 1.4) there is a change in the contribution of inorganic acid substances observable in the precipitation. In the northeastern parts of the United States the importance of sulfuric acid to the acidity in rain water has decreased during the period 1964–1979 by 30% relative to nitric acid, whereas nitric acid increased by 50% relative to sulfuric acid.[355] The relative contribution of SO_4^{2-} to the acidity of rain in New York decreased from 78 to 65% (1955–1973), whereas the contribution of NO_3^- increased by 8 up to 30% in the same time.[325] The contribution of sulfate to the ambient acidity of precipitation at Hubbard Brook, NH, dropped from 83% in 1964–1965 to 66% in 1973–1974 but the nitrate contribution increased from 15% to 30%.[302] At one station in the Western part of the United States the concentration of NO_3^- has more than doubled within 3 years (1975–1978).[375] Rain water in Chembur, a highly industrialized area near Bombay, India, which was reported acidic from 1974 to 1980, turned alkaline in 1990. This fact is ascribed to the declining SO_2 and NO_x emission trends (see section 1.1).[86]

The maximum contributions of H_2SO_4 and HNO_3 to acid precipitation during summer in the United States are 73 and 31%, respectively, and during winter 59 and 61%, respectively.[265,355] The higher contribution of HNO_3 during the winter is likely due to the higher emission rates of NO_x, e.g. due to combustion processes for heating. Measurements of NO_x concentrations in the air of rural areas[376] as well as of cities[77] indicate a higher NO_x concentration during winter. In addition, the atmospheric SO_2 concentration in Europe during the winter is more than two times higher than during the summer (see also Table 1.3). Of course, the conversion rate of SO_2 to SO_4^{2-} is a factor of 2 higher during the summer than during the winter.[68] On the contrary, in the remote area of Amsterdam Island (Indian Ocean) the atmospheric SO_2 concentration in summer is about 6 times higher than in winter (see Table 1.3).[66]

Table 2.1. Solubility of Some Gases in Water (p_{gas} = 1 atm)

	solubility in water (g L^{-1}) at			
gas	0 °C	10 °C	20 °C	25 °C
O_2[a]	0.0701[b]	0.0545[b]	0.0443[b]	0.0406[b]
O_3	1.051[c]	0.802[c]	0.610[c]	
SO_2	228[d]	153.9[e]	106.6[e]	94.1[f]
N_2	0.0296[e]		0.0194[e]	0.0175[f]
NO	0.0983[g]	0.0770[g]	0.0630[g]	0.0577[g]
N_2O	2.537[g]	1.728[g]	1.237[g]	1.065[g]
CO_2	3.35[f]		1.69[f]	1.45[f]

[a] See also section 2.3.1. [b] Reference 378. [c] Reference 379. [d] Reference 380. [e] Reference 381. [f] Reference 382. [g] Reference 383.

According to Radojevic and Clarke,[171] the oxidation process of SO_2 in rain water is too slow in order to produce significant amounts of SO_4^{2-} during the lifetime of a rain drop (approximately 2 min[377]). According to their results 45.5 h are needed to reach the SO_4^{2-} concentrations found in rain water samples (average oxidation rate of 1.34% h^{-1}, LWC = 0.5 g m^{-3}, T = 25 °C) (see also ref 172, p 145). Thus, the reason for high SO_4^{2-} concentrations in rain water is according to Radojevic and Clarke[171] oxidation processes that occur in cloud or fog droplets. A similar conclusion was reached by Tsunogai,[200] who suggested that the sulfate in rain water does not come from the immediate dissolution of SO_2 into falling rain drops, but may come from sulfate in aerosols which has been formed by oxidation in the air or in the cloud droplets prior to incorporation into the rain drops (see also ref 175). Betz[176] calculated that 90% of the sulfate in rain water is due to rainout processes in cloud elements.

2. Aqueous Phase Chemistry

2.1. Sulfur Oxides

In view of the transition metal-catalyzed oxidation of sulfur(IV) oxides a series of sulfur oxides are involved in the overall reaction process, e.g. HSO_3^-, SO_3^{2-}, $SO_3^{\bullet-}$, SO_4^{2-}, $SO_4^{\bullet-}$, SO_5^{2-}, $SO_5^{\bullet-}$, HSO_5^-, $S_2O_6^{2-}$. Sulfate, SO_4^{2-}, and dithionate, $S_2O_6^{2-}$, are the final reaction products (see section 3.5.6) and may have an influence on the overall reaction process (see section 3.5.1). The sulfite radical, $SO_3^{\bullet-}$, the sulfate radical, $SO_4^{\bullet-}$, the peroxomonosulfate radical, $SO_5^{\bullet-}$, and the hydrogen peroxomonosulfate anion, HSO_5^-, are intermediates. Information concerning these species is given in section 3.3.2. Depending on the pH, the hydrogen sulfite anion, HSO_3^-, or the sulfite anion, SO_3^{2-}, are the dominating sulfur(IV) species in atmospheric water droplets. Because of the important role of sulfur(IV) oxides as precursors in the acid rain formation we will only focus on these species in this section.

2.1.1. Hydrolysis of Sulfur Dioxide

In comparison with other atmospheric gases, SO_2 exhibits a rather good solubility in water (Table 2.1; for further information see e.g. refs 384 and 385), which results in an enrichment of sulfur(IV) in

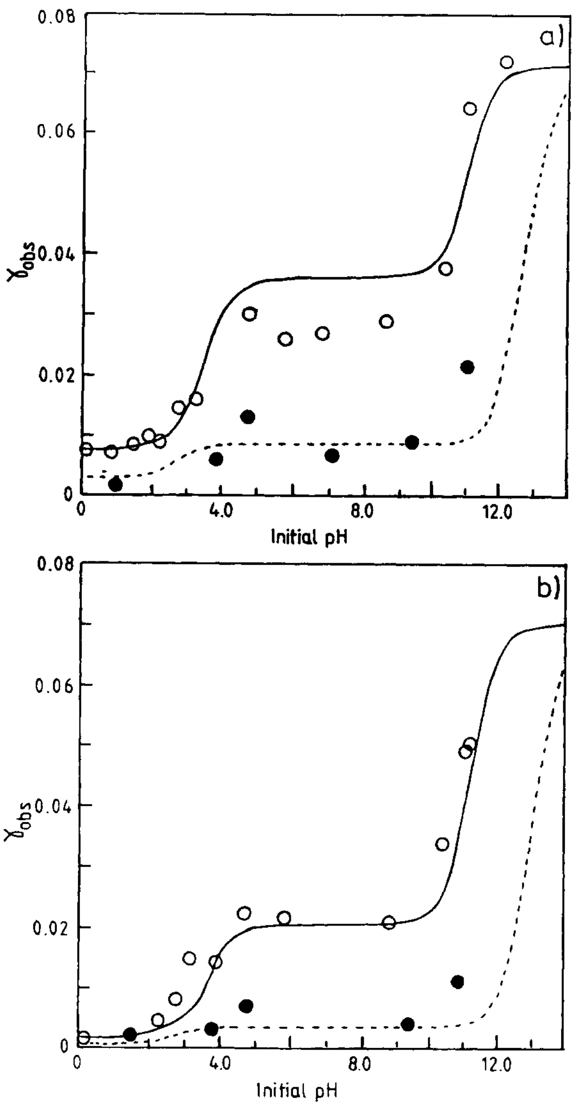


Figure 2.1. Uptake coefficient γ as a function of initial droplet pH (a) gas–droplet interaction time 2 ms; (b) gas–droplet interaction time 10 ms (according to ref 386).

atmospheric water droplets. Due to the fact that the solubility of SO_2 is pH dependent, an acidic atmospheric water droplet can adsorb only a small amount of SO_2 (Figure 2.1). The SO_2 uptake coefficient γ decreases with decreasing pH.[386] At pH > 5 the uptake of SO_2 into a water droplet is limited by the rate of reaction 2.1.

$$SO_2(g) + H_2O \rightarrow HSO_3^- + H^+ \qquad (2.1)$$

During this reaction a $HSO_3^-{-}H^+$ surface complex may be formed, which is in equilibrium with the SO_2 in the gas phase. At pH 4 and a droplet size of 10 μm, 30% of the dissolved sulfur(IV) is estimated to exist as the surface complex.[386] For the salting-out effect (see section 2.3.2) in the case of SO_2 see ref 384.

Depending on pH, the sulfur(IV) species $SO_2{\cdot}H_2O$ (pH < 1.5), HSO_3^- (pH 1.5–6.5) and SO_3^{2-} (pH > 6.5) are the dominant forms in aqueous solution (eq 2.2 to 2.4, Figure 2.2). Equilibrium and rate constants are summarized in Tables 2.2 and 2.3, respectively.

The distribution and reactions of the sulfur(IV) species are further influenced by ionic strength[409] (see also Figure 2.3 and section 3.5.2).

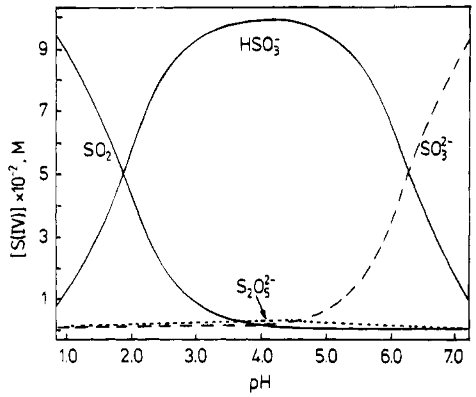


Figure 2.2. Distribution of sulfur(IV) oxide species as a function of pH; $[Na_2S_2O_5] = 5.0 \times 10^{-2}$ M, $T = 25$ °C.[387]

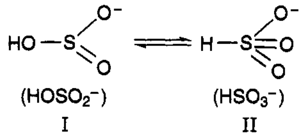
$$SO_2(g) + H_2O \rightleftharpoons SO_2{\cdot}H_2O$$

$$H = 1.23 \text{ M atm}^{-1}\,{}^{388} \qquad (2.2)$$

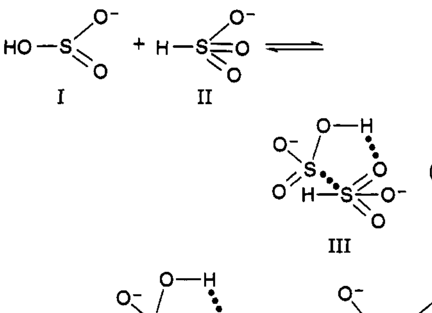
$$SO_2{\cdot}H_2O \rightleftharpoons HSO_3^- + H^+ \qquad pK_a = 1.86^{393} \qquad (2.3)$$

$$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+ \qquad pK_a = 7.2^{408} \qquad (2.4)$$

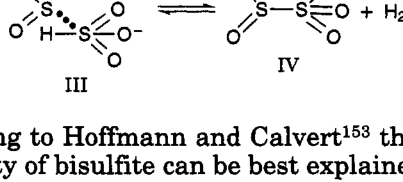
The hydrogen sulfite ion, HSO_3^-, can exist in aqueous solution in two tautomeric forms, I and II.[399,402,405,410–412] According to Simon and Waldmann[411b] and Guthrie[405] the tautomeric form I is present in aqueous solution only in very small concentrations as compared to form II. Baird and Taylor[413] suggested that the H–S bonded tautomer is the most energetically favorable. In contrast, ab initio calculations by Strömberg et al.[414] indicated that the tautomeric form I is lower in energy than the form II. Furthermore, depending on the concentration a dimerization can also occur.[399,404] The so-called Golding-dimer III, $(HSO_3^-)_2$, is in equilibrium with the disulfite ion IV, $S_2O_5^{2-}$:[399,401,411]



low concentration (3×10^{-3} M) (2.5)



(high concentration) (10^{-2} M) (2.6)



(2.7)

According to Hoffmann and Calvert[153] the chemical reactivity of bisulfite can be best explained in terms of the tautomeric form I as the predominant species provided that the two tautomers are in rapid equilibrium. For example, the kinetics and mechanism of the hydrogen peroxide–bisulfite reaction (see

Table 2.2. Equilibrium Constants for Different Sulfur(IV) Species in Aqueous Solution

K	conditions	ref
	$SO_2(g) + H_2O \rightleftharpoons SO_2{\cdot}H_2O$	
1.13 M atm^{-1}	$T = 25$ °C	384
1.23 M atm^{-1}	$T = 25$ °C	388
1.3 M atm^{-1}	$T = 25$ °C	389
	$SO_2{\cdot}H_2O \rightleftharpoons HSO_3^- + H^+$	
1.39×10^{-2} M	$T = 25$ °C, $\mu = -$	390
1.72×10^{-2} M	$T = 25$ °C, $\mu = -$	391
1.32×10^{-2} M	$T = 25$ °C, $\mu = 0$ M	392
1.39×10^{-2} M	$T = 25$ °C, $\mu \leq 0.1$ M	393
1.68×10^{-2} M	$T = 25$ °C, $\mu = 0.2$ M	394
1.78×10^{-2} M	$T = 25$ °C, $\mu = 0.5$ M	394
2.14×10^{-2} M	$T = 25$ °C, $\mu = 0.5$ M	384
2.88×10^{-2} M^a	$T = 25$ °C, $\mu = 0.5$ M	395
2.40×10^{-2} M^a	$T = 25$ °C, $\mu = 1.0$ M	395
1.26×10^{-2} M	$T = 25$ °C, $\mu = 1.0$ M	396
2.34×10^{-2} M	$T = 25$ °C, $\mu = 1.0$ M	384
	$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+$	
6.24×10^{-8} M	$T = 25$ °C, $\mu = -$	391
7.58×10^{-8} M	$T = 25$ °C, $\mu = 0$ M	384
6.42×10^{-8} M	$T = 25$ °C, $\mu = 0$ M	392
1.29×10^{-7} M	$T = 25$ °C, $\mu = 0$ M	397
1.67×10^{-7} M	$T = 25$ °C, $\mu = 0.2$ M	394
2.0×10^{-7} M	$T = 25$ °C, $\mu = 0.5$ M	394
3.31×10^{-7} M	$T = 25$ °C, $\mu = 0.5$ M	384
7.41×10^{-7} M^a	$T = 25$ °C, $\mu = 0.5$ M	394
1.86×10^{-6} M^b	$T = 25$ °C, $\mu = 0.5$ M	398
3.02×10^{-6} M^c	$T = 25$ °C, $\mu = 0.5$ M	398
3.98×10^{-7} M	$T = 25$ °C, $\mu = 1.0$ M	384
5.01×10^{-7} M	$T = 25$ °C, $\mu = 1.0$ M	396
6.98×10^{-7} M^a	$T = 25$ °C, $\mu = 1.0$ M	395
1.62×10^{-6} M^b	$T = 25$ °C, $\mu = 1.0$ M	398
2.14×10^{-6} M^c	$T = 25$ °C, $\mu = 1.0$ M	398
2.34×10^{-6} M^d	$T = 25$ °C, $\mu = 1.0$ M	398
	$2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$	
7.0×10^{-2} M^{-1}	$T = 20$ °C, $\mu = -$	399
7.6×10^{-2} M^{-1}	$T = 25$ °C, $\mu = 0$ M	400
6.2×10^{-2} M^{-1}	$T = 20$ °C, $\mu = 1.0$ M	401
8.2×10^{-2} M^{-1}	$T = 25$ °C, $\mu = 1.0$ M	402
8.8×10^{-2} M^{-1}	$T = 25$ °C, $\mu = 1.0$ M	403
3.4×10^{-1} M^{-1}	$T = 25$ °C, $\mu = 2.0$ M	400
2.5×10^{-1} M^{-1}	$T = 20$ °C, $\mu = 5.0$ M	401
	$2HSO_3^- \rightleftharpoons (HSO_3^-)_2$	
1.75×10^{3} M^{-1}	$T = 25$ °C, $\mu = 0$ M	404
2.42×10^{3} M^{-1}	$T = 25$ °C, $\mu = 0.2$ M	404
	$HSO_3^- \rightleftharpoons SO_3H^-$	
3.98	$T = 25$ °C, $\mu = -$	405
4.9	$T = 25$ °C, $\mu = 1.0$ M	402

^{a} In NaCl solutions and presence of Mg^{2+}. ^{b} In NaCl solutions and presence of Ni^{2+}. ^{c} In NaCl solutions and presence of Mn^{2+}. ^{d} In NaCl solutions and presence of Co^{2+}.

Table 2.3. Rate Constants for the Solvolysis of Sulfur Dioxide and the Dimerization of Bisulfite

k	conditions	ref
	$SO_2{\cdot}H_2O \underset{2}{\overset{1}{\rightleftharpoons}} HSO_3^- + H^+$	
(1) 3.4×10^{6} s^{-1}	$T = 20$ °C, $\mu = 0.1$ M	406
1.06×10^{8} s^{-1}	$T = 24.7$ °C, $\mu = 0.9$ M	407
(2) 2.0×10^{8} M^{-1} s^{-1}	$T = 20$ °C, $\mu = 0.1$ M	406
2.48×10^{8} M^{-1} s^{-1}	$T = 24.7$ °C, $\mu = 0.9$ M	407
	$2HSO_3^- \underset{2}{\overset{1}{\rightleftharpoons}} S_2O_5^{2-} + H_2O$	
(1) 7.0×10^{2} M^{-1} s^{-1}	$T = 24.7$ °C, $\mu = 0.9$ M	407
(2) 1.0×10^{4} s^{-1}	$T = 24.7$ °C, $\mu = 0.9$ M	407

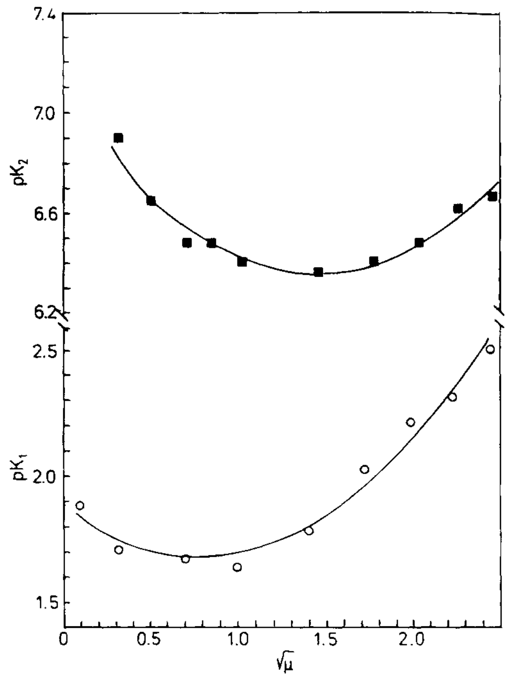


Figure 2.3. Dependence of the first and second dissociation constant of H_2SO_3 in NaCl solutions on ionic strength at $T = 25$ °C ($K_1 = ([H^+][HSO_3^-]/[SO_2])$; $K_2 = ([H^+][SO_3^{2-}]/[HSO_3^-])$ (according to ref 384).

Table 2.4. Lewis Base Strength of Different Ligands[417] (see also ref 418, p 54)

ligand L^{n-}	Lewis base strength of L^{n-}	K_a of the corresponding oxoacid HL
ClO_4^-	0.25	10^8
NO_3^-	0.33	10^3
ClO_3^-	0.33	10^3
H_2O	0.40	
SO_4^{2-}	0.50	10^{-2}
NO_2^-	0.50	5.0×10^{-4}

section 3.2.3) suggest that the pyramidal $HOSO_2^-$ form would provide a stereochemically more tractive site for attack by a nucleophile than the tetrahedral tautomer HSO_3^-. The latter would be more sterically hindered and consequently require a higher activation energy.

2.2. Transition Metals

2.2.1. Solvolysis of Transition Metal Ions

The solvolysis of transition metal ions in water can be described by eq 2.8, where A^{n-} represents the anion of the dissolved metal salt. Equation 2.8 can

$$M^{z+} + yH_2O + aA^{n-} \rightleftharpoons [M(H_2O)_{y-v}(OH)_vA_a]^{(z-v-an)+} + vH^+ \quad (2.8)$$

be simplified to eq 2.9 when noncomplexing anions,

$$M^{z+} + yH_2O \rightleftharpoons [M(H_2O)_{y-v}(OH)_v]^{(z-v)+} + vH^+ \quad (2.9)$$

such as perchlorate,[f] ClO_4^-,[415-417] are used (see Table 2.4). During the solvolysis of a metal salt in water

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[f] Perchlorate also exhibits a slight ability to form complexes, but it is less than for other anions. Feng and Waki[415] reported the following stability constants for iron(III) ($T = 20$ °C, $\mu = 0.4$ M): $FeClO_4^{2+}$; 2.1 M^{-1}; $FeNO_3^-$; 3.2 M^{-1}; $FeCl^{2+}$; 7.2 M^{-1}.

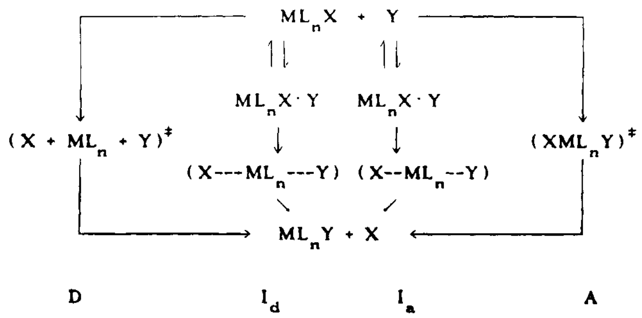


Figure 2.4. Ligand exchange mechanisms for metal complexes.

the O atoms of the water molecules coordinate directly to the metal ions (inner sphere).[419,420]

The behavior of dissolved metal ions in water can be described as a function of charge, ionic radius, and electronic structure.[421] The aquated metal ions exhibit characteristic acid–base equilibria. Water molecules, bound to a metal ion, are often much more acidic than uncoordinated (free) water molecules, usually by several orders of magnitude. For example, the pK_a of uncoordinated water (15.7) decreases to 9 for the $[Ni(H_2O)_6]^{2+}$ and to 3 for the $[Fe(H_2O)_6]^{3+}$ complex, respectively.[422] Substitution reactions of ligands proceed according to different mechanisms.[423–425] In general, substitution mechanisms can be divided into dissociative (d) and associative (a) processes. A transition between both forms are the so called interchange mechanisms (I_d and I_a).[426] These mechanisms are summarized in Figure 2.4. Experimental evidence for the mechanism of a substitution reaction can be obtained from the rate law and the associated activation parameters $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$. Significantly positive values for $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ indicate a dissociative, whereas significantly negative values an associative mechanism, respectively.

The water exchange rate has been measured for many metal ions and water exchange can be the rate-limiting factor in a substitution reaction. It is assumed[427] that the mechanism of many substitution reactions involves the fast association of the anion A^{a-} with the hydrolyzed metal ion in the second coordination (solvation) sphere of the metal ion (encounter complex formation), followed by a rate-determining interchange of ligands:

$$[M(H_2O)_n]^{m+} + A^{a-} \xrightleftharpoons{\text{very fast}} \{[M(H_2O)_n]^{m+}{\cdot}A^{a-}\} \qquad (2.10)$$

$$\{[M(H_2O)_n]^{m+}{\cdot}A^{n-}\} \xrightarrow{\text{slow}} [M(H_2O)_{n-1}A]^{(m-a)+} + H_2O \qquad (2.11)$$

The substitution mechanism depends on the nature of the metal ion. For example, the substitution of a water ligand by an entering nucleophile proceeds according to an associative interchange mechanism (I_a) for the iron(III) hexaaqua ion, $[Fe(H_2O)_6]^{3+}$, but according to a dissociative interchange mechanism for the iron(III) pentaaquahydroxo ion, $[Fe(H_2O)_5OH]^{2+}$ [428,429] (see also ref 430 for water exchange reactions by divalent metal ions).

The metal aqua–hydroxo complexes may dimerize or polymerize,[431] depending on pH and concentration (see section 2.2.2). The resulting species can contain μ-oxo or μ-hydroxo bridges (eqs 2.12 and 2.13).

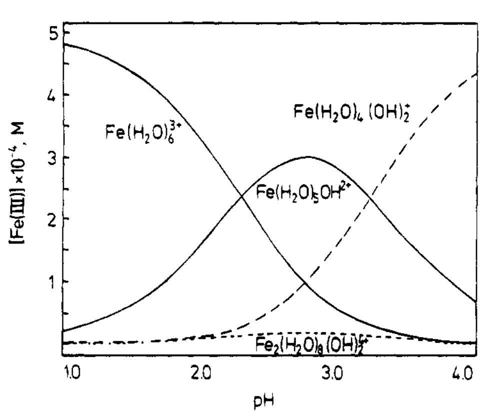
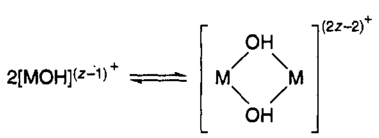


Figure 2.5. Distribution of iron(III) species as a function of pH; [Fe(III)] = 5.0 × 10⁻⁴ M, T = 25 °C.[387]

$$2[MOH]^{(z-1)+} \rightleftharpoons [M{-}O{-}M]^{(2z-2)+} + H_2O \qquad (2.12)$$



$$2[MOH]^{(z-1)+} \rightleftharpoons \left[M(\mu\text{-}OH)_2M \right]^{(2z-2)+} \qquad (2.13)$$

According to Mattock[432] the tendency for dimerization of metal ions increases with increasing covalency of the metal hydroxy bond.

The influence of oxo anions on the formation of ligand-bridged double salts in $M_nL_2{-}M'_nL_2{-}H_2O$ systems (M, M′ = Mn, Fe, Co, Ni, Cu, etc.) depends on the Lewis base strength of the oxo anions (Table 2.4).[417] Double salts are formed when the Lewis base strength of the oxo ligand is higher than that of water. In addition, the ability of double salt formation correlates with the K_a values for the corresponding oxo acids.[417]

2.2.2. Solvolysis of Iron and Manganese

Iron and manganese are the most abundant transition metals in the atmosphere (see section 4). Their solvolysis chemistry in water is rather complex and cannot be treated in detail in this review. For further information see e.g. refs 419 and 433–442. Stability constants of some iron and manganese complexes are summarized in Table 2.5.

Manganese(II) at normal concentrations is not hydrolyzed appreciably before precipitation occurs at pH near 8.[437] For iron(II) the dominant species in aqueous solution up to pH 7 is the iron(II) hexaaqua ion, $Fe(H_2O)_6^{2+}$.[449] This is in contrast to the behavior of iron(III) in aqueous solution, which exists in many different forms, depending on the concentration and the pH (see Figure 2.5). These iron(III) complexes all exhibit different stabilities and reactivities (Tables 2.5 and 2.6). The iron(III)–pentaaquahydroxo complex is about 1000 times more reactive than the hexaaqua complex (see e.g. refs 508–510), which is probably due to the translabilization effect of the hydroxy ligand.

Important features for the atmospheric significance of transition metal ions as catalysts during the

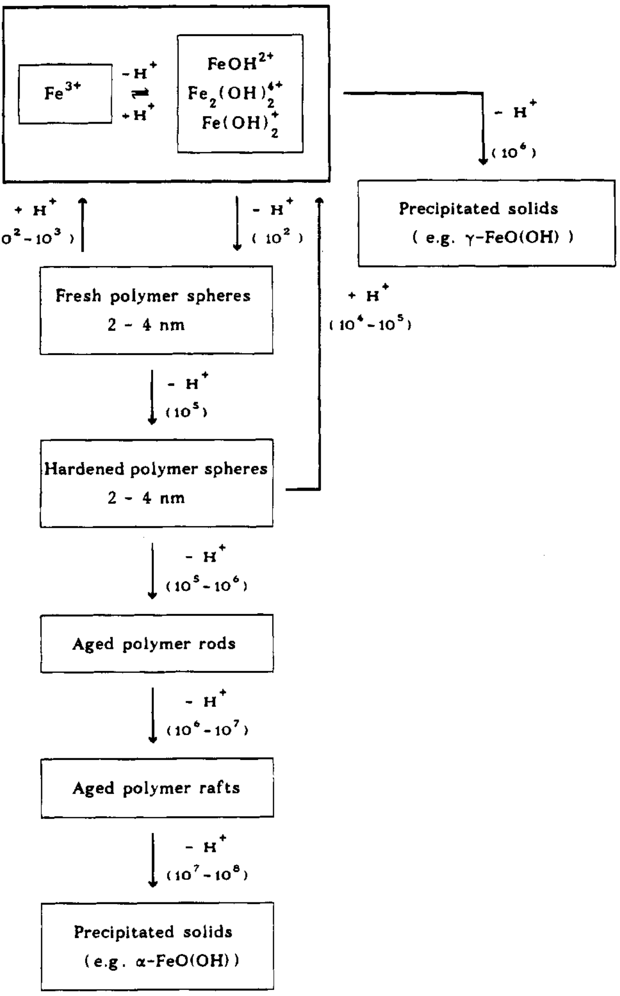


Figure 2.6. Hydrolysis processes in iron(III) solutions. Numbers in parentheses give reaction time in seconds at 25 °C.[419]

oxidation of sulfur(IV) oxides are the dimerization (polymerization) and aging processes of dissolved metal ions, which have an important influence on the overall redox reactions.[511] Aqua hydroxo complexes of iron are inclined to dimerize or polymerize at concentrations $>10^{-3}$ M.[454,512–514] At an iron(III) concentration of 1.1×10^{-4} M, the fraction of dinuclear and trinuclear species is reported to be as high as 0.52 at pH 2.5[515] (see also ref 450). In contrast, Kraft[387] estimated for a 5.0×10^{-4} M solution at 2.5 that only 2% of the iron is in the dimeric form. The dimerization/polymerization results with time, also in acidic solutions, in the precipitation of iron hydroxides (see Figure 2.6).[419,513,516] The structure of the precipitated iron hydroxides depends on the anions present in solution. Addition of base to aqueous solutions of iron(III) perchlorate results in the precipitation of α-FeO(OH), whereas in the case of iron(III) chloride, β-FeO(OH) precipitates.[517–519] β-FeO(OH) converts into α-FeO(OH) during the further aging process. Depending on the degree of neutralization, α-Fe_2O_3 is also formed.[520] In addition, the precipitation temperature has a direct influence on the crystallization of the amorphic precipitate during the aging process. Depending on the temperature, the precipitation from iron(III) nitrate solutions can consist of Fe_2O_3 (hematite) and α-FeO(OH) (goethite).[521] The influence of pH, temperature and other reaction parameters on the formation of α-FeO(OH) from $Fe(OH)_2$ have been studied recently.[522]

Sulfate acts in a labilizing way on the stability of iron(III) solutions. The solution ages faster and the produced precipitate consists of α-FeO(OH) and α-Fe_2O_3.[523,524] Furthermore, the formation of the dimeric species $(FeOH)_2^{4+}$ occur more rapidly in the presence of sulfate.[454,457] Recently, Lepentsiotis[525] observed, that a high excess of sulfate (10^3–10^4) suppresses precipitation in iron(III) solutions with a pH ≤ 4.5 over several hours. Chloride stabilizes the formed polymers, because the Cl^- ions are still incorporated in the structure and are easily displaced by OH^-.[519] Figure 2.6 summarizes the aging processes of aqueous iron(III) solutions.

The dimer $(H_2O)_4Fe(OH)_2Fe(H_2O)_4^{4+}$ which is the third most abundant iron species (after $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5(OH)^{2+}$) in aqueous solution of low acidity,[453,456] dissociates by two parallel pathways, an acid-independent (k_a) and an acid-dependent one (k_b):[454,526–528]

$$(H_2O)_4Fe(OH)_2Fe(H_2O)_4^{4+} + 2H_2O \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} 2Fe(H_2O)_5(OH)^{2+}$$

$$(H_2O)_4Fe(OH)_2Fe(H_2O)_4^{4+} + H^+ + 2H_2O \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} Fe(H_2O)_6^{3+} + Fe(H_2O)_5(OH)^{2+}$$

2.3. Oxidants

The oxidation of sulfur(IV) oxides in the atmosphere can be induced by several oxidants, e.g. O_2, O_3, H_2O_2, via uncatalyzed and catalyzed pathways (see section 3). Besides these, some other oxidants are formed as intermediates, e.g. SO_3^-, SO_5^-, HSO_5^-. The latter species will be treated in section 3.3.2. Sulfite can also act as oxidant and its role in oxidizing reduced transition metal ions is discussed in section 3.3.4. Whether or not transition metal ions have a catalytic effect on the oxidation of sulfur(IV) oxides by O_3 or H_2O_2 is still a subject of controversy (see sections 3.2.2 and 3.2.3). The oxygen-induced oxidation (autoxidation) of sulfur(IV) oxides has been known for over a hundred years to be sensitive toward the presence of transition metal ions (see Introduction). In addition, for atmospheric oxidation processes, oxygen is an ambient oxidant which plays an important role in the overall transition metal-catalyzed oxidation process (see sections 3.3.2 and 3.3.4). For further information on oxygen chemistry see also ref 529.

2.3.1. Redox Behavior of Oxygen

The dioxygen molecule ($^{\bullet}O_2^{\bullet}$, triplet ground state) is a unique reagent with two unpaired electrons (biradical) and a bond order of 2.[529] All the chemistry of oxygen is characterized by these properties and only spin-allowed reactions are possible.[530]

Under mild conditions, oxygen reacts slowly in oxidation processes since the reduction of oxygen

Table 2.5. Equilibrium Constants for Some Transition Metal Complexes in Aqueous Solution

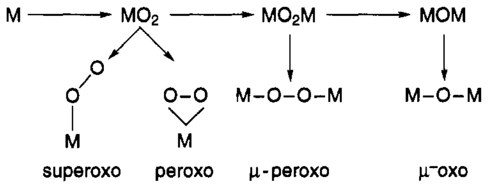
K	conditions	ref	K	conditions	ref
(a) Iron(III) Complexes					
$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+$					
6.0×10^{-3} M	$T = 25$ °C, $\mu = 0$ M	443	1.72×10^{-3} M	$T = 25$ °C, $\mu = 0.68$ M^b	448
2.5×10^{-3} M	$T = 25$ °C, $\mu = 0.1$ M	444	2.3×10^{-3} M	$T = 25$ °C, $\mu = 0.68$ M^c	448
6.4×10^{-3} M	$T = 25$ °C, $\mu = 0.1$ M	445	1.99×10^{-3} M	$T = 25$ °C, $\mu = 0.7$ M	443
1.39×10^{-3} M	$T = 25$ °C, $\mu = 0.2$ M	394	1.7×10^{-3} M	$T = 25$ °C, $\mu = 0.8$ M	449
2.2×10^{-3} M	$T = 25$ °C, $\mu = 0.25$ M	446	1.73×10^{-3} M	$T = 25$ °C, $\mu = 1.0$ M	444
4.0×10^{-3} M	$T = 25$ °C, $\mu = 0.3$ M	443	6.2×10^{-4} M	$T = 25$ °C, $\mu = 1.0$ M^d	450
1.03×10^{-3} M	$T = 25$ °C, $\mu = 0.5$ M	394	1.7×10^{-3} M	$T = 25$ °C, $\mu = 1.0$ M^e	450
1.8×10^{-3} M	$T = 25$ °C, $\mu = 0.5$ M	444	1.9×10^{-3} M	$T = 25$ °C, $\mu = 1.0$ M^a	450
2.3×10^{-3} M	$T = 25$ °C, $\mu = 0.5$ M	447	9.0×10^{-4} M	$T = 25$ °C, $\mu = 3.0$ M	434
1.68×10^{-3} M	$T = 25$ °C, $\mu = 0.68$ M^a	448			
$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_4(OH)_2]^+ + 2H^+$					
4.33×10^{-7} M^2	$T = 25$ °C, $\mu = 0.2$ M	394	5.1×10^{-7} M^2	$T = 25$ °C, $\mu = 1.0$ M^a	450
1.07×10^{-7} M^2	$T = 25$ °C, $\mu = 0.5$ M	394	2.5×10^{-7} M^2	$T = 25$ °C, $\mu = 1.0$ M^e	450
5.3×10^{-8} M^2	$T = 25$ °C, $\mu = 0.68$ M^a	448	1.9×10^{-7} M^2	$T = 25$ °C, $\mu = 1.0$ M^d	450
9.1×10^{-8} M^2	$T = 25$ °C, $\mu = 0.68$ M^c	448	2.0×10^{-6} M^2	$T = 25$ °C, $\mu = 2.67$ M	444
9.9×10^{-8} M^2	$T = 25$ °C, $\mu = 0.68$ M^b	448	4.9×10^{-7} M^2	$T = 25$ °C, $\mu = 3.0$ M	434
$[Fe(H_2O)_5(OH)]^{2+} \rightleftharpoons [Fe(H_2O)_4(OH)_2]^+ + H^+$					
7.6×10^{-4} M	$T = 25$ °C, $\mu \leq 3 \times 10^{-4}$ M	451	9.8×10^{-4} M	$T = 25$ °C, $\mu = 1.0$ M	452
$2[Fe(H_2O)_6]^{3+} \rightleftharpoons [(H_2O)_5Fe(OH)Fe(H_2O)_5]^{5+} + H^+ + H_2O$					
0.105	$T = 20$ °C, $\mu = -$ M	453			
$2[Fe(H_2O)_6]^{3+} \rightleftharpoons [(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{4+} + 2H^+ + 2H_2O$					
1.0×10^{-3} M	$T = 20$ °C, $\mu = -$	453	6.0×10^{-4} M	$T = 25$ °C, $\mu = 1.0$ M^e	450
2.3×10^{-2} M	$T = 25$ °C, $\mu = 0$ M	454	6.3×10^{-4} M	$T = 25$ °C, $\mu = 1.0$ M^a	450
6.91×10^{-4} M	$T = 25$ °C, $\mu = 0.2$ M	394	6.0×10^{-4} M	$T = 25$ °C, $\mu = 2.67$ M	444
1.8×10^{-3} M	$T = 25$ °C, $\mu = 0.25$ M	446	1.2×10^{-3} M	$T = 25$ °C, $\mu = 3.0$ M	434
6.18×10^{-4} M	$T = 25$ °C, $\mu = 0.5$ M	394	4.4×10^{-3} M	$T = 25$ °C, $\mu = 3.0$ M	455
8.1×10^{-5} M	$T = 25$ °C, $\mu = 1.0$ M^d	450	8.1×10^{-3} M	$T = 25$ °C, $\mu = 3.0$ M	452
$2[Fe(H_2O)_5(OH)]^{2+} \rightleftharpoons [(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{4+} + 2H_2O$					
44 M^{-1}	$T = 25$ °C, $\mu = 0$ M	456	450 M^{-1}	$T = 25$ °C, $\mu = 0.5$ M	457
370 M^{-1}	$T = 25$ °C, $\mu = 0.25$ M	446	700 M^{-1}	$T = 25$ °C, $\mu = 1.0$ M	456
$[Fe(H_2O)_6]^{3+} + Cl^- \rightleftharpoons [Fe(H_2O)_5Cl]^{2+} + H_2O$					
20 M^{-1}	$T = 25$ °C, $\mu = 0$ M	443	5.3 M^{-1}	$T = 25$ °C, $\mu = 2.7$ M	462
7.6 M^{-1}	$T = 20$ °C, $\mu = 0.4$ M	415	5.7 M^{-1}	$T = -$, $\mu = 3.0$ M	458
2.8 M^{-1}	$T = 25$ °C, $\mu = 0.68$ M	448	9.8 M^{-1}	$T = 25$ °C, $\mu = 3.0$ M	460
3.3 M^{-1}	$T = -$, $\mu = 1.0$ M	458	10.7 M^{-1}	$T = 25$ °C, $\mu = 3.7$ M	463
4.3 M^{-1}	$T = 25$ °C, $\mu = 1.0$ M	459	7.6 M^{-1}	$T = 25$ °C, $\mu = 4.0$ M	464
5.2 M^{-1}	$T = 25$ °C, $\mu = 1.0$ M	460	17.3 M^{-1}	$T = 25$ °C, $\mu = 4.0$ M	460
58 M^{-1}	$T = -$, $\mu = 1.0$ M	458	36.3 M^{-1}	$T = 25$ °C, $\mu = 5.0$ M	460
1.5 M^{-1}	$T = 25$ °C, $\mu = 1.5$ M	461			
$[Fe(H_2O)_5OH]^{2+} + Cl^- \overset{H^+}{\rightleftharpoons} [Fe(H_2O)_5Cl]^{2+} + H_2O$					
11.7 M^{-1}	$T = 25$ °C, $\mu = 1.5$ M	461			
$[Fe(H_2O)_6]^{3+} + 2Cl^- \rightleftharpoons [Fe(H_2O)_4Cl_2]^+ + 2H_2O$					
0.44 M^{-2}	$T = 25$ °C, $\mu = 0.68$ M	448	0.43 M^{-2}	$T = -$, $\mu = 3.0$ M	458
0.28 M^{-2}	$T = 25$ °C, $\mu = 1.0$ M	462	6.3 M^{-2}	$T = 25$ °C, $\mu = 4.0$ M	464
1.82 M^{-2}	$T = 25$ °C, $\mu = 2.7$ M	462	2.45 M^{-2}	$T = -$, $\mu = 6.0$ M	458
$[Fe(H_2O)_6]^{3+} + HSO_3^- \rightleftharpoons [Fe(H_2O)_5(HSO_3)]^{2+} + H_2O$					
55 M^{-1}	$T = 25$ °C, $\mu = 0.2-0.5$ M	394	72.0 M^{-1}	$T = 24$ °C, $\mu = -$	466
66.8 M^{-1}	$T = 25$ °C, $\mu = 0.4$ M	465	79.4 M^{-1}	$T = 25$ °C, $\mu = 1.0$ M	397
$[Fe(H_2O)_5(OH)]^{2+} + HSO_3^- \rightleftharpoons [Fe(H_2O)_4(HSO_3)(OH)]^+ + H_2O$					
600 M^{-1}	$T = 25$ °C, $\mu = 0.1$ M	445	850 M^{-1}	$T = 25$ °C, $\mu = 0.2-0.5$ M	394
700 M^{-1}	$T = 24$ °C, $\mu = -$	466			
$[Fe(H_2O)_6]^{3+} + SO_3^{2-} \rightleftharpoons [Fe(H_2O)_5(SO_3)]^+ + H_2O$					
7.0×10^6 M^{-1}	$T = 25$ °C, $\mu = -$	394	1.58×10^7 M^{-1}	$T = 25$ °C, $\mu = 1.0$ M	397
3.98×10^6 M^{-1}	$T = 25$ °C, $\mu = 0.4$ M	465			
$[Fe(H_2O)_5(OH)]^{2+} + H_2O{\cdot}SO_2 \rightleftharpoons [Fe(H_2O)_5(SO_3H)]^{2+} + H_2O$					
700 M^{-1}	$T = 25$ °C, $\mu = -$	394			
$[Fe(H_2O)_5(OH)]^{2+} + SO_3^{2-} \rightleftharpoons [Fe(H_2O)_4(SO_3)(OH)] + H_2O$					
1.99×10^7 M^{-1}	$T = 25$ °C, $\mu = 0.4$ M	465			
$[Fe(H_2O)_6]^{3+} + HSO_4^- \rightleftharpoons [Fe(H_2O)_5(SO_4)]^+ + H_2O + H^+$					
8.9	$T = 25$ °C, $\mu = 0.5$ M	467	4.0	$T = 25$ °C, $\mu = 2.67$ M	444
8.8	$T = 25$ °C, $\mu = 1.2$ M	467	33.8	$T = 25$ °C, $\mu = 3.0$ M	452
9.15	$T = 25$ °C, $\mu = 2.0$ M	467			

Table 2.5. (Continued)

K	conditions	ref	K	conditions	ref
$[Fe(H_2O)_6]^{3+} + SO_4^{2-} \rightleftharpoons [Fe(H_2O)_5(SO_4)]^{+} + H_2O$					
2.63×10^2 M^{-1}	T = 25 °C, μ = 0.25 M	468	1.2×10^2 M^{-1}	T = 25 °C, μ = 1.0 M	469
3.83×10^2 M^{-1}	T = 20 °C, μ = 0.4 M	415	1.1×10^2 M^{-1}	T = 25 °C, μ = 2.0 M	467
1.8×10^2 M^{-1}	T = 25 °C, μ = 0.5 M	469	0.84×10^2 M^{-1}	T = 25 °C, μ = 2.67 M	444
1.62×10^2 M^{-1}	T = 25 °C, μ = 0.75 M	468			
$[Fe(H_2O)_6]^{3+} + 2SO_4^{2-} \rightleftharpoons [Fe(H_2O)_4(SO_4)_2]^{-} + 2H_2O$					
1.7×10^3 M^{-1}	T = 20 °C, μ = 0.5 M	469	9.0×10^2 M^{-1}	T = 25 °C, μ = 1.0 M	469
$[Fe(H_2O)_6]^{3+} + HCOOH \rightleftharpoons [Fe(H_2O)_5(HCOO)]^{2+} + H_2O + H^+$					
50	T = –, μ = 1.0 M	470	1260	T = 20 °C, μ = 1.0 M	471
$[Fe(H_2O)_6]^{3+} + H_3CCOOH \rightleftharpoons [Fe(H_2O)_5(H_3CCOO)]^{2+} + H_2O + H^+$					
1.12×10^3	T = 25 °C, μ = 0 M	472	1.58×10^3	T = 20 °C, μ = 1.0 M	471
2.4×10^3	T = –, μ = 0.1 M	473	1.7×10^3	T = 25 °C, μ = 3.0 M	474
1.58×10^3	T = –, μ = 1.0 M	473			
(b) Iron(II), Manganese(III), and Manganese(II) Complexes[g]					
$[Fe(H_2O)_6]^{2+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{+} + H^+$					
5.01×10^{-10} M	T = 25 °C, μ = –	479	2.57×10^{-10} M	T = 25 °C, μ 0.1 M	483
1.20×10^{-8} M	T = 25 °C, μ = –	480	3.16×10^{-10} M	T = 25 °C, μ = 1.0 M	433
1.82×10^{-7} M	T = 25 °C, μ = –	481	5.0×10^{-9} M	T = 25 °C, μ = 2.0 M[f]	484
3.23×10^{-10} M	T = 25 °C, μ = 0 M	482	8.5×10^{-9} M	T = 25 °C, μ = 2.0 M[a]	484
$[Fe(H_2O)_6]^{2+} \rightleftharpoons [Fe(H_2O)_4(OH)_2] + 2H^+$					
2.51×10^{-21} M	T = 25 °C, μ = –	437			
$[Fe(H_2O)_6]^{2+} + Cl^- \rightleftharpoons [Fe(H_2O)_5Cl]^{+} + H_2O$					
3.2 M^{-1}	T = 25 °C, μ = 0 M	472	6.0 M^{-1}	T = 25 °C, μ = 1.0 M	485
$[Fe(H_2O)_6]^{2+} + SO_4^{2-} \rightleftharpoons [Fe(H_2O)_5(SO_4)] + H_2O$					
158.5 M^{-1}	T = 25 °C, μ = 0 M	486			
$[Fe(H_2O)_6]^{2+} + H_3CCOOH \rightleftharpoons [Fe(H_2O)_5(H_3CCOO)]^{+} + H_2O + H^+$					
25.1	T = 25 °C, μ = 0 M	472	2.0	T = 20 °C, μ = 1.0 M	471
$[Mn(H_2O)_6]^{3+} \rightleftharpoons [Mn(H_2O)_5(OH)]^{2+} + H^+$					
2.5 M	T = 25 °C, μ = –	438	1.7 M	T = 23 °C, μ = 5.3 M	489
0.88 M	T = 25 °C, μ = 4.0 M	487	5.0 M[h]	T = 23 °C, μ = 6.0 M	490
0.93 M	T = 25 °C, μ = 4.0 M	488	1.3 M	T = 23 °C, μ = 6.1 M	489
$[Mn(H_2O)_6]^{2+} \rightleftharpoons [Mn(H_2O)_5(OH)]^{+} + H^+$					
2.82×10^{-11} M	T = 25 °C, μ = 0.015 M	491	1.74×10^{-11} M	T = 20 °C, μ = 1.5 M	491
2.57×10^{-11} M	T = 25 °C, μ = 0.04 M	491	3.16×10^{-11} M	T = 25 °C, μ = 1.0 M	492
$[Mn(H_2O)_6]^{2+} \rightleftharpoons [Mn(H_2O)_4(OH)_2] + 2H^+$					
1.09×10^{-13} M	T = 25 °C, μ = –	435	1.26×10^{-10} M	T = 25 °C, μ = 1.0 M	492
$2[Mn(H_2O)_6]^{2+} \rightleftharpoons [(H_2O)_4Mn(OH)Mn(H_2O)_4]^{3+} + H^+ + H_2O$					
1.35×10^{-10}	T = 25 °C, μ = 1.0 M	492			
$[Mn(H_2O)_6]^{2+} + Cl^- \rightleftharpoons [Mn(H_2O)_5Cl]^{+} + H_2O$					
3.85 M^{-1}	T = 20 °C, μ = 0.69 M	493	1.1 M^{-1}	T = 25 °C, μ = 1.1 M	494
46.8 M^{-1}	T = 25 °C, μ = 1.0 M	476			
$[Mn(H_2O)_6]^{2+} + 2Cl^- \rightleftharpoons [Mn(H_2O)_4Cl_2] + 2H_2O$					
1.80 M^{-2}	T = 20 °C, μ = 0.69 M	493			
$[Mn(H_2O)_6]^{2+} + SO_4^{2-} \rightleftharpoons [Mn(H_2O)_5(SO_4)] + H_2O$					
133 M^{-1}	T = 25 °C, μ = –	495	724.4 M^{-1}	T = 25 °C, μ = 0 M	486
280 M^{-1}	T = 25 °C, μ = –	496			
$[Mn(H_2O)_6]^{2+} + H_3CCOOH \rightleftharpoons [Mn(H_2O)_5(H_3CCOO)]^{+} + H_2O + H^+$					
0.04	T = 25 °C, μ = 0 M	477	4.07	T = 25 °C, μ = 0.16 M	497
25.1	T = 25 °C, μ = 0 M	472	4.9	T = 25 °C, μ = 1.0 M	476
6.3	T = 25 °C, μ = 0.1 M	478			

[a] In NaClO$_4$ solution. [b] In NaCl solution. [c] In NaNO$_3$ solution. [d] In KCl solution. [e] In KNO$_3$ solution. [f] In $(NH_4)_2SO_4$ solution. [g] For chloro and sulfato complexes of cobalt(II), copper(II), and nickel(II) see e.g. refs 475 and 476; for acetato complexes of these metals see e.g. refs 477 and 478. [h] Estimated value.

occurs stepwise (Figure 2.7).[532,533] The complete redox potential can only be used when the oxidation occurs in a more or less simultaneous four-electron process.[532] The oxidation potential of oxygen can be increased by the presence of metal ions.[530,534,535] The role of the metal ion in the activation of oxygen can be explained by the formation of metal oxygen complexes, in which the chemical character of the oxygen has changed.[536,537] The intermediate complexes must contain either a superoxo, peroxo, or an oxo ligand,[538] as shown in eq 2.14.



(2.14)

The complex has superoxo or peroxo structure when the metal is a one or two electron donor, respectively. These oxygen adducts can react with another metal to form the μ-peroxo species, MO_2M.

Table 2.6. Rate Constants for the Formation of Some Iron(III) Complexes in Aqueous Solution

k	conditions	ref	k	conditions	ref
$[Fe(H_2O)_6]^{3+} + H_2O \rightarrow Fe(H_2O)_6]^{3+} + H_2O$					
$1.6 \times 10^2\ s^{-1}$	$T = 25\ °C, \mu = 1.0\ M$	498	$1.67 \times 10^2\ s^{-1}$	$T = 25\ °C, \mu = 1.5\ M$	499
$[Fe(H_2O)_6]^{3+} \rightarrow Fe(H_2O)_5(OH)]^{2+} + H^+$					
$2.6 \times 10^6\ s^{-1}$	$T = 25\ °C, \mu = -$	500			
$[Fe(H_2O)_6]^{3+} + [Fe(H_2O)_5(OH)]^{2+} \rightarrow [(H_2O)_6Fe(OH)Fe(H_2O)_5]^{5+}$					
$2.5 \times 10^{-2}\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 0\ M$	454			
$[Fe(H_2O)_5(OH)]^{2+} \rightarrow [Fe(H_2O)_4(OH)_2]^+ + H^+$					
$6.1 \times 10^4\ s^{-1}$	$T = 25\ °C, \mu \leq 3 \times 10^{-4}\ M$	451			
$[Fe(H_2O)_5(OH)]^{2+} + H_2O \rightarrow [Fe(H_2O)_5(OH)]^{2+} + H_2O$					
$1.2 \times 10^5\ s^{-1}$	$T = 25\ °C, \mu = 1.0\ M$	498	$1.4 \times 10^5\ s^{-1}$	$T = 25\ °C, \mu = -$	428
$[Fe(H_2O)_5(OH)]^{2+} + H^+ \rightarrow [Fe(H_2O)_6]^{3+}$					
$1.5 \times 10^9\ s^{-1}$	$T = 25\ °C, \mu = 0.8\ M$	449			
$2[Fe(H_2O)_5(OH)]^{2+} \rightarrow [(H_2O)_5Fe(OH)_2Fe(H_2O)_5]^{4+}$					
$35\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 0\ M$	454	$450\ M^{-1}\ s^{-1}$	$T = 24.5\ °C, \mu = 0.5\ M$	457
$400\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 0.5\ M$	454			
$[Fe(H_2O)_4(OH)_2]^+ \xrightarrow{H^+} [Fe(H_2O)_5(OH)]^{2+}$					
$8.0 \times 10^9\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu \leq 3 \times 10^{-4}\ M$	451			
$[Fe(H_2O)_6]^{3+} + Cl^- \rightarrow [Fe(H_2O)_5Cl]^{2+} + H_2O$					
$4.8\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.0\ M$	498	$19\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.0\ M$	502
$9.4\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.0\ M$	501	$4.8\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.5\ M$	461
$[Fe(H_2O)_5(OH)]^{2+} + [Fe(H_2O)_5Cl]^{2+} \rightarrow [(H_2O)_5Fe(OH,Cl)Fe(H_2O)_5]^{4+}$					
$8.8\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 0\ M$	454	$100\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 0.5\ M$	454
$[Fe(H_2O)_5(OH)]^{2+} + Cl^- \rightarrow [Fe(H_2O)_4(OH)Cl]^+ + H_2O$					
$5.5 \times 10^4\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.0\ M$	498	$1.15 \times 10^4\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.0\ M$	502
$1.1 \times 10^4\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.0\ M$	501	$5.5 \times 10^3\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.5\ M$	461
$[Fe(H_2O)_6]^{3+} + HSO_3^- \rightarrow [Fe(H_2O)_5(SO_3)]^+ + H_2O + H^+$					
$<270\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.0\ M$	503			
$[Fe(H_2O)_5(OH)]^{2+} + HSO_3^- \rightarrow [Fe(H_2O)_5(SO_3)]^+ + H_2O$					
$\sim 4 \times 10^6\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = -$	394			
$[Fe(H_2O)_6]^{3+} + SO_4^{2-} \rightarrow [Fe(H_2O)_5(SO_4)]^+ + H_2O$					
$3.2 \times 10^3\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 0.5\ M$	469	$2.3 \times 10^3\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.0\ M$	498
$4.6 \times 10^3\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 0.5\ M$	467	$3.2 \times 10^3\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.2\ M$	467
$6.37 \times 10^3\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 0.5\ M$	504	$2.8 \times 10^3\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 2.0\ M$	467
$[Fe(H_2O)_5(OH)]^{2+} + [Fe(H_2O)_5(SO_4)]^+ \rightarrow [(H_2O)_5Fe(OH,SO_4)Fe(H_2O)_5]^{3+}$					
$30\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 0\ M$	454	$110\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 0.3\ M$	454
$[Fe(H_2O)_5(OH)]^{2+} + SO_4^{2-} \rightarrow [Fe(H_2O)_4(OH)(SO_4)] + H_2O$					
$2.3 \times 10^5\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 0.5\ M$	467	$1.1 \times 10^5\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.2\ M$	467
$1.1 \times 10^5\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.0\ M$	498	$7.8 \times 10^4\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 2.0\ M$	
$[Fe(H_2O)_6]^{3+} + HSO_4^- \rightarrow [Fe(H_2O)_5(SO_4)]^+ + H_2O + H^+$					
$\sim 38\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.2\ M$	467	$51\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 2.0\ M$	467
$[Fe(H_2O)_5OH]^{2+} + HCOOH \rightarrow [Fe(H_2O)_5(HCOO)]^+ + H_2O$					
$2.5 \times 10^3\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 1.0\ M$	505			
$[Fe(H_2O)_6]^{2+} + H_3CCOOH \rightarrow [Fe(H_2O)_5(H_3CCOO)]^+ + H_2O + H^+$					
$27\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 0.5\ M$	506	$4.8\ M^{-1}\ s^{-1}$	$T = 20\ °C, \mu = 1.0\ M$	507
$[Fe(H_2O)_5OH]^{2+} + H_3CCOOH \rightarrow [Fe(H_2O)_5(H_3CCOO)]^+ + H_2O$					
$2.8 \times 10^3\ M^{-1}\ s^{-1}$	$T = 25\ °C, \mu = 0.5\ M$	506	$5.3 \times 10^3\ M^{-1}\ s^{-1}$	$T = 20\ °C, \mu = 1.0\ M$	507

The latter species can be transformed into the oxo form, MO, by scission of the O–O bond or into the μ-oxo species, MOM, by loss of one oxygen atom.[538]

Oxygen can be reduced electrochemically to the peroxide anion without scission of the O–O bond:[530]

$$O_2 \rightarrow \underset{\text{superoxide}}{O_2^{\bullet -}} \rightarrow \underset{\text{peroxide}}{O_2^{2-}} \tag{2.15}$$

The first one-electron process is energetically unfavorable: the oxygen molecule is a weak oxidant if the product is superoxide or hydrogen superoxide, HO_2. In contrast, the superoxide anion is a strong reductant.[539] In the case of a complete reduction of the oxygen molecule the O–O bond must be cleaved in one of the reaction steps. Due to the fact that the scission of a single bond in the peroxide anion is energetically easier than the scission of a double bond, the scission of the O–O bond occurs following electron transfer to the oxygen molecule.[532]

2.3.2. Solubility of Oxygen

The solubility of a gas in pure water can be described by Henry's law (eq 2.16), according to which

$$c = Hp_g = Hy_g p \tag{2.16}$$

the concentration c of a gas in solution is proportional to its partial pressure p_g or the total gas pressure p above the solution. (For general information on gas

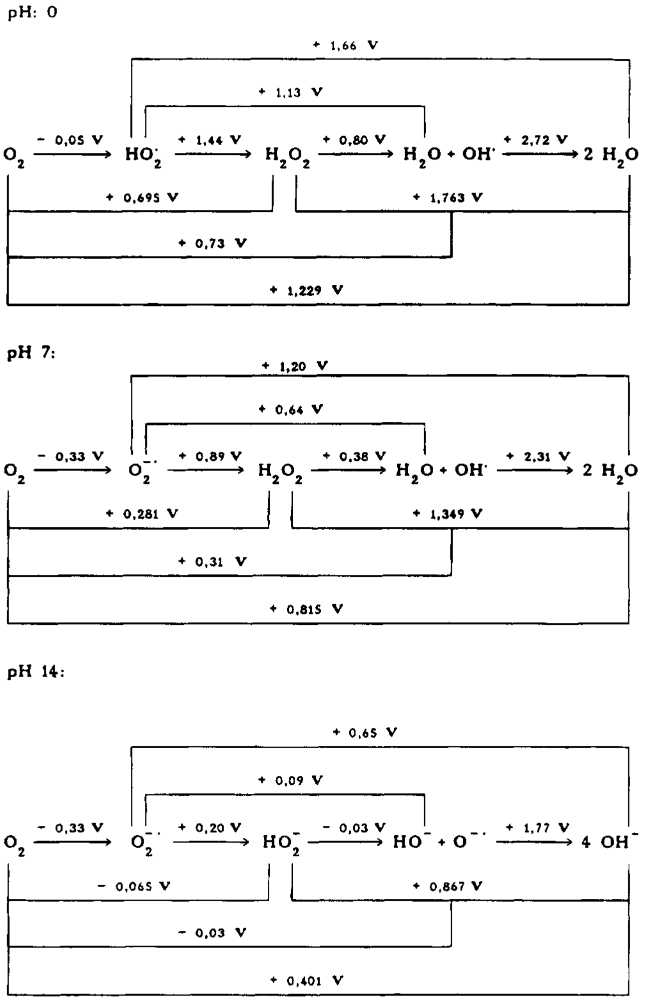


Figure 2.7. Reduction potentials of oxygen in water at $p_{O_2} = 1$ atm.[531]

solubility see e.g. refs 540 and 541; for the solubility of oxygen in sea water see ref 542.) If other substances are dissolved in the solution, the solubility of the gas decreases (salting-out effect; see Table 2.7 and refs 548 and 549) and may not follow Henry's law any longer.

The solubility of oxygen in aqueous sulfite media can be described by Henry's law ($T = 0-30$ °C, $P_{O_2} = 0.6-2$ bar, $c_{SO_3^{2-}} = 0.05-1.2$ M, pH ≈ 8).[546] Slight deviations from Henry's law have been observed in aqueous sulfate solutions.[550] For the solubility of oxygen in aqueous sulfate media, Linek and Vacek[547] reported an empirical equation (valid for $T = 15-35$ °C, $c_{SO_4^{2-}} = 0-1$ M) which can be used to calculate the oxygen concentration in an aqueous sulfate solution as a function of the $[SO_4^{2-}]$ (see Table 2.7):

$$c_{O_2} = (5.909 \times 10^{-6})p_{O_2} \times \exp\left[\frac{1602.1}{T} - \frac{0.9407c_{SO_4^{2-}}}{1 + 0.1933c_{SO_4^{2-}}}\right]M \quad (2.17)$$

With the assumption that the solubility of oxygen in sodium sulfite is equal to that in sodium sulfate (at 25 °C the solubility in aqueous sodium sulfite solutions is about 10% higher than in aqueous sodium sulfate solutions of the same concentration,[511,546] the oxygen solubility in aqueous sodium sulfite solutions has also been estimated for some concentrations in Table 2.7 with the aid of eq 2.17.

Table 2.7. Solubility of Oxygen in Aqueous Salt Solutions at 25 °C (p_{O_2} = 1 atm)

salt	[salt] (M)	[O2] (M)	ref
		1.25×10^{-3}	543
		1.27×10^{-3}	544
		1.27×10^{-3}	378
		1.27×10^{-3}	545
Na_2SO_3	0.05	1.25×10^{-3} [a]	546
	0.1	1.15×10^{-3} [b]	544
	0.125	1.25×10^{-3}	511
	0.2	1.12×10^{-3} [a]	546
	0.25	1.22×10^{-3}	511
	0.5	8.13×10^{-4} [b]	544
	0.5	1.08×10^{-3}	511
	0.6	8.72×10^{-4} [a]	546
	0.8	6.00×10^{-4} [a]	546
	1.0	5.56×10^{-4} [b]	544
	1.2	4.63×10^{-4}	546
Na_2SO_4	0.005	1.25×10^{-3}	511
	0.155	1.12×10^{-3}	544
	0.155	1.11×10^{-3} [c]	511
	0.25	1.08×10^{-3}	511
	0.25	1.02×10^{-3} [c]	511
	0.5	1.02×10^{-3}	511
	0.51	8.25×10^{-4}	544
	0.51	8.23×10^{-4} [c]	511
	0.998	5.95 t 10^{-4}	544
	1.0	8.57×10^{-4}	511
NaCl	0.25	1.24×10^{-3}	511
	0.5	1.07×10^{-4}	543
	0.5	1.16×10^{-3}	511
	1.0	8.92×10^{-4}	543
	1.0	1.09×10^{-3}	511
$NaClO_4$	0.1	1.22×10^{-3}	511
	0.3	1.17×10^{-3}	511
	0.5	1.15×10^{-3}	511
	1.0	1.11×10^{-3}	511
$NaHCO_3$	0.025	1.21×10^{-3}	511
	0.05	1.22×10^{-3}	511
	0.075	1.21×10^{-3}	511
	0.1	1.22×10^{-3}	511

[a] Calculated by Henry's law. [b] Estimated value. [c] Calculated value by an empirical equation of Linek and Vacek;[547] see text for further information.

In the case of atmospheric water droplets, salting-out effects may play an important role, because atmospheric water droplets may contain various dissolved ions. Thus, the concentration of dissolved gases may be less than theoretically expected. Different theories have been proposed, e.g. the hydration theory,[551] the electrostatic theory,[552] or the van der Waals theory,[553] to account for the salting-out effect.

The salting-out effect can be described for most electrolyte solutions by the relationship (eq 2.18) originally suggested by Setschenow,[554,555] where c_0

$$\log(c_0/c) = Kc_{el} \quad (2.18)$$

represents the solubility of the gas in water, c the concentration of the gas in the electrolyte solution with the concentration c_{el}, and K the Setschenow constant. This relationship was improved by van Krevelen and Hoftijzer[556] to include the ionic strength

Table 2.8. Solubility of Oxygen in Aqueous Solution at 25 °C as a Function of pH

pH	$[O_2]$, M	remarks	ref
6.5	1.52×10^{-4} [a]	0.8 M Na_2SO_3 solution; air saturated	559
6.5	1.53×10^{-4} [b]	0.8 M Na_2SO_3 solution; air saturated	559
7.5	1.53×10^{-4} [a]	0.8 M Na_2SO_3 solution; air saturated	559
7.5	1.53×10^{-4} [b]	0.8 M Na_2SO_3 solution; air saturated	559
8.0	1.54×10^{-4} [a]	0.8 M Na_2SO_3 solution; air saturated	559
8.0	1.53×10^{-4} [b]	0.8 M Na_2SO_3 solution; air saturated	559
9.0	1.54×10^{-4} [a]	0.8 M Na_2SO_3 solution; air saturated	559
9.0	1.53×10^{-4} [b]	0.8 M Na_2SO_3 solution; air saturated	559
5.0	1.25×10^{-3}	0.05 M KH_2PO_4–NaOH buffer;[c] O_2 saturated	511
6.0	1.26×10^{-3}	0.05 M KH_2PO_4–NaOH buffer;[c] O_2 saturated	511
7.0	1.24×10^{-3}	0.05 M KH_2PO_4–NaOH buffer;[c] O_2 saturated	511
8.0	1.26×10^{-3}	0.05 M KH_2PO_4–NaOH buffer;[c] O_2 saturated	511

[a] Calculated value by a relation of Schumpe et al.[550] [b] Calculated value by an empirical equation of Linek and Vacek;[547] see text for further information. [c] Buffer according to Perrin and Dempsey.[560]

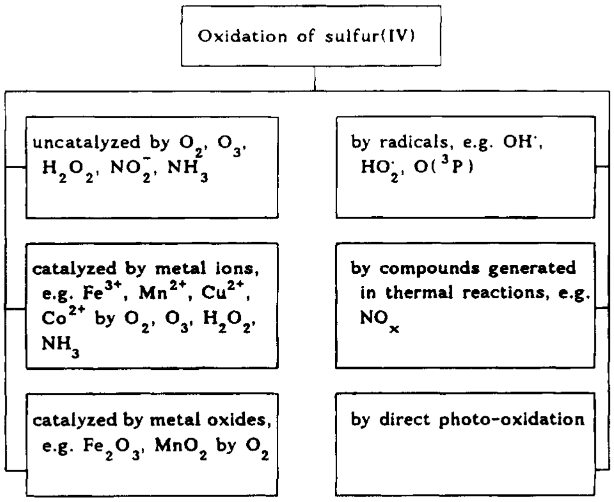


Figure 3.1. Pathways for the atmospheric oxidation of sulfur(IV) oxides.

μ and the salting-out constant h as given in eqs 2.19 and 2.20. The electrolyte activity can be better

$$\log(c_0/c) = h\mu \qquad (2.19)$$

$$h = h_G + h_+ + h_- \qquad (2.20)$$

described as function of the ionic strength and the salting-out constant h, which consists of the fractions of the dissolved gas (h_G), the dissolved cations (h_+), and the dissolved anions (h_-). For typical values of h_G, h_+, and h_- see refs 549, 550, 557, and 558. When using the salting-out theories it must be kept in mind, that nonpolar gases (e.g. O_2, H_2) dissolve as molecules, whereas polar gases undergo hydrolysis in aqueous solution.[558]

The pH of the aqueous solution has almost no influence on the stability of oxygen (Table 2.8; see also ref 549). A pH dependence was predicted by Tamura et al.[561] who used a carbonic acid–bicarbonate buffer system in their experiments. However, the partial pressure of oxygen changes with the partial pressure of carbon dioxide, which is much more soluble in water than oxygen (Table 2.1). Thus, the dissolved oxygen decreases with decreasing pH and reaches a value of 4.0×10^{-4} M at pH 6.0 and p_{O_2} = 1 atm.[561]

3. Mechanistic Considerations

3.1. General Information

The oxidation of sulfur(IV) species in the atmosphere follows different reaction pathways (Figure 3.1). Because of the very complex processes in the atmosphere it is impossible to distinguish between single reaction steps. Many processes run parallel, and may influence each other or depend on meteorological conditions (Table 3.1). A theoretical evaluation of the single processes is only possible by comparing the individual rate constants of these reactions. In addition, the chemistry in atmospheric water droplets is determined by their origin (continental or marine).[564,565] Water droplets with marine origin contain for instance much higher concentrations of chloride ions than continental water droplets. The latter usually exhibit higher concentrations of transition metal ions or oxides. Furthermore, it is important to distinguish between rain, cloud, and fog water. Measurements in North America indicate, that the concentrations of H^+, NO_3^-, and SO_4^{2-} ions are 5 to 10 times higher in cloud water than in rain water.[365,566,567] These ions can affect the oxidation of sulfur(IV) oxides (see section 3.5).

For a detailed discussion on atmospheric relevant S(IV) oxidation reactions see e.g. refs 153, 280, 568, and 569. The most important oxidizing agents in the case of the atmospheric oxidation of sulfur(IV) oxides are ozone, O_3 (see section 3.2.2),[570,571] hydrogen peroxide, H_2O_2 (see section 3.2.3),[570,571] and hydroxyl radicals, OH• (see section 3.2.4).[247,572] The possible catalytic role of transition metal ions in these processes and the contribution of the transition metal-catalyzed autoxidation to the overall reaction process still remains uncertain (see further Discussion).

In a dry atmosphere, SO_2 oxidation occurs via the gas phase reaction with e.g. OH• radicals. If clouds or fog are present, liquid-phase oxidation of SO_2 becomes the primary pathway for sulfate formation.[573] Furthermore, during the nighttime atmospheric SO_4^{2-} production is dominated by aqueous phase pathways.[569]

The fractional contribution of O_3 on the oxidation of sulfur(IV) oxides in fog is around 4% in 3 h.[243] For cloud water (pH $\geq$ 4), Seigneur and Saxena[573] calculated a contribution of 1 to 10% h^{-1} from O_3 on the SO_4^{2-} formation. In remote (normally rural) areas the O_3-induced oxidation can be compared with the

Table 3.1

(a) Contributions of Different SO_4^{2-} Formation Mechanisms after 5 min for Different Atmospheric Conditions (according to ref 562)

reaction pathway	formed SO_4^{2-} (μg m^{-3}) after 5 min: summer day	winter day	night
H_2O_2	0.5–1	4–6	10^{-4}–10^{-1}
Fe	10^{-5}–10^{-2}	10^{-5}–10^{-2}	5×10^{-4}–8×10^{-2}
Mn	7×10^{-7}–1×10^{-1}	7×10^{-7}–1×10^{-1}	1×10^{-8}–2×10^{-1}
O_3	10^{-6}–10^{-3}	8×10^{-6}–1×10^{-7}	5×10^{-7}–8×10^{-6}
C	2×10^{-3}–2×10^{-2}	3×10^{-3}–3×10^{-2}	5×10^{-2}–2×10^{-1}
uncat.	3×10^{-8}–1×10^{-5}	5×10^{-7}–1×10^{-6}	5×10^{-8}–5×10^{-4}

(b) Calculated Percentage of S(IV) Oxidation by Various Reactant Pathways[563] (see also Figure 3.3)

reactant	pH = 3		pH = 4	
	day	night	day	night
H_2O_2	>99	>99	71	63
Fe^{3+}	<1	<1	7	8
Mn^{2+}	<1	<1	22	29

Table 3.2. Estimated Oxidation Rates in Aqueous Solution for $[SO_2] = 10$ ppb[576]

catalyst or oxidant	oxidation rate (% h^{-1})					
	LWC[a] = 50 μg m^{-3}		LWC = 0.1 g m^{-3}		LWC = 1 g m^{-3}	
	pH = 2	pH = 3	pH = 2	pH = 3	pH = 2	pH = 3
Mn(II)[b]	10	10^3	2×10^4	2×10^6	2×10^5	2×10^7
Fe(III)[b]	0.5	5×10^3	10^3	10^7	10^4	10^8
C[b]	30	30	6×10^4	6×10^4	6×10^5	6×10^5
O_3						
40 ppb[c]	2×10^{-6}	2×10^{-4}	4×10^{-3}	4×10^{-1}	4×10^{-2}	4
120 ppb	6×10^{-6}	6×10^{-4}	1.2×10^{-2}	1.2	0.12	12
H_2O_2						
1 ppb[c]	3×10^{-2}	3×10^{-2}	60	60	6×10^2	6×10^2
10 ppb	0.2	0.3	4×10^2	6×10^2	4×10^3	6×10^3

[a] LWC = liquid water content. [b] $[Fe^{3+}] = 2$ μg m^{-3}, $[Mn^{2+}] = 2 \times 10^{-2}$ μg m^{-3}, [C] = 10 μg m^{-3} [c] 1 ppb $SO_2 \approx 2.66$ μg m^{-3}, 1 ppb $O_3 \approx 1.99$ μg m^{-3}, 1 ppb $H_2O_2 \approx 1.41$ μg m^{-3}, at $T = 20$ °C, $p = 1.013$ bar.[577]

synergistic catalyzed (see section 3.5.5) oxidation in the pH range 3–4.5.[574]

According to Saxena and Seigneur,[569] the aqueous phase reaction of SO_2 with H_2O_2 becomes important only at low temperatures, when the solubility of these gases is relatively high.

For polluted areas (e.g. cities) the uncatalyzed autoxidation is comparable with the iron-catalyzed reaction. In the presence of manganese ($c > 10^{-6}$ M, $3 \leq pH \leq 5$), the catalyzed reaction dominates.[569] Computer simulations[575] indicate that the contribution of the transition metal-catalyzed pathway on the SO_4^{2-} formation amounts to between 30–55% at pH 4 (see also Table 3.1b). Due to the low concentrations of transition metal ions in the atmosphere (see Table 1.7), this pathway plays, according to Cocks and McElroy,[563] only a minor role in the United States, whereas in England the iron-catalyzed autoxidation of SO_2 is as important as the oxidation by O_3.

The most important factors influencing the importance of the various SO_2 oxidation pathways are the meteorological conditions (e.g. the relative humidity), the season (e.g. the formation of OH• radicals depending on the solar radiation; see also Table 3.1), and the pollution level (e.g. the ambient concentration of trace metals; see Tables 1.7 and 1.8). Table 3.2 summarizes calculated SO_2 oxidation rates as function of the relative humidity. It is obvious that both the liquid water content (LWC) and the pH (see section 3.5.5 and Figure 3.2) have a certain influence on the SO_2 oxidation rate. With increasing LWC the oxidation rate increases. The importance of manganese catalysis decreases compared to the iron catalysis with increasing pH. The same results for the influence of LWC and pH were obtained by Cocks and McElroy,[563] who performed a similar calculation (LWC 0.5–1 g m^{-3}, pH 3–4) as shown in Table 3.2.

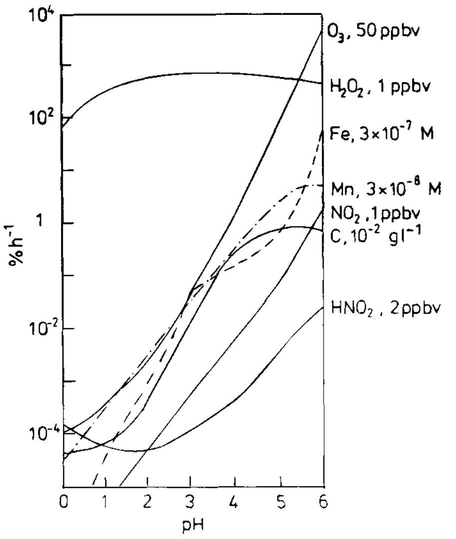


Figure 3.2. Percent per hour oxidation of total sulfur(IV) in a cloud. Conditions: $[SO_2] = 5$ ppbV, LWC = 1 mL m^{-3}, $T = 25$ °C; assumption: no rate limitations due to mass transport.[578]

Table 3.3 Rate Constants for Some Uncatalyzed Oxidation Reactions of Sulfur(IV) Oxides

k	reaction conditions	ref	*k*	reaction conditions	ref
S(IV) + O_2					
$1.18 \times 10^{-7}\ \mathrm{s^{-1}}$	pH 3.0, $T = 25$ °C	332	$9.5 \times 10^{-5}\ \mathrm{s^{-1}}$ [b]	pH 8.2–8.9, $T = 25$ °C	584
$1.72 \times 10^{-7}\ \mathrm{s^{-1}}$	pH 4.0, $T = 25$ °C	332	$1.7 \times 10^{-3}\ \mathrm{s^{-1}}$	pH 6.8, $T = 25$ °C	585
$9.19 \times 10^{-7}\ \mathrm{s^{-1}}$	pH 5.0, $T = 25$ °C	332	$3.0 \times 10^{-3}\ \mathrm{s^{-1}}$	pH 2–4, $T = 25$ °C	586
$1.63 \times 10^{-6}\ \mathrm{s^{-1}}$	pH 6.0, $T = 25$ °C	332	$3.5 \times 10^{-3}\ \mathrm{s^{-1}}$	pH 7.0, $T = 25$ °C	587
$1.3 \times 10^{-5}\ \mathrm{s^{-1}}$ [a]	pH 8.2–8.9, $T = 25$ °C	584	$1.3 \times 10^{-2}\ \mathrm{s^{-1}}$	pH 8.2–8.8, $T = 25$ °C	588
S(IV) + $O_2^{\bullet -}$					
$82\ \mathrm{M^{-1}\ s^{-1}}$	pH 9.8	589			
S(IV) + O_3					
$1.5 \times 10^{4}\ \mathrm{M^{-0.5}\ s^{-1}}$	pH 1–5, $T = 25$ °C	570	$3.2 \times 10^{5}–1.0 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$		
$1.9 \times 10^{4}\ \mathrm{M^{-0.5}\ s^{-1}}$	pH 0–3, $T = 25$ °C	578	$2.7 \times 10^{4}\ \mathrm{M^{-1}\ s^{-1}}$	pH 1.0, $T = 20$ °C	593
$2.9 \times 10^{4}\ \mathrm{M^{-0.5}\ s^{-1}}$	pH 2.2–3.5, $T = 18$ °C	590	$1.4 \times 10^{5}\ \mathrm{M^{-1}\ s^{-1}}$	pH 2.5, $T = 20$ °C	593
$4.4 \times 10^{4}\ \mathrm{M^{-0.9}\ s^{-1}}$	pH 4–7, $T = 25$ °C	591	$2.1 \times 10^{5}\ \mathrm{M^{-1}\ s^{-1}}$ [c]	pH 2.5, $T = 20$ °C	593
$2.0 \times 10^{4}–3.2 \times 10^{5}\ \mathrm{M^{-1}\ s^{-1}}$	pH 1.2–5, $T = 22$ °C	592	$3.7 \times 10^{5}\ \mathrm{M^{-1}\ s^{-1}}$	pH 4.0, $T = 20$ °C	593
	pH >5, $T = 22$ °C	592	$1.25 \times 10^{4}\ \mathrm{M^{-1}\ s^{-1}}$ [c]	pH 4.0, $T = 20$ °C	593
S(IV) + H_2O_2					
$3.0 \times 10^{7}\ \mathrm{M^{-2}\ s^{-1}}$	pH 3.3, $T = 25$ °C	590	$765\ \mathrm{M^{-1}\ s^{-1}}$	pH 5.06, $T = 22$ °C	595
$4.2 \times 10^{7}\ \mathrm{M^{-2}\ s^{-1}}$	pH 0–3	594	$1410\ \mathrm{M^{-1}\ s^{-1}}$	pH 4.7, $T = 22$ °C	595
$8.0 \times 10^{7}\ \mathrm{M^{-2}\ s^{-1}}$	pH 4–5.8, $T = 22$ °C	595	$6950\ \mathrm{M^{-1}\ s^{-1}}$	pH 4.04, $T = 22$ °C	595
$62\ \mathrm{M^{-1}\ s^{-1}}$	pH 5.85, $T = 22$ °C	595			
S(IV) + $S_2O_8^{2-}$					
$4.6 \times 10^{-4}\ \mathrm{M^{-1}\ s^{-1}}$	pH 4.0, $T = 25$ °C	596	$8.2 \times 10^{-3}\ \mathrm{M^{-1}\ s^{-1}}$	pH 9.0, $T = 25$ °C	596
$2.4 \times 10^{-3}\ \mathrm{M^{-1}\ s^{-1}}$	pH 6.0, $T = 25$ °C	596	$8.3 \times 10^{-3}\ \mathrm{M^{-1}\ s^{-1}}$	pH 5.0, $T = 40$ °C	597
$3.2 \times 10^{-3}\ \mathrm{M^{-1}\ s^{-1}}$	pH 1.5–4.3, $T = 40$ °C	597			
S(IV) + $SO_3^{\bullet -}$					
$7.0 \times 10^{6}\ \mathrm{M^{-1}\ s^{-1}}$		598			
S(IV) + $SO_4^{\bullet -}$					
$2.6 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$	pH 7–8, $T = 20$ °C	599	$7.5 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$	pH 4.8, $T = 25$ °C	583
$3.1 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$	pH 9.0,	600	$1.1 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$	pH 4.0, $T = 20$ °C	601
$3.7 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$	pH 9.0, $T = 20$ °C	601	$2.0 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$	pH 8.7,	582
$5.3 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$	pH >7,	408	$>2 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$	$T = 22$ °C	602
$6.8 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$	pH ~4,	600			
S(IV) + HSO_5^-/SO_5^{2-}					
$1.23 \times 10^{2}\ \mathrm{M^{-1}\ s^{-1}}$ [d]	pH alkaline	603	$5.95 \times 10^{3}\ \mathrm{M^{-1}\ s^{-1}}$ [e]	pH alkaline	603
S(IV) + $SO_5^{\bullet -}$					
$3.0 \times 10^{5}\ \mathrm{M^{-1}\ s^{-1}}$	pH 4.9	582	$1.3 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$	pH 8.7	582
S(IV) + $OH^{\bullet}$					
$7.3 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$		604	$4.5 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$	pH 4.4	582
$2.7 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$	pH 4.5	605	$5.2 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$	pH 11.2	582
$4.1 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$	pH 9.0	605	$9.5 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$		573
S(IV) + $Cl_2^{\bullet -}$					
$3.3 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$	pH 7.0	606	$1.7 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$		607
$7.0 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$		572	$3.4 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$	pH 3.0	582
S(IV) + ClO^-					
$1060\ \mathrm{s^{-1}}$ [f]	pH 9–13, $T = 18$ °C	608	$1230\ \mathrm{s^{-1}}$ [g]	pH 9–13, $T = 18$ °C	608
S(IV) + NO_2					
$1.24 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$	pH 5.3[h]	609	$2.14 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$	pH 11.8[k]	609
$1.34 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$	pH 6.8[i]	609	$2.95 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$	pH 13.0[l]	609
$1.54 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$	pH 6.7[h]	609	$3.5 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$	pH 12.1	610
$1.68 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$	pH 9.3[j]	609			
S(IV) + $NO_3^{\bullet}$					
$2.3 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$	pH 1.0, $T = 5$ °C	611	$8.4 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$	pH 4.5, $T = 5$ °C	611
$2.6 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$	pH 1.0, $T = 25$ °C	611	$1.4 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$	pH 4.5, $T = 25$ °C	611
$3.0 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$	pH 10.0, $T = 5$ °C	611	$2.0 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$	$T = 22$ °C	602
S(IV) + HNO_4					
$1.9 \times 10^{5}\ \mathrm{M^{-1}\ s^{-1}}$	pH 2–4, $T = 12$ °C	612			

[a] In Milli-R/Q-water. [b] In destilled water. [c] Presence of 0.1 M acetate buffer. [d] S(IV) + HSO_5^-. [e] S(IV) + SO_5^{2-}. [f] Ionic strength 0.5–1 M. [g] Ionic strength 1.5 M. [h] Presence of 0.5 M phosphate. [i] No buffer. [j] Presence of borate. [k] Presence of 1 mM phosphate + KOH. [l] Presence of 0.1 M KOH.

Furthermore, the SO_2 oxidation by radicals, e.g. $OH^{\bullet}$, $Cl_2^{\bullet -}$ or $SO_4^{\bullet -}$ [564,579–583] should also be mentioned here (see section 3.2.4 for further information).

3.2. The Uncatalyzed Oxidation of Sulfur(IV) Oxides

Rate constants for some uncatalyzed oxidation reactions of sulfur(IV) oxides are summarized in Table 3.3 The reaction rate of the uncatalyzed oxidation of S(IV) is often too high, because traces of transition metals in the water enhance the "uncatalyzed" process.[613] Addition of complexing agents such as EDTA or 1,10-phenanthroline, in order to mask possibly present metal ions, reduces the rate of the "uncatalyzed" process significantly.[613] These sub-

Table 3.4. Selected Literature on the Oxidation of Sulfur(IV) Oxides in Atmospheric Water Samples

water sample	remarks	ref
rain water	half-life time for sulfite is ca. 10 h; (pH ~ 7); oxidation rate corresponds to a metal concentration of 0 M	200
rain water	oxidation rate of sulfite is directly proportional to the manganese concentration and independent of pH (3.7−4.4). At [Mn] = 0−5 μM oxidation rate in distilled water significantly lower than in rain water	172
rain water	oxidation rate of sulfite oxidation in rain water is 50 to 100 times faster than the rate of the uncatalyzed oxidation; pH 3−5	175
rain water	half-life time of sulfite ca. 2.1 h (pH 4.4); oxidation rate is determined by the iron(III) and manganese(II) concentration; oxidation rate in rain water is around 1000 times faster than in pure water	332
rain water	oxidation rate is primarily determined by the iron concentration and the pH; poor correlation between the oxidation rate and the manganese, copper and zinc concentrations	614
fog water	oxidation rate significantly lower than those expected for the iron catalyzed autoxidation of sulfite; pH 2.9−4.2	181

stances do not act as radical scavengers. This is important if free radicals are involved in the overall redox reaction (see section 3.3). Thus for the study of the uncatalyzed oxidation process the pureness of the water is an important factor. Selected literature on the oxidation of sulfur(IV) oxides in atmospheric water samples is summarized in Table 3.4. Clarke and Radojevic[584] obtained a 7 times slower rate constant for the uncatalyzed reaction when using Milli-R/Q water instead of deionized water (see Table 3.3). No influence of the water quality was observed in the case of the cobalt(II)- and iron(III)-catalyzed autoxidation reaction.[511,615] The iron and copper concentrations in deionized water are approximately 5×10^{-8}–5×10^{-7} M and 6×10^{-8}–2×10^{-7} M, respectively,[613,616] which can probably catalyze the overall reaction process. First hints concerning the influence of the water quality on the rate constant of the SO_2 oxidation were given by Titoff.[617] The origin of the sulfite salt can also have an influence on the overall reaction rate.[615,618,619]

Sulfur(IV) oxides form addition products with formaldehyde depending on the pH, viz. hydroxymethane sulfonate, HMS, or hydroxymethane sulfonic acid, HMSA.[620−630] Both HMS/HMSA and formaldehyde have been found in atmospheric water samples.[369,630,631−637] HMS/HMSA is not oxidized by either hydrogen peroxide or ozone[592,627,632] but reacts with hydroxyl radicals.[629,638] According to Chapman,[639] more than 60% of the total sulfur(IV) in wintertime precipitation is present in a form other than dissolved SO_2. The most likely form is HMS, although other aldehyde−sulfur(IV) adducts may also be present. Facchini et al.[630] determined in fog water samples with a pH > 4.5 that on average 95% of the formaldehyde is present as HMSA (compare also with ref 628). At lower pH HMSA formation is limited by the availability of sulfur(IV) in solution. Equilibrium computations by Munger et al.[633] indicate that high concentrations of sulfur(IV) in atmospheric water droplets cannot be achieved without the formation of S(IV)−RCHO adducts. Laboratory experiments have confirmed that S(IV) and H_2O_2 can coexist for hours in the presence of formaldehyde, even when the HCHO and S(IV) concentrations were both as low as 10 μM.[627] It follows that sulfur(IV) oxides can be stabilized by formaldehyde in atmospheric water droplets. Whether transition metal ions have any influence on this situation is presently unknown.

The mechanism of the uncatalyzed oxidation of sulfur(IV) oxides by O_2, O_3, H_2O_2, radicals or NO_x, have been discussed in the literature in detail and will only be summarized here. For mechanistic studies on the oxidation of HMS by OH radicals see refs 629 and 638.

3.2.1. Oxidation of Sulfur(IV) Oxides by Oxygen

One of the first studies on the influence of O_2 on the oxidation of S(IV) was performed by Bigelow.[640] In the case of the uncatalyzed oxidation reactions, the oxygen concentration dependence is discussed in a contradictory way in the literature (see Table 3.18). In some cases, no oxygen dependence was observed in the range $3 \leq pH \leq 7$,[587,641] whereas an oxygen dependence was found at pH > 8.[574,591] In other cases, a number of authors[559,642,643] found a first-order dependence on O_2 but no dependence on the initial pH (see Table 3.18). The pH dependence of the uncatalyzed oxidation and the iron(III)-catalyzed oxidation of sulfur(IV) oxides is summarized in Figure 3.3. The pH dependence can be explained by the redox potentials of O_2 (see Figure 2.7) and that of the different sulfur(IV) species (see Figure 2.2 and Table 3.5). It is evident that SO_3^{2-} is easier oxidized by oxygen than HSO_3^- (see section 3.5.5).

The pH profile for the uncatalyzed autoxidation reaction (Figure 3.4) shows that the pH of the solution decreases during the reaction, but that the reaction rate is not influenced by the pH change during the first part of the reaction until the pH decreases below a value between 5.7 and 5.9.[559] This pH profile indicates that the sulfite oxidation mechanism depends on the HSO_3^- concentration. It should be noted here that similar pH profiles have been reported for the iron(II, III)-catalyzed reaction when starting with an initial pH around 6 (Figure 3.4).[511,660] It is suggested that during the uncatalyzed autoxidation of sulfur(IV) oxides the disulfate ion, $S_2O_7^{2-}$, is formed, which decomposes via hydrolysis into products (reaction 3.1):[661,662]

$$S_2O_7^{2-} + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \qquad k = 0.013\ s^{-1\,a} \tag{3.1}$$

[a] Reference 662 ($T = 25$ °C, $\mu = 0.5$ M, independent of pH in the range $2 \leq pH \leq 5$)

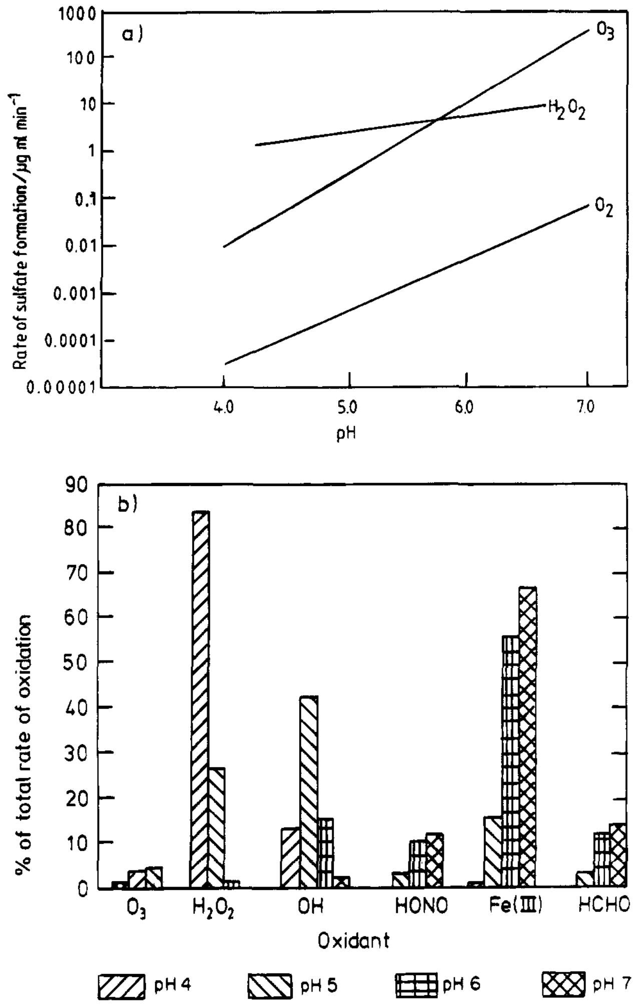


Figure 3.3. Comparison of the atmospheric oxidation rates of SO_2 as a function of pH: (a) ref 570, and (b) ref 153.

In the gas phase sulfur dioxide can be oxidized by oxygen to sulfur trioxide, SO_3, which reacts very rapidly with water to form sulfuric acid.[663-665]

3.2.2. Oxidation of Sulfur(IV) Oxides by Ozone

O_3 is a water-soluble gas (see Table 2.1), which can decompose in water under formation of OH• radicals (OH^- catalysis),[666-668] as shown in the following reactions:

$$O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2$$

$$k = 70\ M^{-1}\ s^{-1}\ {}^{669}$$

$$k = 3.7 \times 10^2\ M^{-1}\ s^{-1}\ {}^{670} \quad (3.2)$$

$$O_3 + HO_2 \rightarrow OH^{\bullet} + 2O_2$$

$$k = 4.0 \times 10^6\ M^{-1}\ s^{-1}\ {}^{671} \quad (3.3)$$

$$O_3 + OH^{\bullet} \rightarrow HO_2 + O_2$$

$$k < 1.0 \times 10^4\ M^{-1}\ s^{-1}\ {}^{672}$$

$$k = 2.0 \times 10^9\ M^{-1}\ s^{-1}\ {}^{673} \quad (3.4)$$

$$OH^{\bullet} + HO_2 \rightarrow O_2 + H_2O$$

$$k = 3.1 \times 10^9\ M^{-1}\ s^{-1}\ {}^{674}$$

$$k = 7.0 \times 10^9\ M^{-1}\ s^{-1}\ {}^{675} \quad (3.5)$$

Table 3.5. Redox Potentials of Some Sulfur Oxides

redox couple	$E°$ (V)	pH	ref
SO_2/SO_2^-	−0.17	0	644
	−0.262		645
	−0.288	1.0	644
	−0.31	2.0	644
SO_3^-/SO_3^{2-}	0.63	>7.0	646
	0.72		647
	0.76		648
	0.89[b]		649
SO_3^-/HSO_3^-	0.84	3.6	646
SO_4^-/SO_4^{2-}	2.43		650
	2.52−3.08[a]		651
	2.6		652
SO_4^{2-}/SO_3^{2-}	−0.93		653
SO_4^{2-}/H_2SO_3	0.172		653
$2SO_4^{2-}/S_2O_6^{2-}$	−0.22		653
$2SO_4^{2-}/S_2O_8^{2-}$	1.939		654
	2.01		380
$2HSO_4^-/S_2O_8^{2-}$	2.057		654
SO_5^-/HSO_5^-	1.1	7.0	646
HSO_5^-/HSO_4^-	1.81		655
	1.82		656
	1.842		657
HSO_5^-/SO_4^{2-}	1.75	3−9	655
SO_5^{2-}/SO_4^{2-}	1.22	>10	655
$S_2O_4^{2-}/HSO_3^-$	−0.386[a]	7	658
$S_2O_6^{2-}/2SO_3^{2-}$	0.07		659
$S_2O_6^{2-}/SO_3^-, SO_3^{2-}$	−0.49		650
$S_2O_6^{2-}/2H_2SO_3$	0.564		653
$S_2O_8^{2-}/SO_4^-, SO_4^{2-}$	1.39		652

[a] Estimated value. [b] Calculated upper limit.

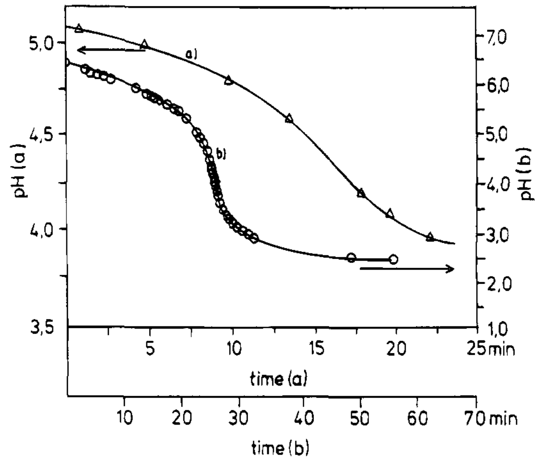


Figure 3.4. pH profile for the uncatalyzed[559] (time scale a) and the Fe(II,III)-catalyzed[660] oxidation of sulfur(IV) oxides (time scale b). Conditions for the uncatalyzed process: [S(IV)] = 0.79 M, T = 20 °C, pH = 6.4. Conditions for the Fe(II,III)-catalyzed process: $[Fe]_{total}$ = 0.2 µg mL⁻¹, [S(IV)] = 8 µg mL⁻¹, T = 25 °C, pH = 5.0.

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$k = 7.6 \times 10^5\ M^{-1}\ s^{-1}\ {}^{674}$$

$$k = 8.6 \times 10^5\ M^{-1}\ s^{-1}\ {}^{676} \quad (3.6)$$

The mechanism of the oxidation of S(IV) by ozone remains uncertain.[565] A simple oxygen transfer reaction is discussed[677] as well as an electrophilic attack of ozone on the sulfur atom of the sulfur(IV) oxide species.[592,678] A free radical mechanism has also been proposed.[570,590,591,593] The reaction is described uniformly in the literature as first order in [S(IV)] and $[O_3]$.[570,578,590,677] In contrast, there are different results concerning the pH dependence of the process (see e.g. refs 590 and 677).

The influence of metal ions on the overall reaction rate has been studied, but the results are controversial. Martin,[578] Lagrange et al.[590] and Botha et al.[593] observed no influence of transition metal ions (Cr^{3+}, Fe^{3+}, Fe^{2+}, Mn^{2+}, Cu^{2+}), whereas Harrison et al.[679] found a catalytic effect of Mn^{2+} and Fe^{3+}. In the latter case the oxidation rate increased linearly with increasing iron(III) concentration.

The influence of oxygen on the oxidation of sulfur(IV) oxides by ozone has been studied recently.[593] An increase in oxygen concentration results in an increase in the overall oxidation rate, indicating that oxygen plays a role in the overall mechanism. For this reason, Botha et al.[593] proposed a reaction mechanism which includes the oxidation of sulfur(IV) oxides by HSO_5^-. The HSO_5^- anion is formed by the reaction of the $OH^\bullet$ radical (e.g. from reaction 3.3) with the sulfur(IV) oxides (see section 3.2.4).

3.2.3. Oxidation of Sulfur(IV) Oxides by Hydrogen Peroxide

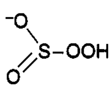
For a detailed treatment of the atmospheric chemistry of hydrogen peroxide see refs 680 and 681. For an overview about the role of hydrogen peroxide in aquatic systems see ref 682. Recently, the photochemical formation of hydrogen peroxide has been identified as an important source in atmospheric water droplets.[683-687] Hydrogen peroxide hydrolyzes in aqueous solution:[688,689]

$$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^- \qquad K = 2.4 \times 10^{-12}\ \mathrm{M}^{380} \quad (3.7)$$

The oxidation of sulfur(IV) oxides by hydrogen peroxide is characterized by a strong pH dependence (Figure 3.3).[564,690-693] For the pH range 2–6, Drexler et al.[691] found the following rate law (see also refs 564 and 690):

$$r = (k_H[H^+] + k_{HX}[HX] + k_p)[HSO_3^-][H_2O_2]$$

where H = proton activity, HX = buffer (e.g. formic or acetic acid), and k_p = water induced reaction path. The reaction mechanism for the oxidation of sulfur(IV) oxides by hydrogen peroxide is still uncertain. Probably a peroxomonosulfurous acid intermediate



is formed via a rapid nucleophilic displacement of H_2O by H_2O_2 on HSO_3^-, followed by a rate-determining rearrangement that results in the production of sulfuric acid.[564,690-692,694,695] There is presently no evidence for the participation of the pyrosulfite ion, $S_2O_5^{2-}$, in the overall reaction scheme[695] and it has not been taken into account in recent literature.[680,691-693,696-698]

The influence of the ionic strength on the overall reaction rate depends on the pH. Drexler et al.[691] observed no influence of the ionic strength in the range 4.6 ≤ pH ≤ 4.8. Penkett et al.[570] reported no influence of the ionic strength at pH 6.6, but observed a decrease in the reaction rate with increasing ionic strength at pH 8.2. Breytenbach et al.[693] found a decrease of about 20% in the observed pseudo-first-order rate constants when they increased the ionic strength from 0.1 to 1.0 M (pH 3.5–5.0). Lagrange et al.[698] reported different influences of the ionic strength depending on the employed electrolyte medium. In an aqueous $NaClO_4$ medium the third-order rate constant exhibits a nearly bell-shaped ionic strength dependence with a maximum between 0.2 and 0.4 M. When aqueous NaCl solution is used as medium Lagrange et al.[698] find no dependence of the third-order rate constant on the ionic strength. In an aqueous Na_2SO_4 solution the third-order rate constant decreases by 40% when the ionic strength is increased from 0.4 to 1.0 M.

The influence of buffers on the oxidation of sulfur(IV) oxides by hydrogen peroxide has been studied in detail. For example, Lagrange et al.[698] obtained higher reaction rates in phosphate buffer than in acetate buffers. A linear increase of the reaction rate with increasing formate or acetate concentration has been reported by Drexler et al.[691] Formic acid has a stronger influence on k_{obs} than acetic acid.

As in the case of O_3 (see section 3.2.2), the influence of metal ions on the overall oxidation process of the S(IV)–H_2O_2 reaction is a subject of controversy. In general, metal ion concentrations between 4 and 40 μM are required for a significant catalytic effect,[680] especially when the Fenton-type reactions (transition metal catalyzed decomposition of H_2O_2; see e.g. refs 699–701) are taken into account. No influence of Fe^{3+}, Cr^{3+}, Cu^{2+}, and Mn^{2+} was reported by Lagrange et al.[698] These authors observed only a small catalytic effect in the presence of Fe^{2+}. Drexler et al.[702] found no influence of Fe^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, and Cu^{2+}. No catalysis in the presence of Fe^{3+} or Mn^{2+} was found by Martin and Damschen.[690] In contrast, Ibusuki et al.[697] reported catalytic effects by addition of Fe^{3+}, Fe^{2+}, Co^{2+}, Mn^{2+}, and Ni^{2+}. Fe^{2+} exhibits the strongest catalytic activity (see also Table 4.1). Breytenbach et al.[693] observed an acceleration of the reaction by iron(II), if the iron is added to the H_2O_2 solution. No kinetic effect was observed when the iron(II) is added to the sulfur(IV) solution under argon atmosphere. No surface catalytic effects were observed when the S(IV)–H_2O_2 system was studied in aqueous suspensions of SiO_2, Al_2O_3, or TiO_2.[703]

3.2.4. Oxidation of Sulfur(IV) Oxides by Radicals

The most important reaction of sulfur(IV) oxides with radicals in the atmosphere is the one with the hydroxyl radicals, $OH^\bullet$,[247] which are mainly produced via photochemical processes.[564,685,687,704-706] For a detailed account on atmospheric $OH^\bullet$ chemistry see refs 705, 707, and 708. Other radical sources are for instance the reaction of O_3 with organic compounds[709] and the reaction of HO_2 with NO.[704] During the reaction of sulfur(IV) oxides with $OH^\bullet$ radicals the sulfite radical, $SO_3^{\bullet-}$, is formed:[581,705,710,711]

$$HSO_3^- + OH^\bullet \rightarrow SO_3^{\bullet-} + H_2O$$
$$k = 2.7 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}\ ^{605}$$
$$k = 4.5 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}\ ^{582} \quad (3.8)$$

$$SO_3^{2-} + OH^{\bullet} \rightarrow SO_3^{\bullet -} + OH^-$$
$$k = 4.1 \times 10^9\ M^{-1}\ s^{-1}\ [605]$$
$$k = 5.2 \times 10^9\ M^{-1}\ s^{-1}\ [582] \qquad (3.9)$$

The mechanism of the S(IV)–OH• reaction is still uncertain. For a discussion see refs 581 and 712.

The influence of chloride on the overall reaction rate (see also section 3.5.1) has been studied. It inhibits the oxidation rate and it is suggested that it acts as a radical scavenger.[581]

The influence of the ionic strength on the oxidation of sulfur(IV) oxides by radicals was recently studied.[607,713] This study indicates an increase of the reaction rate with increasing ionic strength.

3.2.5. Oxidation of Sulfur(IV) Oxides by Nitrogen Oxides

In aqueous solution only NO, NO_2, N_2O, and the dimeric species N_2O_2 and N_2O_4 are stable species. NO and NO_2 are in equilibrium with their corresponding dimers:

$$2NO \rightleftharpoons N_2O_2 \qquad (3.10)$$

$$2NO_2 \rightleftharpoons N_2O_4 \qquad (3.11)$$

According to Kameoka and Pigford,[714] N_2O_4 reacts more rapidly with water and electrolyte solutions than does NO_2 when absorbed into water or aqueous solutions, respectively.

Nitrous acid, HNO_2, formed in the gas phase, dissociates in aqueous solution into the nitrite ion, which is a strong oxidizing agent.

$$NO(g) + OH^{\bullet} \rightarrow HNO_2 \qquad (3.12)$$

$$HNO_2 \rightleftharpoons H^+ + NO_2^- \qquad (3.13)$$

In view of flue gas desulfurization and atmospheric processes, the reactions of NO_y with sulfur(IV) oxides are important. The influence of NO_x on the oxidation of SO_2 in artificial flue gases exhibits for NO_2 an acceleration of the process whereas NO inhibits the reaction.[715] The oxidation of sulfur(IV) oxides by NO_y results in many sulfur–nitrogen (S–N) compounds (see Figure 3.5) which can undergo further reactions. During the hydrolysis of these substances SO_4^{2-} and $S_2O_6^{2-}$ (dithionate) can be formed as possible products (see also section 3.5.6).

S–N compounds have been reported since the 19th century.[717–721] The decomposition of S–N compounds was probably studied the first time by Wagner.[721] For review articles concerning S–N chemistry see e.g. refs 578 and 722–724.

In principle, the reactions of S(IV) oxides with NO_y can be divided into different groups: (1) reactions with N(II) oxides, e.g. NO;[715,725–728] (2) reactions with N(III) oxides, e.g. NO_2^- and HONO;[726,729–733] and (3) reactions with N(IV) oxides, e.g. NO_2.[609,610,715,734–736] The reactions mentioned in Figure 3.5 cannot be discussed in detail in this review. By way of example only the reaction of the nitrite ion, NO_2^-, with sulfur(IV) will be mentioned here. The main S–N compound formed during this reaction is hydroxylamine disulfonate, HADS.[729–733] Ion chromatographic studies[733] in Ar-saturated aqueous solutions suggest the following reaction mechanism:

$$NO_2^- + H^+ \rightleftharpoons HONO \qquad (3.13)$$

$$HONO + HSO_3^- \rightarrow ONSO_3^- + H_2O \qquad (3.14)$$

$$ONSO_3^- + HSO_3^- \rightarrow HON(SO_3)_2^{2-} \qquad (3.15)$$

$$2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O \qquad (3.16)$$

$$HONO + S_2O_5^{2-} \rightarrow HON(SO_3)_2^{2-} \qquad (3.17)$$

The effect of metal ions (Fe^{3+}, Mn^{3+}, Fe^{2+}, Mn^{2+}, Co^{2+},

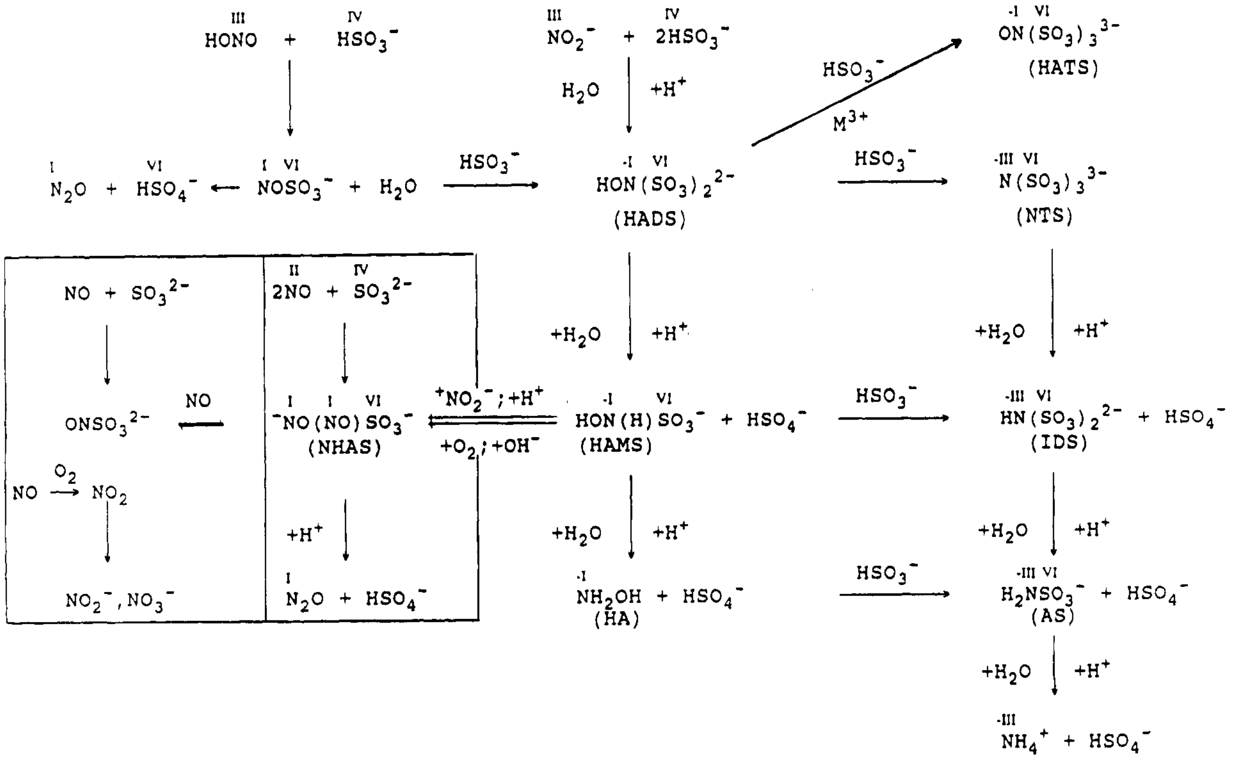


Figure 3.5. Formation and hydrolysis reactions of N–S compounds.[716]

Cu^{2+}) on this reaction has also been studied.[726,733] In air-saturated aqueous solutions the reaction rate decreases with increasing [Fe^{n+}], whereas in Ar-saturated solutions no influence of Fe^{3+} was observed.[733] In contrast, increasing Fe^{2+} concentration resulted in an increase in the reaction rate when a certain [Fe^{2+}] is reached.[733] Martin et al.[726] observed no influence on the reaction rate when adding Fe^{3+} or Mn^{2+}.

Nash[734] studied the influence of Fe^{2+}, Mn^{2+}, and Cu^{2+} on the oxidation of sulfur(IV) oxides by nitrogen dioxide. Iron exhibits a strong catalytic effect and it was suggested that iron(III) is the catalytic active species (see section 3.3.3). Copper and manganese had no catalytic effect. In addition, no catalytic effect of transition metal ions was also reported for the reaction of S(IV) with NO_3^- [726] and NO_2.[737] In a reverse manner, Ellison and Eckert[738] observed no catalytic influence of NO_2 on the Fe^{2+}- and Mn^{2+}-catalyzed oxidation of sulfur(IV) oxides (see section 3.3).

3.3. Homogeneous Catalysis

Three types of mechanisms are discussed in the literature for the transition metal catalyzed oxidation of sulfur(IV) oxides: (1) nonradical mechanisms,[151,152,235,465,739–742] (2) radical mechanisms,[649,743–754] and (3) combined nonradical and radical mechanisms.[755,756]

In general, the nonradical mechanisms postulate an inner-sphere complexation of the metal ion by sulfite followed by an electron transfer (ET) reaction. In the presence of oxygen, the latter is suggested to bind to the metal sulfito complex.

Most of the published reaction mechanisms for the homogeneous transition metal catalyzed autoxidation of sulfur(IV) oxides suggest radical mechanisms that are based on the scheme given by Backström:[743]

$$SO_3^{2-} + M^{n+} \rightleftharpoons SO_3^{\bullet-} + M^{(n-1)+} \qquad (3.18)$$

$$SO_3^{\bullet-} + O_2 \rightleftharpoons SO_5^{\bullet-} \qquad (3.19)$$

$$SO_5^{\bullet-} + HSO_3^- \rightleftharpoons HSO_5^- + SO_3^{\bullet-} \qquad (3.20)$$

$$SO_5^{\bullet-} + SO_3^{2-} \rightleftharpoons SO_5^{2-} + SO_3^{\bullet-} \qquad (3.21)$$

$$SO_5^{\bullet-} + HSO_3^- \rightleftharpoons HSO_4^- + SO_4^{\bullet-} \qquad (3.22)$$

$$SO_5^{\bullet-} + SO_3^{2-} \rightleftharpoons SO_4^{2-} + SO_4^{\bullet-} \qquad (3.23)$$

$$SO_3^{2-} + HSO_5^- \rightleftharpoons HSO_4^- + SO_4^{2-} \qquad (3.24)$$

$$SO_3^{2-} + SO_5^{2-} \rightleftharpoons 2SO_4^{2-} \qquad (3.25)$$

$$SO_4^{\bullet-} + HSO_3^- \rightleftharpoons HSO_4^- + SO_3^{\bullet-} \qquad (3.26)$$

$$SO_4^{\bullet-} + SO_3^{2-} \rightleftharpoons SO_4^{2-} + SO_3^{\bullet-} \qquad (3.27)$$

Radical scavengers such as mannitol,[588] *tert*-butyl alcohol,[754,757] ethanol,[743,752,758] and hydroquinone[752,759,760] inhibit the overall S(IV) oxidation process (negative catalysis). This can be interpreted as evidence for a free radical chain reaction during the transition metal-catalyzed autoxidation of S(IV) oxides (see also section 3.5.3). The inhibiting effect of some substances on the autoxidation of S(IV) oxides was studied systematically the first time by Bigelow.[640]

Table 3.6. Theoretical Rate Expressions Obtained from the Backström Mechanism (eqs 3.18–3.27) for Some Termination Steps[761]

termination step	rate constant k^a	α	β	γ
eq 3.25	$k_{3.18}(2k_{ox}/k_{3.25})^{1/2}$	$^1/_2$	$^1/_2$	1
eq 3.28	$(2k_{ox}k_{3.18}k_{3.19}/k_{3.28})^{1/2}$	$^1/_2$	1	$^1/_2$
eq 3.29	$k_{3.19}(2k_{ox}/k_{3.29})^{1/2}$	$^1/_2$	$^3/_2$	0

[a] k_{ox}: $H_nOSO_2^{(2-n)-} + 0.5O_2 \rightarrow H_nSO_4^{(2-n)-}$.

Table 3.7. Examples of Metal–Sulfito Complexes

	sulfito group bounded via		
complex	O	S	ref
$[FeSO_3]^+$		x	503
$[FeSO_3]$	x		762
$[Fe(SO_3)_n]^{(3-2n)}$		x	445
$[HOFeSO_3]$		x	465
$[(NH_4)_9(Fe(SO_3)_6)]$	x		763
$[MnSO_3]$	x		764
$[O_3MnOSO_3]^{3-}$	x		765
$[Co(CN)_4(SO_3)_2]^{5-}$		x	766
$[Co(NH_3)_5SO_3]^+$		x	767
$[Co(NH_3)_5SO_3]^+$	x		396
$[OCoOSO_2H]^-$	x		643
$[Rh(NH_3)_5SO_3]^+$	x		768
$[Cr(NH_3)_5SO_3]^+$	x		768
$[CrOSO_2]^+$	x		769
$[Cu(SO_3)_n]^{2-2n}$		x	770

Using the simple model of Backström,[743] eqs 3.18–3.27, different theoretical rate expressions can be obtained for the general rate law, if different rate-determining and termination steps (eqs 3.28–3.30) for the Backström mechanism are assumed (Table 3.6).

$$-d[SO_3^{2-}]/dt = k[M^{n+}]^{\alpha}[SO_3^{2-}]^{\beta}[O_2]^{\gamma}$$

$$SO_3^{\bullet-} + SO_3^{\bullet-} \rightarrow S_2O_6^{2-} \qquad (3.28)$$

$$SO_3^{\bullet-} + SO_5^{\bullet-} \rightarrow S_2O_6^{2-} + O_2 \qquad (3.29)$$

$$SO_5^{\bullet-} + SO_5^{\bullet-} \rightarrow S_2O_6^{2-} + 2O_2 \qquad (3.30)$$

3.3.1. Formation of Transition Metal–Sulfito Complexes

The transition metal-catalyzed oxidation of sulfur(IV) oxides follows a complex reaction mechanism with several distinguishable steps starting with the formation of a metal–sulfito complex (see Tables 3.7 and 3.8).[387,394,445,465,740,770] Meyer[783] already proposed the formation of metal–sulfito complexes during the oxidation of SO_2 in the presence of iron or manganese. Depending on the [S(IV)], different metal–sulfito complexes are formed (Figure 3.6).[445,770,773]

$$M^{n+} + mSO_3^{2-} \rightleftharpoons [M(SO_3)_{m-a}]^{n-2(m-a)} + aSO_3^{2-} \qquad (3.31)$$

Recently, Betterton[394] studied the pH-dependent

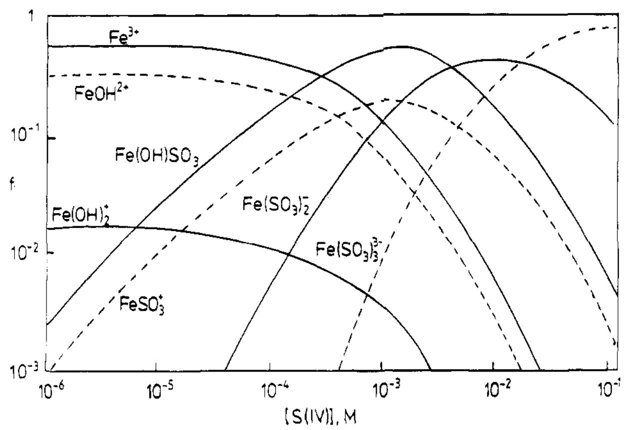
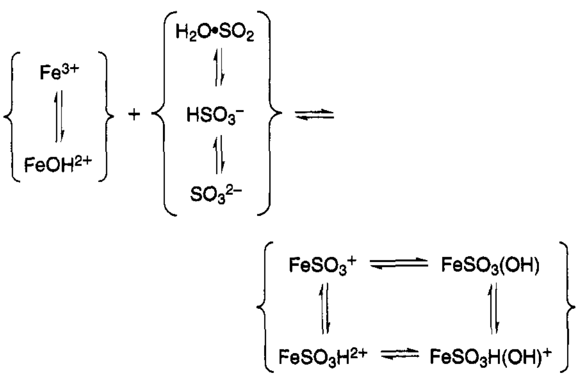


Figure 3.6. Iron(III)–sulfito complex speciation at pH 2.0, ionic strength μ = 0.01 M.[756]

formation of the iron(III)–sulfito complexes. He suggested the formation of different 1:1 iron(III)–sulfito complexes:



$$\left\{\begin{array}{c}\mathrm{Fe^{3+}}\\ \Updownarrow\\ \mathrm{FeOH^{2+}}\end{array}\right\} + \left\{\begin{array}{c}\mathrm{H_2O{\cdot}SO_2}\\ \Updownarrow\\ \mathrm{HSO_3^-}\\ \Updownarrow\\ \mathrm{SO_3^{2-}}\end{array}\right\} \rightleftharpoons \left\{\begin{array}{ccc}\mathrm{FeSO_3^+} & \rightleftharpoons & \mathrm{FeSO_3(OH)}\\ \Updownarrow & & \Updownarrow\\ \mathrm{FeSO_3H^{2+}} & \rightleftharpoons & \mathrm{FeSO_3H(OH)^+}\end{array}\right\} \qquad (3.32)$$

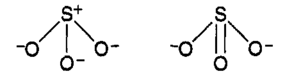
In the case of the 1:2 iron(III)–sulfito complex, $Fe(SO_3)_2^-$, the occurrence of cis- and trans-isomers has been suggested.[445] A similar concentration dependence for the formation of e.g. iron–sulfate complexes ($FeSO_4^+$, $Fe(SO_4)_2^-$, $FeSO_4{\cdot}HSO_4$) is also described in the literature.[468,784]

The formation of metal–sulfito complexes has been reported for many transition metals (see Table 3.7). On the basis of stability constants for transition metal–sulfito complexes reported in the literature,[465,770] the following stability order can be given (log *K* values): $FeSO_3^+$ (6.6) > $CuSO_3$ (4.2, 3.62) > $NiSO_3$ (1.33) > $CoSO_3$ (1.28) > $FeSO_3$ (0.77) > $MnSO_3$ (0.48). By using the stability constants obtained by Roy et al.,[398] the following stability order can be given (log *K* values): $CoSO_3$ (3.08) > $MnSO_3$ (3.00) > $NiSO_3$ (2.88). By way of comparison, the stability order of metal–sulfato complexes can be given as (log *K* values): $MnSO_4$ (2.86) > $NiSO_4$ (2.81) > $CoSO_4$ (2.69) > $FeSO_4^+$ (2.42) > $CuSO_4$ (2.26) > $FeSO_4$ (2.20).[468,486]

The calculation of the pH-dependent distribution of copper(I)–sulfito complexes indicates an increase in stability for the 1:2 copper(I)–sulfito complex, $Cu(SO_3)_2^{3-}$, with increasing pH.[312]

For details on the structure and binding of transition metal-sulfito complexes see ref 785. In principle, a sulfito group can be coordinated to a metal center via the S, O, or, in a bidentate way, via S and O or via two O atoms. Nyberg and Larsson[786] divide metal–sulfito complexes into three categories: (1) complexes without sulfur coordination, (2) complexes with both sulfur and oxygen coordination, and (3) complexes with dominant sulfur coordination.

The sulfite ion can be written in two mesomeric forms (see also section 2.1.1):



I II

The coordination of an O atom on a positively charged metal center is more likely for structure I, whereas structure II promotes the formation of a metal–sulfur bonded species[786] (see also ref 776).

Due to its stronger electron-donor ability and its higher polarizability, sulfur is more likely to form stronger bonds with metals than oxygen.[770] According to Vepřek-Šiška et al.[787] inert metal complexes (see ref 788) (e.g. $[Fe(CN)_6]^{3-}$, $[Mn(CN)_6]^{3-}$) form S-bonded and labile metal complexes (e.g. $[Fe(H_2O)_6]^{3+}$, $[Cu(H_2O)_4]^{2+}$) form O-bonded metal–sulfito complexes. Recent results point at a pH-dependent structure. Metal aqua–hydroxo complexes react fast with $SO_2(aq)$ under formation of O-bonded metal–sulfito complexes (3 < pH < 8). At pH > 9 the reaction is much slower (substitution controlled) and results in the formation of S-bonded metal–sulfito complexes.[789] See Table 3.7 for the coordination mode of some metal–sulfito complexes.

Carlyle[503] as well as Kraft and van Eldik[445] have considered the possibility of an O-coordination, but suggest on the basis of theoretical considerations, a coordination of the sulfito group via the S atom. Conklin and Hoffmann[465] suggest a linkage isomerization reaction from O to S bonded.

The atmospheric stability and the possible influence of metal–sulfito complexes on atmospheric processes is still unknown. Because of the high content of copper(I) in fog water (4 to >90% of the total copper concentration), Xue et al.[312] suggest that copper(II) [which is much more stable than copper(I)] is reduced mainly by sulfite to copper(I), which is than stabilized as a copper(I)–sulfito complex. Conklin and Hoffmann[770] calculated that at pH 3.5 in aqueous solution 15% of the copper(II) exists as a copper(II)–sulfito complex, $CuSO_3$, whereas 77.2% of the copper(II) is uncomplexed. At pH 6.3, 98.5% of the copper(II) is complexed by sulfite. According to Weschler et al.,[790] copper and iron will partly exist in the atmosphere as sulfito complexes, whereas manganese and nickel exist only as aqua complexes (see also ref 169). Hoffmann and Jacob[761] propose that in the pH range 1–4 most of the iron, and in the pH range 4–6 most of the manganese ions exist as metal–sulfito complexes in the presence of S(IV). The solubility of some metal complexes as function of the pH is summarized in Table 3.9.

The formation of a pure iron–sulfito complex in the presence of high chloride concentrations (for the influence of anions on the overall reaction see section 3.5.1) is unlikely according to Bassett and Parker,[151] because of the high stability of the iron(III)–tetrachloro complex, $FeCl_4^-$. They postulate the formation of a mixed iron–chloro–sulfito complex, e.g. $FeCl_2(SO_3)^-$ (see also section 2.2). Erel et al.[791] calculate for an atmospheric water sample (pH 3.4) in the

Table 3.8. Selected Literature on the Formation and Decomposition of Transition Metal–Sulfito Complexes

complex	remarks	ref
	Co^{2+}	
$[CoSO_3]$	observed induction period is associated with formation of the complex	760
$[OCoOSO_2H{\cdot}O_2]^-$, $[OCoOSO_2{\cdot}O_2]^{2-}$	surface complexation on CoO; complex decomposes under formation of HSO_5^- or SO_5^{2-}, respectively	643
$[Co(OH)SO_3]^-$	formation of complex is rate-determining step for the autoxidation of Co(II) in the presence of S(IV)	771
	Cu^+, Cu^{2+}	
$[Cu(SO_3)_2]^{2-}$	decomposes under formation of Cu^+, SO_4^{2-} $S_2O_6^{2-}$	151
$[Cu(SO_3)_2]^{3-}$	in the presence of O_2 formation of $[O_2{\rightarrow}Cu(SO_3)_2]^{3-}$, which decomposes under formation of SO_4^{2-}	151
$[Cu(SO_3)_2]^{3-}$	in the presence of O_2 formation of $[Cu(SO_3)_2O_2]^{2-}$	739
$[Cu(SO_3)_n]^{2-2n}$	$n = 1-3$, depending on the [S(IV)] and pH; formation of a dimeric complex: $[CuSO_3Cu]^{2+}$	740, 770
$[CuSO_3]^-$, $[Cu(SO_3)_2]^{3-}$	stability of complex is pH dependent	312
$[CuSO_3]$	stability of complex is pH dependent	312
$[CuO{\cdot}O_2{\cdot}SO_3H]^-$, $[CuO{\cdot}O_2{\cdot}SO_3]^{2-}$	surface complexation on CoO; complex decomposes under formation of HSO_5^- or SO_5^{2-}, respectively	242
$[Cu(HSO_3)_2]$	formed during the dissolution of CuO in the presence of sulfur(IV) oxides	772
	Fe^{2+}, Fe^{3+}	
$[O_2{\rightarrow}Fe(SO_3)_2]^{2-}$	decomposes under formation of Fe^{3+} and SO_4^{2-}	151
$[Fe(SO_3)_2]^-$	decomposes under formation of $S_2O_6^{2-}$	151
$[Fe(SO_3)_n]^{3-2n}$	$n = 1-3$, depending on the [S(IV)]	773
$[Fe(HSO_3)]^{2+}$	decomposition under formation of Fe^{2+} and $HSO_3^{\bullet}$	744
$[FeSO_3]^+$	electron transfer following inner-sphere complexation	774
$[FeS_2O_5]^+$, $[FeHSO_3]^{2+}$	decomposition under formation of Fe^{2+} and $SO_3^{\bullet -}$	775
$[FeOSO_2H]^{2+}$, $[FeSO_3H]^{2+}$	nature of formed iron(III)–sulfito complex depends on the tautomeric forms of bisulfite ion	776
$[FeSO_3]^+$	complex formation is rate-determining step	758
$[FeSO_3]^+$	complex formation can be followed by an increase and complex decomposition by a decrease in absorbance at 390 nm	387
$[HOFeOSO_2]$	complex formation can be followed by an increase and complex decomposition by a decrease in absorbance at 350 nm and 450 nm	465
$[FeOSO_2]^-$	surface complexation on Fe_2O_3 colloids in aqueous suspensions	777
$[Fe(SO_3)_n]^{3-2n}$	$n = 1-3$, depending on the [S(IV)] and pH	445
$[FeSO_3]^+$, $[FeSO_3H]^{2+}$	formation of a 1:1 iron(III)–sulfito complex; formation constant depends on pH, wavelength	394
$[Fe(SO_3)_n]^{3-2n}$	absorbance–time traces ($\lambda = 390$ nm) of the complex decomposition exhibit, in the presence of oxygen, an additional step, which is terminated by a characteristic break at the time when all the oxygen in the solution is consumed	752
	Fe^{6+}	
$[O_3Fe{-}O{-}SO_3H]^3$	direct transfer of an oxygen from ferrate(VI) to the sulfur center	778
	Mn^{2+}, Mn^{3+}	
$[O_2{\rightarrow}Mn(SO_3)_2]^{2-}$	rapid rearrangement into $[Mn(SO_4)_2]^{2-}$	151
$[Mn{\cdot}SO_2]^{2+}$	4-step mechanism with formation of a $[(Mn{\cdot}SO_2^{2+})_2{\cdot}O_2]$ complex	235
$[Mn^{2+}(SO_3^{2-})_3]^{4-}$	formation of complex before catalytic activity	745
$[Mn_2HSO_3]^{3+}$, $[Mn(HSO_3)_2]$	complex reacts with oxygen under formation of $OH^{\bullet}$ and $SO_4^{\bullet -}$ radicals; minor contribution of $[Mn(HSO_3)_2]$ on reaction mechanism	755
$[Mn(HSO_3)_x]^{2-x}$	complex more favorable for oxidation reaction than $[Mn(SO_3)_x]^{2-2x}$	779
$[Mn^{2+}(SO_3^-)] \rightleftharpoons [Mn^{3+}(SO_3^{2-})]$	manganese–sulfito radical complex inhibits at pH 10.1 autoxidation of sulfite	780
$[Mn_2OHSO_3]^+ \rightleftharpoons [Mn_2OH(SO_3)_2]^-$	rate-determining step: $MnOH^+ + Mn^{2+} \rightleftharpoons MnOHMn^{3+}$	758
$[MnHSO_3]^+$, $[MnSO_3Mn]^{2+}$	complex reacts with Mn(III) or $SO_5^{\bullet -}$ under formation of $SO_3^{\bullet -}$ radical (pH 2.4); at pH 4 also formation of a bridged Mn(II) dimer complex with the same reaction behavior	750
$[MnSO_3]^+$	complex decomposes under quantitative formation of dithionate; inner-sphere oxidation process in which free sulfur(V) radicals are not scavenged	781
	Ni^{3+}	
$[Ni(O_2)(OSO_2)]$	surface complexation on Ni_2O_3; complex decomposes under formation of HSO_5^-	782

presence of oxalate that nearly all of the iron(III) is complexed by oxalate (98.7%) while iron(II) mainly exists as hexaaqua complex (95.2%), followed by the iron(II)–sulfate complex (3.2%) (see also ref 169).

3.3.2. Decomposition of Transition Metal–Sulfito Complexes

The transition metal–sulfito complexes formed in the first step during the overall oxidation of sulfur(IV) oxides decompose spontaneously under formation of the reduced metal species and sulfite radicals, $SO_3^{\bullet -}$.[465,775,789] The rate of decomposition for instance of the iron(III)–sulfito complexes is in the range of 2×10^{-3}–$0.2\ s^{-1}$,[387,465,752,792] and has been studied in detail.[387,751,752,792]

For the manganese(II)-catalyzed oxidation of sulfur(IV) oxides, Berglund et al.[750] suggest a second pathway at higher pH (pH 4), during which $SO_3^{\bullet -}$ is generated parallel to the redox decomposition. For this pathway the formation of a bridged manganese(II) complex is suggested, which can be attacked by manganese(III) (compare also with refs 793 and 794):

Table 3.9. Expected Upper Limit Concentrations for Different Metal Complexes in Atmospheric Droplets as a Function of the pH[575,790]

	concentration, M		
metallocomplex	pH 3	pH 4	pH 5
$Fe(H_2O)_6^{3+}$	2×10^{-6}		
$Fe(H_2O)_5(OH)^{2+}$	1×10^{-5}	3×10^{-6}	5×10^{-8}
$Fe(H_2O)_5(SO_3)^{+}$	2.2×10^{-6}	6×10^{-6}	1×10^{-6}
$Fe(H_2O)_4(OH)(SO_3)$		6×10^{-7}	1×10^{-7}
$Fe(H_2O)_5(SO_4)^{+}$	1×10^{-6}		
$Cu(H_2O)_6^{2+}$	1×10^{-6}	2×10^{-6}	2×10^{-6}
$Ni(H_2O)_6^{2+}$	2×10^{-6}	2×10^{-6}	2×10^{-6}
$Mn(H_2O)_6^{2+}$	2×10^{-6}	2×10^{-6}	2×10^{-6}

$$MnHSO_3^{+} + Mn^{2+} \rightleftharpoons MnSO_3Mn^{2+} + H^{+} \quad (3.33)$$

$$MnSO_3Mn^{2+} + Mn^{3+} \rightarrow 3Mn^{2+} + SO_3^{\bullet -} \quad (3.34)$$

In the absence of oxygen, the produced $SO_3^{\bullet -}$ radical can react via different ways (k in $M^{-1}\,s^{-1}$):

$$\begin{aligned} &SO_3^{\bullet -} + SO_3^{\bullet -} \rightarrow S_2O_6^{2-} \\ &\qquad 2k = 3.6 \times 10^{8} \quad (pH\ 4.3)^{795} \\ &\qquad 2k = 5.0 \times 10^{8} \quad (pH\ 9.0)^{600} \\ &\qquad 2k = 5.4 \times 10^{8} \quad (pH\ 9.0)^{796} \\ &\qquad 2k = 6.8 \times 10^{8} \quad (pH\ 9.8)^{589} \\ &\qquad 2k = 7.2 \times 10^{8} \ (pH\ 10.7)^{797} \\ &\qquad 2k = 8.5 \times 10^{8} \quad (pH\ 5.0)^{798} \\ &\qquad 2k = 1.1 \times 10^{9} \quad (pH\ 9.8)^{408} \\ &\qquad 2k = 1.4 \times 10^{9\ 799} \\ &\qquad 2k = 1.4 \times 10^{9} \quad (pH\ 10.0)^{798} \\ &\qquad 2k = 1.6 \times 10^{9} \ (pH\ 14.0)^{800} \\ &\qquad 2k = 1.9 \times 10^{9} \quad (pH\ 11.8)^{801} \quad (3.28) \end{aligned}$$

$$\begin{aligned} &SO_3^{\bullet -} + SO_3^{\bullet -} \rightarrow SO_3^{2-} + SO_3\ (\text{or } SO_2 + SO_4^{2-}) \\ &\qquad\qquad 2k = 4.6 \times 10^{8\ 795} \quad (3.35) \end{aligned}$$

$$SO_3^{\bullet -} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_7^{-} \quad (3.36)$$

$$SO_3^{\bullet -} + SO_4^{2-} \rightarrow SO_3^{2-} + SO_4^{\bullet -} \quad (3.37)$$

In Ar-saturated solutions the recombination of $SO_3^{\bullet -}$ radicals proceeds by two channels (eqs 3.28 and 3.35) with almost equal probability.[795]

According to Luňák and Vrepřek-Šiška[802] the reaction of iron(II) with the $SO_3^{\bullet -}$ radicals is also a possible sink for these radicals. Thus, reaction 3.38

$$Fe^{2+} + SO_3^{\bullet -} \rightarrow Fe^{3+} + SO_3^{2-} \quad (3.38)$$

(see Table 3.11 for rate constants) should inhibit the iron(III)-catalyzed oxidation of sulfur(IV) oxides, as it has been observed.[752,803,804] In addition, a similar behavior was observed for the copper(III) catalysis. Addition of copper(II) effectively suppressed the reaction rate (copper(III) as well as copper(II) as tetraglycine complexes).[649] Siskos et al.[781] reported for the manganese(III)-catalyzed reaction a small inhibition by manganese(II). The oxidation of manganese(II) by the $SO_3^{\bullet -}$ radical has also been proposed:[780]

$$\begin{aligned} &Mn^{2+} + SO_3^{\bullet -} \rightleftharpoons [Mn^{II}(SO_3^{-})]^{+} \rightleftharpoons \\ &\qquad [Mn^{III}(SO_3^{2-})]^{+} \rightleftharpoons Mn^{3+} + SO_3^{2-} \quad (3.39) \end{aligned}$$

In the presence of oxygen (see section 3.5.2) the reactions 3.38 and 3.39, respectively, are in competition with reaction 3.19, because the $SO_3^{\bullet -}$ radical reacts very fast with the oxygen dissolved in water to form the peroxomonosulfate radical, $SO_5^{\bullet -}$:[408,646,743,805]

$$\begin{aligned} &SO_3^{\bullet -} + O_2 \rightarrow SO_5^{\bullet -} \\ &\qquad k = 1.1 \times 10^{9}\ M^{-1}\,s^{-1} \quad (pH \approx 1.0)^{799} \\ &\qquad k = 1.2 \times 10^{9}\ M^{-1}\,s^{-1\ 758} \\ &\qquad k = 1.5 \times 10^{9}\ M^{-1}\,s^{-1} \quad (pH\ 6.8)^{646} \\ &\qquad k = 2.5 \times 10^{9}\ M^{-1}\,s^{-1\ 605} \quad (3.19) \end{aligned}$$

The possible formation of the superoxide anion, O_2^{-}, as in reaction 3.40 is unlikely based on experimental results with ascorbate.[646]

$$SO_3^{\bullet -} + O_2 \rightarrow SO_3 + O_2^{\bullet -} \quad (3.40)$$

Beside the formation of the $SO_5^{\bullet -}$ radical, the formation of the hydrogenperoxomonosulfate anion, HSO_5^{-}, also plays an important role in the atmospheric sulfur chemistry[705] (k in $M^{-1}\,s^{-1}$):

$$\begin{aligned} &SO_5^{\bullet -} + O_2^{\bullet -} \xrightarrow{H_2O} HSO_5^{-} + OH^{-} + O_2 \\ &\qquad k = 1.0 \times 10^{8\ 705} \\ &\qquad k = 3.3 \times 10^{8} \quad (pH\ 9.0)^{605} \\ &\qquad k = 8.0 \times 10^{8\ 806} \quad (3.41) \end{aligned}$$

$$\begin{aligned} &SO_5^{\bullet -} + HSO_3^{-} \rightarrow HSO_5^{-} + SO_3^{\bullet -} \\ &\qquad k = 1.2 \times 10^{4\ 807} \\ &\qquad k = 2.5 \times 10^{4} \quad (pH\ 4.9)^{582} \\ &\qquad k = 3.0 \times 10^{6} \quad (pH\ 6.8)^{646} \\ &\qquad k = 1.3 \times 10^{7} \quad (pH\ 8.7)^{582} \quad (3.20) \end{aligned}$$

$$SO_5^{\bullet -} + M^{2+} \xrightarrow{H^{+}} HSO_5^{-} + M^{3+} \quad (3.42)$$

The $SO_5^{\bullet -}$ radical as well as the HSO_5^{-} anion are strong oxidizing agents (see Table 3.5). Both species, $SO_5^{\bullet -}$ and HSO_5^{-}, formed in the presence of oxygen can undergo many reactions which may influence the decomposition of the metal–sulfito complex and the product formation (see section 3.5.6) (k in $M^{-1}\,s^{-1}$):

$$\begin{aligned} &SO_5^{\bullet -} + HSO_3^{-} \rightarrow HSO_5^{-} + SO_3^{\bullet -} \\ &\qquad k = 2.5 \times 10^{4\ 807} \\ &\qquad k = 2.5 \times 10^{4} \quad (pH\ 4.9)^{582} \\ &\qquad k = 3.0 \times 10^{6} \quad (pH\ 6.8)^{646} \\ &\qquad k = 1.3 \times 10^{7} \quad (pH\ 8.7)^{582} \quad (3.20) \end{aligned}$$

$$\begin{aligned} &SO_5^{\bullet -} + HSO_3^{-} \rightarrow SO_4^{\bullet -} + SO_4^{2-} + H^{+} \\ &\qquad k = 7.5 \times 10^{4\ 582} \\ &\qquad k = 4.0 \times 10^{8\ 808} \quad (3.43) \end{aligned}$$

$$SO_5^{\bullet-} + HSO_3^- \xrightarrow{H_2O} 2SO_4^{2-} + 2H^+ + OH^\bullet \tag{3.44}$$

$$SO_5^{\bullet-} + SO_5^{\bullet-} \rightarrow 2SO_4^{\bullet-} + O_2$$

$2k = 1.1 \times 10^7$ [806]
$2k = 2.0 \times 10^8$ [705]
$2k = 2.0 \times 10^8$ (pH 6.0)[799]
$2k = 2.8 \times 10^8$ [799]
$2k = 6.0 \times 10^8$ [582] (3.45)

$$SO_5^{\bullet-} + SO_5^{\bullet-} \rightarrow S_2O_6^{2-} + 2O_2 \tag{3.30}$$

$$SO_5^{\bullet-} + SO_5^{\bullet-} \rightarrow S_2O_8^{2-} + O_2$$

$2k = 1.4 \times 10^7$ [582]
$2k = 1.5 \times 10^8$ [601]
$2k = 1.9 \times 10^8$ [794]
$2k = 2.6 \times 10^8$ (pH 4.0)[607] (3.46)

$$SO_5^{\bullet-} + SO_5^{\bullet-} \rightarrow S_2O_{10}^{2-}$$

$2k = 9.3 \times 10^7$ (pH 4.3)[809] (3.47)

$$SO_5^{\bullet-} + O_2^- \xrightarrow{H_2O} HSO_5^- + OH^- + O_2$$

$k = 1.0 \times 10^8$ [705]
$k = 3.3 \times 10^8$ (pH 9.0)[605]
$k = 8.0 \times 10^8$ [806] (3.41)

$$HSO_5^- + SO_5^{\bullet-} \xrightarrow{H_2O} OH^\bullet + 2SO_4^{2-} + O_2 + 2H^+ \tag{3.42}$$

$$HSO_5^- + SO_5^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + O_2^{\bullet-} + H^+ \tag{3.48}$$

$$HSO_5^- + HSO_5^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} + O_2^{\bullet-} + 2H^+ \tag{3.49}$$

$$HSO_5^- + HSO_3^- \rightarrow 2SO_4^{2-} + 2H^+$$

$k = 3.5 \times 10^2$ (pH 8.0)[758]
$k = 9.1 \times 10^3$ (pH 2.9)[810]
$k = 7.9 \times 10^4$ (pH 1.5)[810]
$k = 2.0 \times 10^4$ (pH 2.5)[810]
$k = 7.5 \times 10^7$ [705] (3.50)

$$HSO_5^- + OH^\bullet \rightarrow SO_5^{\bullet-} + H_2O$$

$k = 1.7 \times 10^7$ (pH 7.0)[811] (3.51)

$$HSO_5^- + SO_4^{\bullet-} \rightarrow SO_5^{\bullet-} + SO_4^{2-} + H^+$$

$k < 1.0 \times 10^5$ [811] (3.52)

The branching ratio of the $SO_5^{\bullet-}$ radical self-reaction, eqs 3.45 and 3.46, has been determined to be $7(k_{3.45}/k_{3.46})$.[812] See Hui et al.[799] for suggestions on recombination pathways of the $SO_5^{\bullet-}$ radical.

The $SO_5^{\bullet-}$ radical and the HSO_5^- anion are two important oxidizing agents in view of the reoxidation of the reduced transition metal ions (see sections 3.3.4 and 3.3.6 and refs 751 and 752). The oxidation of e.g. iron(II) to iron(III) by HSO_5^- (eq 3.53) follows

$$Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + OH^- + SO_4^{\bullet-}$$

$k = 3.0 \times 10^4\ M^{-1}\ s^{-1}$ [813] (3.53)

a one-electron transfer reaction according to an inner-sphere mechanism.[813] Another possible reaction (eq 3.54) is negligible according to experiments per-

$$Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + OH^\bullet + SO_4^{2-} \tag{3.54}$$

formed in the presence of radical scavengers.[814] For reactions of HSO_5^- with other transition metal ions, see e.g. ref 815.

For the oxidation of manganese(II) by the $SO_5^{\bullet-}$ radical a mechanism has recently been proposed,[794] which involves a bimolecular manganese(II) species (compare also with refs 750, 793, and 816):

$$Mn^{2+} + SO_5^{\bullet-} \rightarrow (MnSO_5)^+ \tag{3.55}$$

$$(MnSO_5)^+ \xrightarrow{H^+} Mn^{3+} + HSO_5^- \tag{3.56}$$

$$(MnSO_5)^+ + Mn^{2+} \rightleftharpoons (MnSO_5Mn)^{3+} \tag{3.57}$$

$$(MnSO_5Mn)^{3+} \rightarrow Mn^{3+} + \text{product} \tag{3.58}$$

For studies on the oxygen consumption during the oxidation of manganese(II), see refs 435 and 817.

The sulfate radical, $SO_4^{\bullet-}$, formed during the decomposition of the metal–sulfito complexes,[754] reacts most likely with the sulfite ions present in solution (eq 3.59; $[S(IV)] \gg [M^{n+}]$) as indicated by computer simulations of the iron(III)-catalyzed oxidation of sulfur(IV) oxides[752] (k in $M^{-1}\ s^{-1}$):

$$SO_4^{\bullet-} + HSO_3^- \rightarrow SO_3^{\bullet-} + HSO_4^-$$

$k = 2.6 \times 10^8$ (pH 7–8)[599]
$k = 3.1 \times 10^8$ (pH 9.0)[818]
$k = 3.8 \times 10^8$ (pH 9.0)[806]
$k = 4.6 \times 10^8$ [582]
$k = 5.3 \times 10^8$ (pH > 7)[408]
$k = 5.5 \times 10^8$ (pH 8.0)[758]
$k = 6.8 \times 10^8$ (pH ≈ 4.0)[600]
$k = 7.5 \times 10^8$ (pH 4.8)[583]
$k = 2.0 \times 10^9$ (pH 8.7)[582]
$k = 3.3 \times 10^9$ [808] (3.59)

A second important sink for the $SO_4^{\bullet-}$ radical has been suggested to be the reaction with the reduced metal ion. (See Table 3.11 for rate constants.) The recombination of the sulfate radical is probably negligible, if the [S(IV)] is in excess[752] (k in $M^{-1}\ s^{-1}$):

Table 3.10. Examples for the M^{2+}-Catalyzed Oxidation of Sulfur(IV) Oxides

	induction period			
M^{2+}	yes	no	remarks	ref
Co^{2+}	x		induction period depends on $[Co^{2+}]$, $[O_2]$, [S(IV)]	760
	x		induction period depends on $[Co^{3+}]$	748
Fe^{2+}	x		induction period up to 2 h; pH dependent	826
	x			827
	x		induction period only for slow reactions	738
	x		induction period is the time SO_2 needs for hydrolysis	828
	x		no induction period if Fe^{3+} is added	829
	x		with increasing the initial concentration of Fe^{3+} the induction period becomes shorter	830
	x		induction period increases with increasing initial pH	660
Mn^{2+}	x		about 2 s	831
	x		induction period up to 4 min in the presence of succinic acid	619
		x	pH 1–4	826
	x		no induction period if Mn^{3+} is added	832
	x		induction period depends on initially added $[Mn^{3+}]$	750
Ni^{2+}		x		832

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-}$$

$$\begin{aligned} 2k &= 3.2 \times 10^8\ {}^{607} \\ 2k &= 3.8 \times 10^8\ {}^{799} \\ 2k &= 5.4 \times 10^8\ {}^{819} \\ 2k &= 6.1 \times 10^8 \quad (\mathrm{pH}\ 1.0)^{820} \\ 2k &= 7.2 \times 10^8 \quad (\mathrm{pH}\ 0.1)^{820} \\ 2k &= 7.8 \times 10^8 \quad (\mathrm{pH}\ 4.8)^{820} \\ 2k &= 8.4 \times 10^8 \quad (\mathrm{pH}\ 5.5)^{821} \\ 2k &= 8.9 \times 10^8 \quad (\mathrm{pH}\ 4.9)^{822} \\ 2k &= 1.6 \times 10^9\ {}^{823} \\ 2k &= 3.6 \times 10^9\ {}^{824} \end{aligned} \qquad (3.60)$$

3.3.3. M^{2+}-Catalyzed Oxidation of Sulfur(IV) Oxides

Most of the transition metal ions that are important for the oxidation of sulfur(IV) oxides (see Table 4.1) in view of a possible catalytic activity, are only stable in the oxidation state +2 in aqueous solution. In order to exhibit catalytic activity, these metal ions probably must be oxidized into a higher oxidation state (+3).[660,771,814,825] Thus, it is reasonable to expect an induction period when a transition metal ion in the oxidation state +2 is used as catalyst for the oxidation of sulfur(IV) oxides under the conditions that the oxidation of the metal ion itself is slow (Table 3.10). There are several suggestions in the literature to account for the general reaction 3.61 and the associated induction period. Coichev and van Eldik[748]

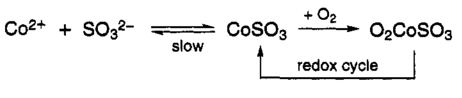
$$M^{2+} \rightarrow M^{3+} + e^- \qquad (3.61)$$

suggest a direct oxidation of the metal ion via oxygen (eq 3.62), whereas Anast and Margerum[649] propose a disproportion reaction (eq 3.63):

$$M^{2+} + O_2 \rightarrow M^{3+} + O_2^- \qquad (3.62)$$

$$2Cu^{2+} \rightarrow Cu^+ + Cu^{3+} \qquad (3.63)$$

According to Hobson et al.[760] a metal–sulfito complex is formed during the induction period, which is then oxidized:



(3.64)

3.3.4. Sulfite-Induced Oxidation of M^{2+} Ions

In the presence of transition metal ions the sulfur(IV)–oxygen system exhibits an interesting dualism. Depending on the reaction conditions, this system can function as an oxidant (metal ions in excess) or as a reductant (S(IV) in excess).[747,748,829,833–835] A mixture of sulfite and oxygen has a stronger oxidizing potential than oxygen alone.[836]

In general, the autoxidation of transition metal ions in the +2 oxidation state is very slow in acidic solution. The oxidation of iron(II) by oxygen at pH 7 is drastically enhanced if the pH is raised by one unit[837,838] (for mechanistic considerations see e.g. ref 839). In contrast, Diem and Stumm[840] observed nearly no oxidation of manganese(II) by oxygen within 7 years in aqueous solutions which are homogeneous with respect to manganese(II) (not oversaturated with regard to $MnCO_3$ or $Mn(OH)_2$) and are sterile (pH = 8.4, $[O_2] = 2.8 \times 10^{-4}$ M). The oxidation rate depends, beside the pH, also on the ionic strength and the ligands coordinated to the metal ion. (For the influence of anions on the oxidation of metal ion, see section 3.5.1.) In the case of the sulfite-induced oxidation of iron(II) an increase in the ionic strength (with $NaClO_4$) from 9.0×10^{-3} M to 1.1×10^{-2} M results in an increase of the half-life of iron(II) from 18 to 38 minutes (T = 25 °C, pH = 6.84, $p_{O_2} = 0.2$ atm).[841]

As mentioned above, the sulfite concentration controls the redox process. An excess of sulfur(IV) oxides results in the reproduction of M^{3+} ions, which will immediately be reduced again by sulfur(IV) oxides to M^{2+} ions.[747,748,834] For this redox process, oxygen must be present.[747,748,752,835] In the case of sulfite-induced oxidation of cobalt(II) for example, the reaction rate is independent of $[O_2]$, but oxygen is essential for the overall reaction process[748] (see also ref 835). The sulfite-induced autoxidation of iron(II) exhibits the following stoichiometry:[833]

$$2Fe^{2+} + SO_2 + O_2 \rightarrow 2Fe^{3+} + SO_4^{2-} \qquad (3.65)$$

The sulfite-induced oxidation of transition metal ions exhibits a characteristic autocatalytic behavior and an induction period is generally observed (see section 3.3.3). The addition of small quantities of the metal ion in its oxidized form, M^{3+}, enhances the reaction.[747,748,829] In contrast, Tiwari et al.[833] observed no influence of added iron(III) on the oxidation rate of the sulfite-induced oxidation of iron(II). Small amounts of copper(II) were found to accelerate the oxidation rate (see further Discussion).[833]

Kinetic analysis of the sulfite-induced oxidation of cobalt(II) and iron(II) results in the same empirical rate law, which illustrates the role of the oxidized

$$k_{obs} = k_1[M^{3+}]_i + k_2[S(IV)]$$

metal ion, M^{3+},[748,829] where $[M^{3+}]_i$ represents the initial concentration of the M^{3+} ions present in solution. Thus, the autocatalytic process is controlled by the nature and the concentration of the M^{3+} ions and their ability to produce $SO_3^{\bullet-}$ radicals, which can rapidly react with O_2 to produce $SO_5^{\bullet-}$ radicals. (See sections 3.3.2 and 3.3.5 for mechanistic details.)

For the autoxidation of cobalt(II) (eq 3.66) in the

$$2Co^{2+} + 2H^+ + O_2 \rightarrow 2Co^{3+} + H_2O_2 \quad (3.66)$$

presence of sulfite Pasiuk–Bronikowska et al.[771] found the rate law

$$d[Co^{2+}]/dt = k_{ox}[Co^{2+}][S(IV)]$$

with k_{ox} values of 7.7×10^{-2} M^{-1} s^{-1} (pH 8.7) and 2.68×10^{-1} M^{-1} s^{-1} (pH 9), respectively. These authors suggest that the formation of a cobalt–sulfito complex (eq 3.67) is the rate-determining step for the autoxidation of cobalt(II) in the presence of sulfite:

$$CoOH^+ + SO_3^{2-} \rightarrow Co(OH)SO_3^- \quad (3.67)$$

The oxidation rate of the reduced metal ion depends on several reaction conditions, e.g. anions present, ionic strength, and pH.

The synergistic effect (see section 3.5.3) of other added metal ions on the sulfite-induced oxidation of M^{2+} ions has been studied for example for the autoxidation of iron(II)[833,842] and cobalt(II).[842] Tiwari et al.[833] studied the influence of copper(II) on the sulfite-induced autoxidation of iron(II). While the addition of small amounts of copper(II) enhances the oxidation process, high copper(II) concentrations inhibit the reaction rate. Tiwari et al.[833] explain this behavior with the equilibria (eqs 3.68 to 3.70) reported by Cher and Davidson:[843]

$$Cu^{2+} + Fe^{2+} \rightleftharpoons Cu^+ + Fe^{3+} \quad (3.68)$$

$$Cu^+ + O_2 + H^+ \rightleftharpoons Cu^{2+} + HO_2 \quad (3.69)$$

$$HO_2 + Fe^{2+} + H^+ \rightleftharpoons Fe^{3+} + H_2O_2 \quad (3.70)$$

An increase in the $[Cu^{2+}]$ results in a saturation of the catalytic effect by shifting the equilibrium in eq 3.69 to the left, followed by a change in equilibrium in eq 3.68, and resulting in the inhibition of the overall iron(II) oxidation rate.[833]

Coichev et al.[842] have studied the synergistic effect of manganese(II) on the sulfite-induced autoxidation of iron(II) and cobalt(II) azide. Their results indicate that manganese(II) has a significant catalytic effect, but the synergistic effect actually occurs in the presence of cobalt(III) and iron(III). It is suggested, that these metal ions can oxidize manganese(II) to manganese(III), which rapidly oxidizes sulfite to the $SO_3^{\bullet-}$ radicals. The latter radicals initiate the autoxidation process via the formation of $SO_5^{\bullet-}$ and HSO_5^- (see section 3.3.5 for mechanistic details). The cooxidation of bivalent metal ions and sulfur(IV) oxides is summarized in Figure 3.7.

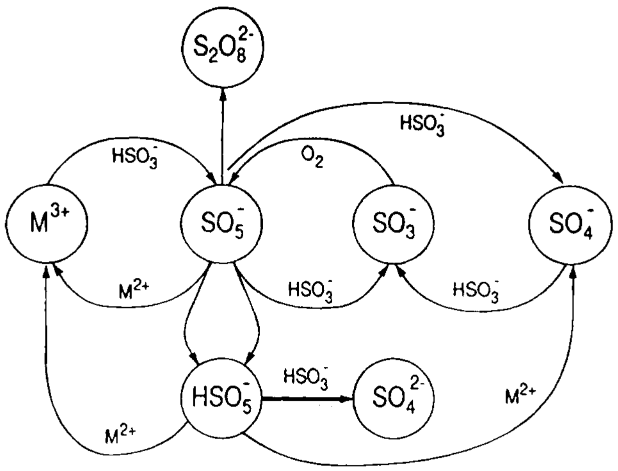


Figure 3.7. Tentative mechanism for the cooxidation of bisulfite and bivalent metal ions.[844]

3.3.5. The Postulated Overall Reaction Mechanism

Sections 3.3.1 and 3.3.2 give detailed information on the formation and decomposition of transition metal–sulfito complexes during the homogeneously catalyzed oxidation of sulfur(IV) oxides. Stoichiometric measurements indicate that the overall reaction can be described by eq 3.71, if SO_4^{2-} is the only

$$2M^{n+} + S(IV) \rightarrow 2M^{(n-1)+} + S(VI) \quad (3.71)$$

oxidation product (see section 3.5.6).[649,742,753,845–847] $S_2O_6^{2-}$ is the only oxidation product, a 1:1 stoichiometry is observed:[781]

$$M^{n+} + S(IV) \rightarrow M^{(n-1)+} + S(V) \quad (3.72)$$

Due to the formation of the $SO_5^{\bullet-}$ radical in the presence of oxygen many reactions are involved in the overall decomposition of the transition metal–sulfito complexes. In view of the proposed atmospheric redox cycle of transition metal ions (see section 3.3.6), the reoxidation of the reduced metal ion into the catalytically active form by $SO_5^{\bullet-}$ or HSO_5^- must be considered. Recently, evidence for the redox cycle of transition metal ions during the catalyzed autoxidation of sulfur(IV) oxides has been reported.[752,835,848,849] The absorption–time traces of the iron(III)-catalyzed oxidation of sulfur(IV) oxides exhibit an additional step in the presence of oxygen, which ends with a peculiar break at the time t_{bp} (Figure 3.8). Measurements with an oxygen-sensitive electrode[850] indicate that the break in the curve appears when the oxygen in the solution is nearly consumed.[751,752] Similar absorbance–time traces have been observed for the nickel(III)-catalyzed reaction,[746] but no explanation for the different absorbance–time traces in the presence and absence of oxygen was offered. Recently, Brandt et al.[752] developed a com-

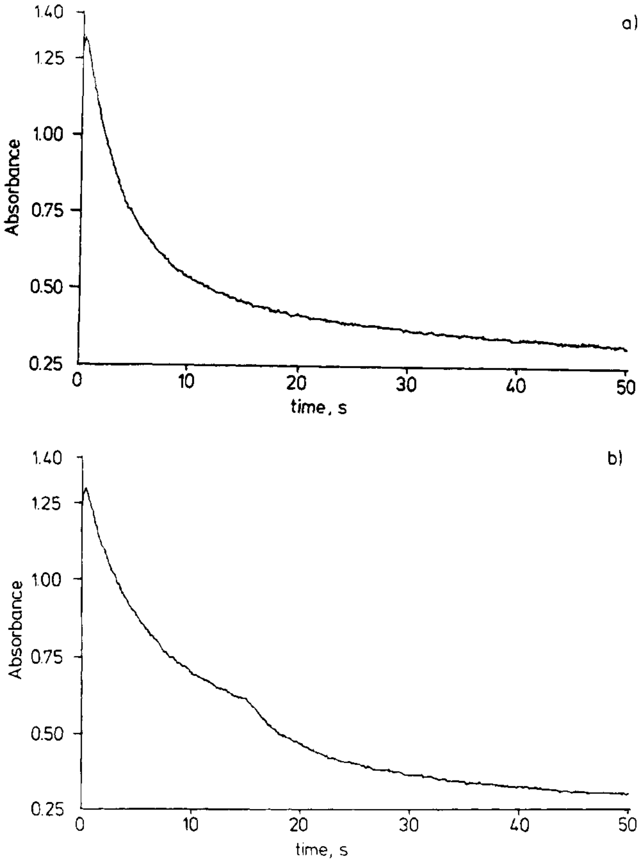


Figure 3.8. Absorbance−time traces of the iron(III)-catalyzed oxidation of sulfur(IV) oxides at pH 2.5 ($\lambda = 390$ nm): (a) in the absence of oxygen (Ar−saturated solution); (b) in the presence of oxygen ($[O_2] = 7.5 \times 10^{-4}$ M).[752]

puter-based model for the iron(III)-catalyzed oxidation of sulfur(IV) oxides, for which the reaction scheme is given below. The simulations indicate that the oxidation of the reduced metal ion into the catalytically active form (M^{3+}) mainly occurs via $SO_5^{\bullet -}$ radicals or the HSO_5^- anion. The regenerated M^{3+} ions can easily form new metal−sulfito complexes which then decompose again. This redox cycle is active as long as oxygen is present in the solution to generate the $SO_5^{\bullet -}$ species, and can account for the additional step shown in Figure 3.8b.

The reaction starts with the rapid formation of the metal−sulfito complex, MSO_3^+ or MSO_3, followed by the redox decomposition of the complex, which produces the $SO_3^{\bullet -}$ radical (eq 3.74). Complex formation between the reduced metal ion and sulfur(IV) is also possible, and the metal−sulfito complex reacts with the $SO_3^{\bullet -}$ radical. In the absence of oxygen the overall reaction can be described by reactions 3.73−3.78 and 3.28. The last one needs to be included in order to account for the formation of dithionate, $S_2O_6^{2-}$, which was experimentally observed at different concentration levels (e.g. refs 151, 752, 758, and 792; see also section 3.5.6).

$$M^{3+} + HSO_3^- \rightleftharpoons MSO_3^+ + H^+ \qquad (3.73)$$

$$MSO_3^+ \rightleftharpoons M^{2+} + SO_3^{\bullet -} \qquad (3.74)$$

$$M^{2+} + HSO_3^- \rightleftharpoons MSO_3 + H^+ \qquad (3.75)$$

$$MSO_3 + M^{3+} \rightarrow 2M^{2+} + SO_3^{\bullet -} \qquad (3.76)$$

$$MSO_3 + SO_3^{\bullet -} \rightarrow M^{3+} + 2SO_3^{2-} \qquad (3.77)$$

$$M^{3+} + SO_3^{\bullet -} \xrightarrow{H_2O} M^{2+} + SO_4^{2-} + 2H^+ \qquad (3.78)$$

$$SO_3^{\bullet -} + SO_3^{\bullet -} \rightarrow S_2O_6^{2-} \qquad (3.28)$$

In the presence of oxygen, the redox cycle is controlled by the formation of the peroxomonosulfate radical, $SO_5^{\bullet -}$ (eq 3.19). This species is a much more reactive oxidant than O_2 and may oxidize either sulfite ion (eqs 3.20 and 3.22) or the reduced metal ion, M^{2+} (eq 3.79). The produced sulfate radical, $SO_4^{\bullet -}$ (eq 3.22) can induce several oxidation processes, e.g. oxidizing either the sulfite ion (eq 3.26) or the reduced metal ion (eq 3.82). Because of the excess of sulfur(IV) and M^{n+} (see Tables 1.3 and 1.7 for atmospheric concentrations) the recombination of the $SO_4^{\bullet -}$ radical (eq 3.60) is unlikely and not included in the reaction scheme. The hydrogenperoxomonosulfate anion, HSO_5^- formed in reactions 3.20 and 3.79 together with the $SO_5^{\bullet -}$ radical open various reaction pathways that may influence both the decomposition process and the product formation.

$$SO_3^{\bullet -} + O_2 \rightarrow SO_5^{\bullet -} \qquad (3.19)$$

$$SO_5^{\bullet -} + HSO_3^- \rightarrow SO_3^{\bullet -} + HSO_5^- \qquad (3.20)$$

$$SO_5^{\bullet -} + HSO_3^- \rightarrow SO_4^{\bullet -} + HSO_4^- \qquad (3.22)$$

$$SO_4^{\bullet -} + HSO_3^- \rightarrow SO_3^{\bullet -} + HSO_4^- \qquad (3.26)$$

$$HSO_5^- + HSO_3^- \rightarrow 2SO_4^{2-} + 2H^+ \qquad (3.50)$$

$$SO_5^{\bullet -} + SO_5^{\bullet -} \rightarrow 2SO_4^{\bullet -} + O_2 \qquad (3.45)$$

$$M^{2+} + SO_5^{\bullet -} \xrightarrow{H^+} M^{3+} + HSO_5^- \qquad (3.79)$$

$$M^{2+} + HSO_5^- \rightarrow M^{3+} + SO_4^{\bullet -} + OH^- \qquad (3.80)$$

$$M^{2+} + HSO_5^- \rightarrow M^{3+} + SO_4^{2-} + OH^{\bullet} \qquad (3.81)$$

$$M^{2+} + SO_4^{\bullet -} \rightarrow M^{3+} + SO_4^{2-} \qquad (3.82)$$

$$M^{2+} + OH^{\bullet} \rightarrow M^{3+} + OH^- \qquad (3.83)$$

$$HSO_3^- + OH^{\bullet} \rightarrow SO_3^{\bullet -} + H_2O \qquad (3.84)$$

$$HSO_5^- + OH^{\bullet} \rightarrow SO_5^{\bullet -} + H_2O \qquad (3.51)$$

$$HSO_5^- + HSO_5^- \rightarrow SO_4^{\bullet -} + SO_4^{2-} + O_2^- + 2H^+ \qquad (3.49)$$

$$SO_3^{\bullet -} + SO_5^{\bullet -} \rightarrow S_2O_6^{2-} + O_2 \qquad (3.29)$$

As mentioned above, the proposed reaction mechanism is based on a computer modeling of the iron(III)-catalyzed oxidation of sulfur(IV) oxides in the presence of oxygen.[752] Computer modeling plays an important role in developing the reaction mechanism for complex systems (see e.g. refs 668, 724, 851, and 852). The limitations of this technique are generally determined by the availability of reliable sets of rate and thermodynamic data.

It should be noted here that some of the reactions included the proposed reaction mechanism as a single step reaction are most likely the composite of various elementary steps. For instance, reaction 3.50 may proceed through a multistep reaction mechanism[603,810,853-855] with the disulfate ion, $S_2O_7^{2-}$, as an intermediate (see also section 3.2.1) and the following reaction sequence:[853]

$$HSO_3^- + HSO_5^- \rightarrow O_3SOOSO_2^{2-} + H_2O \quad (3.50a)$$

$$O_3SOOSO_2^{2-} + H^+ \rightarrow O_3SOSO_3^{2-} + H^+ \quad (3.50b)$$

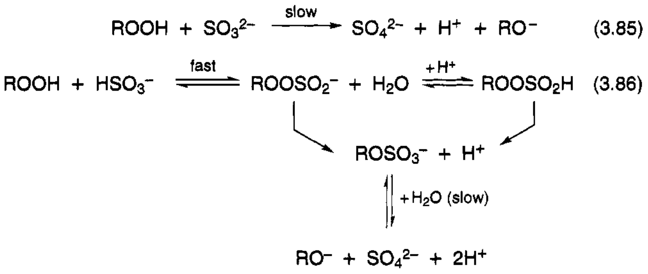
$$O_3SOSO_3^{2-} + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \quad (3.50c)$$

Deister et al.[603] proposed a similar reaction mechanism without providing any information on the formed intermediate (k given for 20 °C and pH 2.9):

$$HSO_3^- + HSO_5^- \rightarrow \text{complex 1} \qquad k = 1.02 \times 10^7\ M^{-1}\ s^{-1} \quad (3.50d)$$

$$\text{complex 1} + H^+ \rightarrow \text{complex 2} + H^+ \qquad k = 0.21\ s^{-1} \quad (3.50e)$$

The oxidation of sulfur(IV) oxides by HSO_5^- and other peroxo compounds has recently been studied over a wide pH range (0–13).[854,855] It is interesting to note, that both sulfur(IV) species, HSO_3^- and SO_3^{2-}, exhibit different mechanistic behavior toward the reaction with ROOH (R = $CH_3C(O)$-, ^-O_3S-, O_2N-), as shown in reactions 3.85 and 3.86 (see also ref 855). For reaction 3.85 it is assumed[854] that the SO_3^{2-} ion is a good S-nucleophile to attack one of the two oxygen atoms in ROOH or ROO^-, respectively, with no formation of any intermediate. In contrast, there is kinetic evidence that the oxidation of HSO_3^- ion proceeds through the formation of at least two intermediates, $ROOSO_2^-$ and $ROSO_3^-$, respectively (eq 3.86).[854]



$$ROOH + SO_3^{2-} \xrightarrow{\text{slow}} SO_4^{2-} + H^+ + RO^- \quad (3.85)$$

$$ROOH + HSO_3^- \underset{}{\overset{\text{fast}}{\rightleftharpoons}} ROOSO_2^- + H_2O \overset{+H^+}{\rightleftharpoons} ROOSO_2H \quad (3.86)$$

$$ROOSO_2^-,\ ROOSO_2H \rightarrow ROSO_3^- + H^+ \xrightleftharpoons{+H_2O\ (\text{slow})} RO^- + SO_4^{2-} + 2H^+$$

The reaction of HSO_3^- with HSO_5^- is subject to general-acid catalysis, and that of the SO_3^{2-} ion not.[855]

The formation of the metal–sulfito complex is a ligand substitution process (see section 2.2.1). Recently, kinetic information was obtained from pH dependencies concerning a substitution-controlled manganese(III)-catalyzed oxidation of sulfur(IV) oxides.[753] During these reactions intermediate association products are formed. The rate-determining steps are the conversion of these intermediates into manganese–sulfito complexes which undergo fast intramolecular redox decomposition. In general, it remains unknown if possible intermediates have any influence on the overall redox process. They can react with the reactants or with each other, thus affecting the course of the overall reactions. The influence of some anions on the transition metal-catalyzed oxidation of sulfur(IV) oxides has been studied in detail, and show that anions can have an influence on the overall reaction rate (see section 3.5.1).

In addition, the possible influence of dimeric species [e.g. the Golding dimer (see section 2.1.1) or μ-oxo and μ-hydroxo bridged metal ions (see section 2.2.1)] is not included in the reaction scheme because of the absence of any reliable kinetic evidence. To the best of our knowledge only one study exists[511] that deals with the reactivity of aged metal hydroxides towards the oxidation of sulfur(IV) oxides (see Figure 2.6). During the aging of iron(III) in aqueous solution, μ-oxo- and/or μ-hydroxoiron(III) dimeric and polymeric species are formed. With increasing time, these dimers and polymers exhibit a decrease in catalytic activity toward the oxidation of sulfur(IV) oxides. The catalytic activity of iron solutions with an initial pH of 3 decreased about 70% within 100 h.[511] It should be noted here, that the aging rate depends on the initial pH of the iron(III) solution.[511]

Finally, it is still uncertain whether the two isomeric forms of hydrogen sulfite, HSO_3^- and SO_3H^- (see section 2.1.1) exhibit similar behavior or not. Both forms can act as general acids, but it was suggested that these two forms react quite differently, since HSO_3^- does not have a pair of electrons available on sulfur for direct transfer to the oxidant.[856]

3.3.6. Redox Cycles

In section 3.3.5 mechanistic details were given for a process that is important for atmospheric relevant redox reactions, viz. the "reproduction" of the oxidant. Kessler[857] already suggested that oxygen transfer during a redox reaction is based on an alternating oxidation and reduction of the catalyst. Beside other oxidants (e.g. HO_2/O_2^-, H_2O_2, O_3, and radicals), sulfur(IV) oxides play an important role in the oxidation of metal ions into the catalytically active, higher oxidation state[858] (see section 3.3.4). In recent literature redox cycles for iron in the atmosphere[157,683,791,829,835,859-862] and in aqueous solution[862-864] have been suggested (see also Figure 3.9).

Redox cycles have also been proposed for cobalt(II), copper(II), and manganese(II).[157,649,747,748,760,848,849] The possible role of S–N compounds (see section 3.2.5) in atmospheric redox cycles still remains uncertain. A recent study[716] indicated that some S–N compounds induce or accelerate the autoxidation of manganese(II) in alkaline medium. It is still unknown whether these reactions also occur in an atmospheric relevant pH range (2 ≤ pH ≤ 6). Lepentsiotis et al.[865] observed that some S–N compounds are able to reduce iron(III) and manganese(III) also in slightly acidic medium (pH ≥ 5.5). The order of reactivity for the reduction of both iron(III)

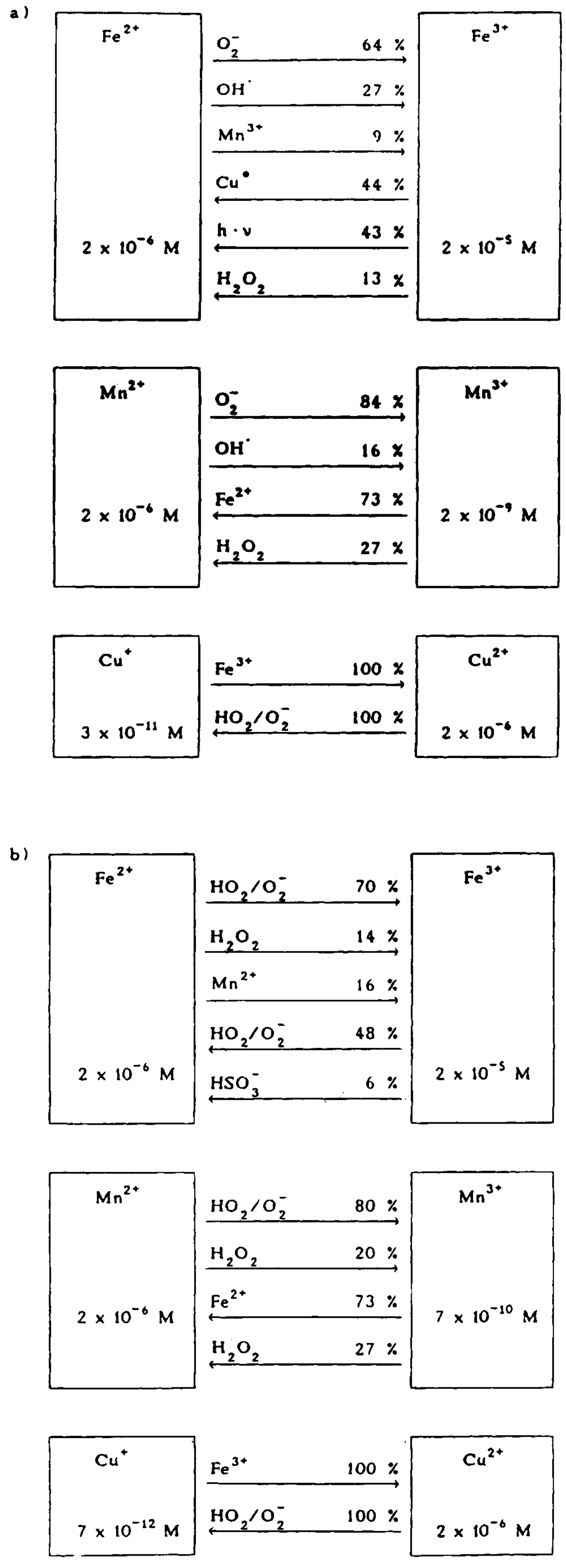


Figure 3.9. Atmospheric transition metal redox reactions at a height of 1 km in a rain drop of 1 mm diameter during the day (a) and at night (b); calculations are based on ion concentrations given in the boxes[157] (for iron compare with ref 741; p 12990).

and manganese(III) is S(IV) > HAMS > HATS > HADS > IDS.[865]

Synergistic reactions (see section 3.5.3) have not been mentioned in the suggested atmospheric redox cycles, except for the studies of Coichev and van Eldik[849] and Sedlak and Hoigné.[861] In the former study the synergistic effect of manganese(II) on the autoxidation of cobalt(II) in the presence of sulfite has been investigated. Sedlak and Hoigné[861] studied the influence of copper on the redox cycle of iron. For synergistic effects during the sulfite-induced oxidation of transition metal ions, see section 3.3.4. Copper(II) and manganese(II) catalyze the oxidation of iron(II) in aqueous solution.[833,843,866,867] Furthermore, in the presence of iron(III) hydroxide the oxidation of iron(II) proceeds along two paths: one is the homogeneous reaction occurring in solution and the other is the heterogeneous one taking place on the iron(III) hydroxide.[561,866] The oxidation of manganese(II) in aqueous solution is catalyzed by several metal oxides.[868,869] Davies and Morgan[869] give the following order for the enhancement of the rate of the manganese(II) oxidation: γ-FeO(OH) > α-FeO(OH) > SiO_2 > δ-Al_2O_3.

The atmospheric redox reactions of iron given in Figure 3.9 indicate a change in the dominating reactions during day and night. The dependence of the atmospheric oxidation processes on meteorological conditions has been discussed earlier (see section 3.1). During the day as well as during the night the reactions of the $HO_2^\bullet$ radical and the O_2^- anion are the most important reactions in the atmospheric redox cycles of iron (Figure 3.9). Copper as well as iron ions act as much as O_3, as a sink for $HO_2^\bullet$ and O_2^- [852] (see also ref 861).

In order to obtain more information on the efficiency of atmospheric redox cycles, it is necessary to determine the fractions of the oxidation states for the individual transition metal ions in atmospheric water droplets.[g] In view of the redox potential of the Fe^{3+}/Fe^{2+} couple a theoretical ratio of $Fe^{3+}/Fe^{2+} \leq 3 \times 10^{-5}$ in the atmosphere is expected.[169] In rain samples collected in Germany both iron(III) and iron(II) were found in nearly equal amounts.[169] In fog and cloud water samples collected in California the ratio of Fe(II)/Fe(total) varied between 0.02 and 0.55.[791] Fog water samples from Switzerland contained 20–90% dissolved iron(II) of the total amount of iron[859] (see also ref 181). In aerosol samples collected in Germany, up to 10% soluble iron(II) (6% of the total iron content) and 75% soluble iron(III) were found.[871] The fraction of iron(II) in the aerosol samples was accounted for by Dedik et al.[871] in terms of a reduction of iron(III) and a dissolution of iron(II) compounds from solid aerosols. Zhuang et al.[860] suggested that the high iron(II) fraction in marine aerosols (average value 49%[h]) was due to a photoinduced reduction of iron(III) (see Figure 3.9 and refs

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[g] It should be noted here that the freezing of aqueous samples containing both iron(II) and iron(III) has no effect on the Fe(II)/Fe(III) equilibrium in the pH range 2–5, irrespective of the freezing temperature.[870]

[h] Based on a personal communication from Zhuang concerning an error in the published text,[860] Zhu et al.[872] give a mean value of 15% for the soluble iron(II) fraction in the marine aerosols studied by Zhuang et al.[860]

872–874). It should be mentioned that the photoreduction of iron(III) is inhibited by inorganic ions (e.g. Cl^-, NO_3^-, SO_4^{2-}) and accelerated by organic substances[791,861,872] (see further Discussion and section 3.5.1). Zhu et al.[874] reported that 7.5% of the soluble iron was in the iron(II) form in marine mineral aerosols. Hofmann et al.[169] assumed that the nearly equal amounts of iron(III) and iron(II) in their rain samples are probably due to the fact that the chemical equilibrium was not established during the rain event.

For the presence of iron(II) in atmospheric water droplets and aerosols different mechanisms have been proposed, e.g. radical reactions.[157,859] In the more recent literature, the role of organic ligands, especially oxalate, in the photoreduction of iron(III) has been discussed.[181,791,861,862,875] In the presence of formate (pH 4.25), Pehkonen et al.[875] reported the following order of reactivity for the photoreduction rates of iron(III) oxyhydroxides: amorphous $Fe(OH)_3 \gg \gamma\text{-}FeO(OH) \geq \alpha\text{-}Fe_2O_3 \geq \alpha\text{-}FeO(OH)$. This reactivity order is suggested to be an indication of the importance of the strength of the Fe–O bond in the different iron phases. Therefore the presence of ligands and the distribution of different iron complexes in atmospheric water droplets and aerosols is of importance (see section 3.5.1).

In addition, pH plays an important role in the iron(III)/iron(II) distribution. Kotronarou and Sigg[181] observed that more than 80% of the dissolved iron was in the oxidation state +2 in fog water samples when the pH of the sample was below 5.

On the basis of the data given above, it is not possible to comment on the efficiency of atmospheric redox cycles for iron. The redox cycle of iron shown in laboratory experiments[751,752,835] cannot be simply extrapolated to atmospheric conditions, since the interaction with other dissolved reactive species can affect the efficiency of the overall redox cycle. Anions can significantly change the redox behavior of transition metal ions (see section 3.5.1).

Table 3.11 summarizes the rate constants for oxidation reactions of some transition metal ions that are most probably of atmospheric relevance.

3.4. Heterogeneous Catalysis

3.4.1. Atmospheric Aspects

Aerosols (see section 1.2) as well as suspended metal oxides and hydroxides in atmospheric water droplets can function as catalysts in atmospheric redox processes. The heterogeneously catalyzed oxidation of sulfur(IV) oxides is slower than the homogeneous one (see further Discussion and ref 511), but the distribution (soluble versus insoluble) and the factors that influence this distribution remain uncertain (see further Discussion). Thus, the contribution of heterogeneous catalysis to the overall oxidation processes of sulfur(IV) oxides remains uncertain.

According to Graedel and Weschler[187] and Weschler et al.,[790] the contribution of iron to the homogeneous transition metal-catalyzed oxidation in the atmospheric relevant pH range (4–6) is negligible in comparison to other metals, because of the low solubility of iron hydroxides (see also refs 756, 905, and 906).

In the atmosphere 80–90% of the manganese and 60–75% of the iron are in a dissolved form.[168,907] In rain samples from Northern Nigeria, Beavington and Cawse[177] found only 16% of the iron in a dissolved form, whereas 61–96% of cobalt, copper, manganese, and zinc were present in a soluble form. Rain samples collected in the United States contained 42% insoluble iron.[908] Approximately 60–75% of the iron and 80–93% of the manganese were dissolved in rain samples collected in Germany;[176] 83% of the iron in precipitation collected at the sea coast in western France was insoluble.[909] Fog water from Switzerland contained 30–80% dissolved iron and 50–100% dissolved copper.[181] In marine aerosol particles collected in Barbados, only 1% of the total iron was in a soluble form.[872] An aerosol sample collected in Germany contained about 84% soluble iron. The remaining iron consisted mainly of Fe_3O_4 (7.6%) and Fe_2O_3 (5.5%).[871] In rain samples from Germany, 40–60% of the detected iron was in the form of fine or coarse particles. This fraction is attributed to polyhydroxo species of iron(III).[169] In contrast, in the case of other metal ions, e.g. Mn^{2+} and Cu^{2+}, the hydrated forms predominated in these samples.[169] The solubility of metals in aerosols and other samples is summarized in Table 3.12.

Giusti et al.[919] pointed out in a review that the most important factors controlling the soluble/insoluble phase distribution are the nature (i.e. the source) of the particles and the pH of atmospheric water droplets during the various stages of atmospheric transport. Anthropogenic and marine sources are generally associated with a higher percentage of soluble phases than crustal sources. Theis and Wirth[917] showed that pH is the major factor controlling the yield of dissolved metal ions from fly ash samples (see Table 3.12b). The amount of dissolved metal ions increased with increasing acidity. According to Gatz and Chu[914] the fraction of soluble and insoluble metal compounds in rain water samples depends not only on the pH and the rainfall quantity but also on the fraction of insoluble matter itself. The metal solubility decreases with increasing concentration of the total insoluble mass (TIM). TIM tends to remove ions from solution through some sort of sorption processes.[914] Furthermore, the sampling technique has an important influence on the fraction of soluble and insoluble mass in the sample (Table 3.12). From Table 3.12 it is evident that the concentrations of insoluble metals are much higher in rain samples collected as bulk sample (wet and dry deposition; see section 1.4) than in samples collected in a wet-only sampler (see also ref 920).

The leaching of metals (see Table 3.12b) from fly ash samples by HCl and some organic chelating agents has been shown to be very effective. In the presence of 0.5 M HCl, 60–70% of total Cu, Fe, Mn, Ni, and Zn was leached within the first 24 h.[911] Sequeira[921] pointed out that the experimentally obtained solubility is generally found to be several orders of magnitude larger than that based on the thermodynamic data. For instance, the experimental solubilities for goethite (FeO(OH)) and albandite (MnS) are 24 and 3.0×10^4 $\mu g\ L^{-1}$, whereas the theoretical values are 2.9×10^{-4} and 12 $\mu g\ L^{-1}$,

Table 3.11. Rate Constants of Oxidation Processes of Iron(II), Manganese(II), and Copper(I,II)

reaction	k	remarks	ref
$Fe^{2+} + SO_3^{\bullet -} \rightarrow Fe^{3+} + SO_3^{2-}$	9.8×10^6 M^{-1} s^{-1}	pH 4.0	605
	1.4×10^7 M^{-1} s^{-1}	pH = 4.0; formation of an intermediate, $Fe^{2+}{\cdot}SO_3^-$, suggested with $K = 770$ M^{-1}	794
$Fe^{2+}{\cdot}SO_3^{2-} + SO_3^{\bullet -} \rightarrow Fe^{3+} + 2SO_3^{2-}$	3.2×10^6 $M-^1$ s^{-1}	pH = 4.0	605
	3.9×10^6 M^{-1} s^{-1}	pH = 4.0	794
$Fe^{2+} + SO_4^{\bullet -} \rightarrow Fe^{3+} + SO_4^{2-}$	9.9×10^8 M^{-1} s^{-1}		876
	4.0×10^7 M^{-1} s^{-1}	$T = 20$ °C; multistep reaction: $Fe^{2+} + SO_4^{\bullet -} \rightleftharpoons [Fe^{II}SO_4]^+ \rightarrow [Fe^{III}SO_4]^+ \rightleftharpoons Fe^{3+} + SO_4^{2-}$	822
$Fe^{2+} + SO_4^{\bullet -} \overset{k}{\rightleftharpoons} X \xrightarrow{k_2}$ products	3.0×10^8 M^{-1} s^{-1}	$T = 20$ °C; $k_2 = 6.5 \times 10^3$ s^{-1}	877
$Fe^{2+} + SO_5^{\bullet -} \xrightarrow{H_2O} FeOH^{2+} + HSO_5^-$	8.0×10^5 M^{-1} s^{-1}	estimated value	878
	3.56×10^4 M^{-1} s^{-1}	pH 4.0	807
$Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + OH^- + SO_4^{\bullet -}$	3.0×10^4 M^{-1} s^{-1}	one-electron transfer reaction	813
	3.56×10^4 M^{-1} s^{-1}	pH = 4.0	807
$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet -}$	12 M^{-1} s^{-1}	pH = 2.4; $T = 22$ °C; negligible effect of adding iron(III)	814
	26 M^{-1} s^{-1}	$T = 25$ °C, $\mu = 0.1$ M	652
$Fe^{2+} + Cl_2^{\bullet -} \rightarrow Fe^{3+} + 2Cl^-$	1.0×10^7 M^{-1} s^{-1}	pH = 1.0; $T = 25$ °C; outer sphere	879
	4.0×10^6 M^{-1} s^{-1}	pH = 1.0; $T = 25$ °C; inner sphere	879
$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^-$	2.3×10^8 M^{-1} s^{-1}	pH = 1.0; independent from temperature in the range 17−67 °C	880
	3.2×10^8 M^{-1} s^{-1}	pH = 7.0; H abstraction; probably no outer-sphere mechanism	449
	4.3×10^8 M^{-1} s^{-1}	pH = 3.0; $T = 20$ °C; temperature dependent	881
	3.0×10^9 M^{-1} s^{-1}		876
	5.0×10^9 M^{-1} s^{-1}		882
$Fe^{2+} + O_2^{\bullet -} \xrightarrow{2H_2O} Fe^{3+} + H_2O_2 + 2OH^-$	1.0×10^7 M^{-1} s^{-1}	pH = 6.8; $T = 25$ °C	883
$Fe^{2+} + HO_2^{\bullet} \xrightarrow{H^+} Fe^{3+} + H_2O_2$	1.2×10^6 M^{-1} s^{-1}	pH = 1.0; $T = 25$ °C; at pH < 4 k_{obs} independent from $[O_2^-]$	883
$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^-$	2.1×10^6 M^{-1} s^{-1}	pH = 0−2.1; presence of O_2	884
$Fe^{2+} + HO_2^{\bullet} \rightarrow (Fe^{III}HO_2)^{2+} \xrightarrow{k} Fe^{3+} + HO_2^-$	1.8×10^3 s^{-1}	$T = 25$ °C; formation of a bridged compound: $(Fe^{III}HO_2)^{2+} + Fe^{2+} \rightleftharpoons [Fe^{III}HO_2Fe^{II}]^{4+} \xrightarrow{k_2} Fe^{3+} + Fe^{II}OH_2^+$, which decomposes with $k_2 = 2.5 \times 10^4$ s^{-1}	885
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^-$	41 M^{-1} s^{-1}	$T = 20$ °C; in 0.1 M $HClO_4$	886
	48 M^{-1} s^{-1}	$T = 25$ °C, $\mu = 1.0$ M	485
	51 M^{-1} s^{-1}	$T = 20$ °C; in 0.4 M H_2SO_4	886
	65 M^{-1} s^{-1}	$T = 25$ °C; $\mu = 3.0$ M; iron(II) in large excess	526
	76 M^{-1} s^{-1}		701
$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^-$	1.6×10^{-7} s^{-1}	pH = 5.0; $T = 25$ °C	838
	8.1×10^{-6} s^{-1}	pH = 6.0; $T = 25$ °C	838
	6.4×10^{-5} s^{-1}	pH = 6.5; in sea water	887
	1.7×10^{-3} s^{-1}	pH = 7.6; in sea water	887
	1.4 M^{-1} s^{-1}	pH = 3.0; $T = 25$ °C	888
$Fe^{2+} + O_2 \rightarrow$ products	1.2×10^{13} M^{-2} atm^{-1} min^{-1}	pH = 6.84; $T = 25$ °C; $\mu = 0.11$ M; $p_{O_2} = 0.2$ atm	841
	2.9×10^{13} M^{-2} atm^{-1} min^{-1}	pH = 6.84; $T = 25$ °C; $\mu = 0.02$ M; $p_{O_2} = 0.2$ atm	841
	1.4×10^{14} M^{-3} s^{-1}	pH = 6.5; $T = 25$ °C; $\mu = 0.11$ M; presence of 0.1 M SO_4^{2-}	889
	1.6×10^{14} M^{-3} s^{-1}	pH = 6.5; $T = 25$ °C; $\mu = 0.11$ M; presence of 0.1 M Cl^-	889
	2.0×10^{14} M^{-3} s^{-1}	pH = 6.5; $T = 25$ °C; $\mu = 0.11$ M; presence of 0.1 M NO_3^-	889
	2.4×10^{14} M^{-3} s^{-1}	pH = 6.5; $T = 25$ °C; $\mu = 0.11$ M; presence of 0.1 M ClO_4^-	889
$Fe^{2+} + O_3 \rightarrow$ products	1.7×10^5 M^{-1} s^{-1}	$T = 25$ °C; $\mu = 3.0$ M	526
	$\geq 5.0 \times 10^5$ M^{-1} s^{-1}	pH = 2.0; $T = 22$ °C	592
	8.2×10^5 M^{-1} s^{-1}	pH = 0−2; $T = 25$ °C	890
$Mn^{2+} + SO_4^{\bullet -} \rightarrow Mn^{3+} + SO_4^{2-}$	1.6×10^7 M^{-1} s^{-1}	average of 3 rate values; rate independent from $[H_2SO_4]$ in the range 2−10 M	891
	3.0×10^7 M^{-1} s^{-1}	pH = 3.0	892
	1.8×10^{10} M^{-1} s^{-1}	estimated value	893
$Mn^{2+} + SO_4^{\bullet -} \rightleftharpoons X \xrightarrow{k_2}$ products	8.3×10^7 M^{-1} s^{-1}	$T = 20$ °C; $k_2 = 4.5 \times 10^4$ s^{-1}	877

Table 3.11. (Continued)

reaction	k	remarks	ref
$Mn^{2+} + SO_5^{\bullet -} \rightleftharpoons Mn^{3+} + SO_5^{2-}$	$>2 \times 10^8$ M^{-1} s^{-1}	calculated value	894
	10^8–10^9 M^{-1} s^{-1}	pH = 3.0; T = 20 °C; presence of sulfite; rate constant depends on dominant manganese(II) complex in solution: $k_{Mn^{2+}}, k_{Mn(HSO_3)^+} > k_{Mn(SO_3)Mn^{2+}}$	816
$Mn^{2+} + OH^\bullet \rightarrow Mn(OH)_2^+$	2.6×10^7 M^{-1} s^{-1}	pH = 9.0	895
	3.4×10^7 M^{-1} s^{-1}	pH = 6.7; T = 24 °C	896
$Mn^{2+} + O_2^{\bullet -} \rightarrow$ products	1.1×10^8 M^{-1} s^{-1}	pH = 6.7; T = 24 °C; $K = 1.5 \times 10^4$ M^{-1}; MnO_2 and $MnOH^{2+}$ are formed as products	896
$Mn^{2+} + O_2^{\bullet -} \xrightarrow{k} MnO_2^+ \xrightarrow{H^+} Mn^{3+} + HO_2^-$	4.6×10^7 M^{-1} s^{-1}	pH = 6–7; T = 25 °C; presence of formate; in the presence of sulfate: $k = 5.4 \times 10^7$ M^{-1} s^{-1}	793
$Mn^{2+} + HO_2^\bullet \xrightarrow{k_1} MnOOH^{2+} \xrightarrow{k_2} Mn^{3+} + HO_2^-$	6.4×10^6 M^{-1} s^{-1} (k_1) 12.7 s^{-1} (k_2)	pH = 1–3; T = 25 °C; in the presence of formate; in the presence of sulfate: $k_1 = 7.0 \times 10^6$ M^{-1} s^{-1}, $k_2 = 79.3$ s^{-1}	793
$Mn^{2+} + NO_3^\bullet \rightarrow Mn^{3+} + NO_3^-$	1.5×10^6 M^{-1} s^{-1}	[HNO$_3$] = 3 M; rate increases with increasing [HNO$_3$]; $k = 9.0 \times 10^6$ M^{-1} s^{-1} at [HNO$_3$] = 16 M	891
Mn^{2+} + NHAS$^a \rightarrow$ products	7.3×10^{-2} M^{-1} s^{-1}	pH = 11.0; T = 25 °C; [O$_2$] = 2.6×10^{-4} M	897
	2.2×10^{-3} M^{-1} s^{-1}	pH = 11.0; T = 25 °C; [O$_2$] = 7.6×10^{-4} M	897
$Mn^{2+} + O_2 \rightarrow Mn^{3+} + O_2^-$	$<3.3 \times 10^{-8}$ s^{-1}	pH = 8.35; T = 25 °C	869
	1.5×10^{-6} s^{-1}	pH = 8.95; T = 25 °C	869
	2.8×10^{-6} s^{-1}	pH = 9.04; T = 25 °C	869
	9.5×10^{-6} s^{-1}	pH = 9.25; T = 25 °C	869
	162 M^{-1} s^{-1}	pH = 8.0; T = 25 °C	898
	105 M^{-1} s^{-1}	pH = 8.9; T = 25 °C	898
$Cu^{2+} + SO_4^{\bullet -} \rightarrow Cu^{3+} + SO_4^{2-}$	8.1×10^7 M^{-1} s^{-1}	T = 20 °C	894
$Cu^{2+} + SO_4^{\bullet -} \overset{k}{\rightleftharpoons} X \xrightarrow{k_2}$ products	8.1×10^7 M^{-1} s^{-1}	T = 20 °C; $k_2 = 5.1 \times 10^3$ s^{-1}	877
$Cu^+ + OH^\bullet \rightarrow Cu^{2+} + OH^-$	2.0×10^{10} M^{-1} s^{-1}		899
$Cu^{2+} + OH^\bullet \rightarrow CuOH^{2+}$	3.1×10^8 M^{-1} s^{-1}	pH 3–6	900
	3.5×10^8 M^{-1} s^{-1}		901
$Cu^+ + HO_2^\bullet \xrightarrow{H^+} Cu^{2+} + H_2O_2$	2.3×10^9 M^{-1} s^{-1}	pH = 2.3; T = 25 °C; inner-sphere reaction	902
$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^\bullet + OH^-$	4.0×10^6 M^{-1} s^{-1}	pH = 8.0; T = 25 °C; in sea water; Cl$^-$ decreases oxidation rate	903
	4.7×10^3 M^{-1} s^{-1}	pH = 2.3; T = 25 °C	902
$Cu^+ + O_2 \rightarrow Cu^{2+} + OH^\bullet + OH^-$	7.8×10^4 s^{-1}	in sea water	904

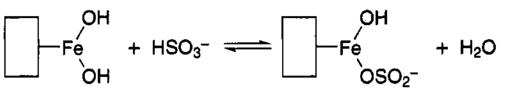
[a] *N*-Nitrosohydroxylamine-*N*-sulfonate.

respectively. However, during the lifetime of aerosols (see Table 1.9) a certain amount of metal ions can be leached from the TIM by acids or organic substances, and participate in homogeneous transition metal-catalyzed oxidation processes. Recently, Çakici et al.[772] reported that copper(II) oxide dissolves completely in water saturated by sulfur dioxide.

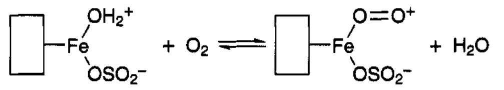
3.4.2. Mechanistic Aspects

Metal oxides play an important role in the industrially employed heterogeneously catalyzed autoxidation of sulfur(IV) oxides, e.g. the production of sulfuric acid with the help of vanadium pentoxide as catalyst. In general, metal oxides exhibit different catalytic activity (Figure 3.10), which is probably related to the different bond strengths of oxygen to the metal surface. The catalytic activity of a metal oxide increases with decreasing energy of the metal–oxygen bond.[923] Prasad et al.[242] observed no significant oxidation of sulfur(IV) oxides using SiO_2 or CuO as catalysts in the absence of oxygen. In addition, Bhagava et al.[924] found no oxidation of sulfite in aqueous suspensions of MgO in the absence of oxygen, although the rate of oxidation was found to be the same in air and oxygen-saturated solutions (see Table 3.18).

For the heterogeneous oxidation of sulfur(IV) oxides, it is assumed that both oxygen and sulfur(IV) are adsorbed on the surface of the metal oxide.[242,777,925]

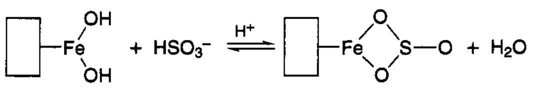


(3.87)



(3.88)

In addition to the monodentate surface complex (eq 3.87), the formation of a bidentate complex is also possible[777] (see also ref 786):



(3.89)

Furthermore, Kent et al.[926] observed three different surface species in their study of the adsorption of SO_2 on CuO.

Table 3.12. Aerosol Solubility and Leaching of Metals (see also ref 910)

(a) Solubility

sample, remarks	metal	total concentration	insoluble fraction	soluble fraction	%	ref
coal fly ash, leached by 0.5 M HCl (24 h values)	Cu	100 ppm	66 ppm^{a}	34 ppm	34	911
	Fe	39000 ppm	29250 ppm^{a}	9750 ppm	25	
	Mn	240 ppm	164 ppm^{a}	76 ppm	31.7	
	Ni	65 ppm	40 ppm^{a}	25 ppm	38.5	
oil fly ash	Fe	0.48%	0.13%		0.33	221
	Ni	1.28%	0.23%		1.05	
coal soot particles, leached by acid at pH 5.5	Cu	0.04 mg g^{-1}	0.03 mg g$^{-1\,a}$	0.01 mg g^{-1}	25	912
	Fe	20 mg g^{-1}	17 mg g$^{-1\,a}$	3.0 mg g^{-1}	15	
	Mn	0.12 mg g^{-1}	0.05 mg g$^{-1\,a}$	0.07 mg g^{-1}	58.3	
	Pb	0.08 mg g^{-1}	0.07 mg g$^{-1\,a}$	0.01 mg g^{-1}	12.5	
power plant fly ash, aqueous extract; values in brackets for leaching with nitric acid at pH 2.0	Cu			0.01 ppm (0.13)		913
	Fe			0.11 ppm (10.64)		
	Ni			*b* (0.30)		
	Pb			*b* (0.05)		
wet precipitation, pH 4.43	Cu	3.86 μg L$^{-1\,a}$	0.77 μg L^{-1}	3.09 μg L^{-1}	80.1	914
	Fe		88.3 μg L^{-1}			
	Pb	12.03 μg L$^{-1\,a}$	2.49 μg L^{-1}	9.54 μg L^{-1}	79.3	
bulk (wet + dry) precipitation, pH 5.95	Cu	8.12 μg L$^{-1\,a}$	4.69 μg L^{-1}	3.43 μg L^{-1}	42.2	914
	Fe		606 μg L^{-1}			
	Pb	37.5 μg L$^{-1\,a}$	32.5 μg L^{-1}	5.0 μg L^{-1}	13.3	
precipitation, North Atlantic 1988, leached with 0.4% HNO_3 for 24 h	Cu			0.09 μg L$^{-1\,c}$		915
	Fe			42.1 μg L$^{-1\,c}$		
	Mn			1.6 μg L$^{-1\,c}$		
	Pb			0.23 μg L$^{-1\,c}$		
precipitation, Ireland, leached with 0.4% HNO_3 for 24 h	Cu			0.77 μg L^{-1}		915
	Fe			2.78 μg L^{-1}		
	Mn			0.42 μg L^{-1}		
	Pb			0.49 μg L^{-1}		
atmospheric particles, La Jolla, CA, leached with sea water (3 h)	Co	<0.4 μg L^{-1}	0.3 μg L^{-1}	<0.1 μg L^{-1}	<25	202
	Cu	16 μg L^{-1}	11 μg L^{-1}	4.5 μg L^{-1}	28.1	
	Fe	610 μg L^{-1}	600 μg L^{-1}	7 μg L^{-1}	1.1	
	Mn	11 μg L^{-1}	5.9 μg L^{-1}	5.2 μg L^{-1}	47.3	
	Ni	11 μg L^{-1}	5.4 μg L^{-1}	5.2 μg L^{-1}	47.3	
	Pb	560 μg L^{-1}	340 μg L^{-1}	220 μg L^{-1}	39.3	
atmospheric particles, Ensenada, Mexico, leached with sea water (3 h)	Co	<0.5 μg L^{-1}	0.4 μg L^{-1}	<0.1 μg L^{-1}	<20	202
	Cu	20 μg L^{-1}	17 μg L^{-1}	2.9 μg L^{-1}	14.5	
	Fe	2100 μg L^{-1}	2100 μg L^{-1}	4 μg L^{-1}	0.2	
	Mn	46 μg L^{-1}	30 μg L^{-1}	16 μg L^{-1}	34.8	
	Ni	2.8 μg L^{-1}	2 μg L^{-1}	0.8 μg L^{-1}	28.6	
	Pb	150 μg L^{-1}	130 μg L^{-1}	20 μg L^{-1}	13.3	
atmospheric aerosol, leached with water or HNO_3 for 2 h^{d}	Mn			330 μg g$^{-1\,e}$		916
	Mn			94 μg g$^{-1\,f}$		
	Mn			58 μg g$^{-1\,g}$		

(b) pH Dependent Leaching of Transition Metals

		concentration of leached metal					
sample, remarks	pH	Cu	Fe	Mn	Ni	Pb	ref
fly ash; leaching time 24 h	3.0	15.60 μg g^{-1}			11.70 μg g^{-1}	9.10 μg g^{-1}	917
	6.0	0.82 μg g^{-1}			3.60 μg g^{-1}	1.40 μg g^{-1}	
	9.0	0.36 μg g^{-1}			0.50 μg g^{-1}	0.73 μg g^{-1}	
	12.0	0.59 μg g^{-1}			0.61 μg g^{-1}	0.91 μg g^{-1}	
fuel ash; pulverized; leaching time 6 h	2.0		0.57%	17.66%			213
	2.5		0.37%	16.73%			
	3.0		0.15%	6.97%			
	4.0		0.05%	3.25%			
	>5.0		0%	0%			
marine aerosols, dissolution by rain water (10 min)	2.0			800 μg L^{-1}			918
	3.4			730 μg L^{-1}			
	5.0			270 μg L$^{-1\,h}$			

[a] Calculated by arithmetic mean. [b] Not traceable. [c] Mean value from six precipitation events. [d] 83% Mn were water + acid leachable. [e] Water soluble. [f] With 0.08 M HNO_3. [g] With 1 M HNO_3. [h] Buffered; 370 μg L^{-1} for unbuffered solution after 6 min.

In contrast to the homogeneous catalysis by transition metals, it is more difficult to present a general reaction mechanism for the heterogeneously catalyzed oxidation of sulfur(IV) oxides, mainly due to the limited information on the adsorption and redox activities of different surface sites. These activities

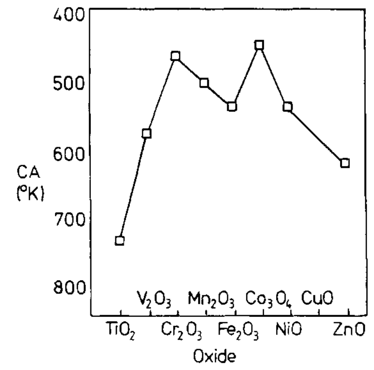


Figure 3.10. Catalytic activity of some metal oxides for the oxidation of NH_3 (expressed as the temperature required to oxidize 5% of the NH_3) (taken from ref 922).

probably depend on the nature of the metal oxide or hydroxide studied (see further Discussion). In the following proposed mechanism,[925] different surface sites were not considered:

$$M_xO_y + O_2 \rightleftharpoons M_xO_y{\cdot}O_2 \tag{3.90}$$

$$M_xO_y{\cdot}O_2 + HSO_3^- \rightleftharpoons M_xO_y{\cdot}O_2{\cdot}SO_3H^- \tag{3.91}$$

$$M_xO_y{\cdot}O_2 + SO_3^{2-} \rightleftharpoons M_xO_y{\cdot}O_2{\cdot}SO_3^{2-} \tag{3.92}$$

$$M_xO_y{\cdot}O_2{\cdot}SO_3H^- \rightarrow M_xO_y + HSO_5^- \tag{3.93}$$

$$M_xO_y{\cdot}O_2{\cdot}SO_3^{2-} \rightarrow M_xO_y + SO_5^{2-} \tag{3.94}$$

$$HSO_5^- + S(IV) \rightarrow 2S(VI) \tag{3.95}$$

$$SO_5^{2-} + S(IV) \rightarrow 2S(VI) \tag{3.96}$$

In contrast to the mechanism given above (eqs 3.90–3.96), Kim and Choi[927] suggested that SO_2 appears to be adsorbed essentially on the O lattice (of α-Fe_2O_3) as a molecular species, whereas O_2 is adsorbed on an O vacancy as an ionic species (O_2^-).

In the case of mixed particles (e.g. atmospheric dust, fly ashes) the composition of the investigated samples (see Table 1.10) is a dominant factor that influences the overall redox process, since synergistic effects complicate the situation.

On the basis of the adsorption behavior of SO_2 on hematite, α-Fe_2O_3, Faust and Hoffmann[874] suggested the existence of two different adsorption sites on the surface with two different adsorption constants. In addition, spectroscopic investigations of the surfaces of α-, β-, and γ-FeO(OH) exhibit differently bound surface hydroxyl groups[928] and therefore probably different adsorption activities. In contrast to α- and β-FeO(OH), γ-FeO(OH) only has one type of surface hydroxyl groups.[928]

Two types of mechanisms for the heterogeneous catalysis are reported in the literature. In the one, the catalytic activity of particles during the oxidation of sulfur(IV) oxides is mainly ascribed to surface catalysis,[242,782,929–931] whereby sulfur and/or oxygen are adsorbed on active surface centers. In the other, the catalytic activity of particles is suggested to be mainly due to leached metal ions (homogeneous catalysis, see section 3.3).[210,239,906,913,932,933] For leaching of metal ions from fly ashes see e.g. refs 910, 911, and 917 and Table 3.12.

Table 3.13. SO_2 Adsorption Capacities of Different Metal Oxides as a Function of the Relative Humidity[934]

metal oxide	relative humidity (%)	surface area ($m^2\ g^{-1}$)	SO_2 adsorption capacity (mg of SO_2/g of metal oxide)
MgO	0		4
	50		12
	95		400
Fe_2O_3	0	27.3	0.6
	50		1.2
Al_2O_3	0	215	25
	53		5
	95		17
MnO_2	0	109	4
	25		78
	58		320
	95		>530

By using atmospheric dust as a catalyst for the oxidation of sulfur(IV) oxides, Rani et al.[210] observed at the beginning of the reaction an induction period (see section 3.3.3) which was suggested to be due to a slow surface catalysis. Due to the leaching of metal ions, the slow surface catalysis is overtaken in time by faster homogeneous catalysis. According to Zhang and Millero[906] only dissolved iron is catalytically active during the oxidation of sulfur(IV) oxides in sea water, whereas colloidal iron exhibits no catalytic activity. This is in agreement with results of Grgić et al.,[905] who observed no catalytic effect of iron(III) on the oxidation of sulfur(IV) oxides at a pH larger than 6 (see also ref 756). Comparative studies by Prasad et al.[242] on the CuO and Cu(II) catalysis provide evidence for both homogeneous (by dissolved copper(II) ions) and heterogeneous (surface catalysis) contributions during the heterogeneous CuO-catalyzed oxidation of sulfur(IV) oxides. Gupta et al.[933] suggested the contribution of the surface catalysis to be in the range of 13–34% during the heterogeneous autoxidation of sulfur(IV) oxides in mineral and stone suspensions. The contribution of the homogeneous catalysis by dissolved metal ions is 66–86%. By using soot particles as catalyst Grgić et al.[912] found at pH 3.9 the same rate constant as for the iron(III)-catalyzed oxidation of sulfur(IV) oxides under the same experimental conditions.

Metal oxides exhibit different adsorption capacities for SO_2 as a function of the relative humidity (Table 3.13). The relative humidity is a major factor in controlling the oxidation rate of sulfur(IV) oxides in the heterogeneously catalyzed oxidation process[935] (see also Table 3.13). For mineral dusts (silcates and calcites), a SO_4^{2-} formation rate of 25–150 mg of SO_4^{2-} (g of mineral)$^{-1}$ ([SO_2] = 0.86 ppm, reaction time 1–5 days, relative humidity 85%) was reported by Mame and Gottlieb.[936] For fly ash, values of 220 mg of SO_4^{2-} (g of fly ash)$^{-1}$ (pH 4.7) up to 600 mg of SO_4^{2-} (g of fly ash)$^{-1}$ (pH 6) were found.[935]

The surface pH is a dominating factor for the overall reaction rate.[934] Due to the formation of H^+ ions during the redox process, the oxidation rate

Table 3.14. Selected Literature on the Heterogeneous Catalyzed Oxidation of Sulfur(IV) Oxides

aerosol/particle	remarks	ref
particle from different sources	influence of pH and relative humidity	232
fly ash	solubility of metal important for catalytic process	240
fly ash/cement dust	influence of pH and relative humidity	935
fly ash (power plant)	influence of buffers, [S(IV)], [fly ash], EDTA	913
mineral particle/cement dust	comparison of SO_2 and NO_x oxidation	936
atmospheric dust	catalytic activity due to dissolved metal ions	210
sea salt particles	influence of SO_2 and relative humidity	937
sea salt particles	influence of NO_2 and relative humidity	216
sea salt particles	influence of water content	938
sea salt particles	influence of relative humidity, [SO_2]	939
carbon particles	influence of LWC and NO_2	940
soot particles	influence of pH	912
soot particles	oxidation by NO_2	941
phosphate aerosols	influence of LWC and pH	942
Al_2O_3, SiO_2, TiO_2	no surface catalysis by H_2O_2-induced oxidation	703
CdO	influence of buffers	943
CoO	influence of buffers, pH, O_2	643
Fe_2O_3, MgO, MnO_2	influence of relative humidity, p_{SO_2}, p_{O_2}, surface catalysis	934
Fe_2O_3	oxidation capacity	241
α-Fe_2O_3	adsorption sites for SO_2 and O_2	927
α-Fe_2O_3	adsorption sites for SO_2	874
α-Fe_2O_3	photoinduced autoxidation of SO_2	777
α-Fe_2O_3, α-FeO(OH), β-FeO(OH), γ-Fe_2O_3, γ-FeO(OH), δ-FeO(OH)	photocatalytic activity	944
MgO	influence of buffers, pH, O_2	924
$MnSO_4$	influence of relative humidity	235
$MnSO_4$, $MnCl_2$	comparison of catalytic activity	945
$MnSO_4$	influence of relative humidity and NH_3	234
$MnSO_4$	change in particle size due to oxidation of SO_2	946
NaCl	influence of relative humidity	238
Ni_2O_3	influence of buffers, pH, O_2	782
SiO_2, CuO	influence of buffers, pH, EDTA, mannitol	242

slows down with time, since the sulfur(IV) oxides are less soluble in acidic solution (see section 2.1).

Selected literature on the heterogeneously catalyzed oxidation of sulfur(IV) oxides is summarized in Table 3.14.

3.5. Miscellaneous Effects

The reaction mechanism given for the homogeneous catalysis by transition metals during the oxidation of sulfur(IV) oxides is only valid under ideal reaction conditions, considering no influence by e.g. anions (section 3.5.1) or other metal ions (section 3.5.3). In addition, the ionic strength (section 3.5.2) and the initial pH of the reaction solution (section 3.5.5) were reported to affect the reaction. In view of an autoxidation process, the initial oxygen concentration (section 3.5.4) may have a certain influence. All the parameters mentioned influence the product formation and/or the product distribution (section 3.5.6).

3.5.1. Influence of Anions and Organic Compounds

The reaction rate of the transition metal-catalyzed oxidation of sulfur(IV) oxides depends on the ligand substitution rate of the metal ion and the stability of the produced complex, the possible translabilization effect of coordinated ligands, and the effect of coordinated ligands on the redox potential of the M^{3+}/M^{2+} system.

The effects of chloride (sea spray), sulfate and dithionate (oxidation products), and acetate and formate (buffer species present in atmospheric water droplets (see Table 1.17) on the transition metal-catalyzed oxidation of sulfur(IV) oxides will be discussed here due to their mechanistic and atmospheric relevance.

Chloride and sulfate are the most important water-soluble components of atmospheric aerosols[180,216] and have been found in high concentrations in rain water[37,169,327] and cloud and fog droplets[179,180,947] (see Table 1.16 for sulfate concentration). In rain water samples collected in northeastern Bavaria (Germany) the contribution of Cl^-, NO_3^-, and SO_4^{2-} to the total anionic equivalent per cubic meter was found to be 15.8, 39.1, and 45.1%,[948] respectively (see also ref 949). As mentioned in section 1.5, acetic and formic acid are the most important organic acids that have an influence on the acidity of wet precipitation. The reported influence of acetate and formate (Table 3.15) is mostly based on data for the influence of the buffer concentration on the reaction rate.[i]

The possible influence of anions can be studied in two different ways, viz. by using different salts of the same transition metal (e.g. $MnCl_2$ and $MnSO_4$) or by addition of the anion in the form of its alkali or earth alkali metal salt. For the possible influence of cations see refs 584, 755, 956, and 957.

Meyer[958] already described that different salts of one transition metal ion exhibit different catalytic activities in the oxidation of sulfur(IV) oxides. The chloride salts of iron and cobalt exhibit a slightly higher catalytic activity than the sulfate salts, whereas

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[i] It should be noted here, that the oxidative degradation of organic acids during the oxidation of sulfur(IV) oxides is accelerated by the presence of iron, cobalt, and nickel, and decreased by manganese and halides (ref 893 and literature cited therein). Possible effects of this pathway on the overall oxidation process of sulfur(IV) oxides are not treated in the further discussion.

Table 3.15. Influence of Anions on the Oxidation of Sulfur(IV) Oxides

anion, concentration range	effect[a] +	effect[a] −	effect[a] O	remarks	ref
Cl^-					
0−0.2%	x			uncatalyzed oxidation by O_2 in tap and river water	950
0−0.5 M	x		x	uncatalyzed oxidation by O_2; acceleration of the reaction at $[Cl^-] > 10^{-3}$ M	584
−	x			uncatalyzed oxidation by O_2; cloud chamber experiment	951
$>5.0 \times 10^{-5}$ M	x			uncatalyzed oxidation by O_2; at $[Cl^-] \approx 10^{-4}$ M catalytic action comparable to that for carbon particles at the same conditions	952
1.0×10^{-10}−5.0×10^{-4} M		x		uncatalyzed oxidation by $OH^•$ radicals; Cl^- acts as radical scavenger	581
0−0.447 M			x	uncatalyzed oxidation by H_2O_2	691
0−1.0 M	x			uncatalyzed oxidation by H_2O_2; maximum value for k_{obs} at 0.4 M Cl^-	698
−	x	x		iron(III) catalysis; acceleration at low $[Cl^-]$, inhibition at high $[Cl^-]$	516
1.0×10^{-4}−1.0 M		x		iron(III) catalysis; inhibition due to increasing ionic strength	953
0−5.0×10^{-2} M			x	iron(III) catalysis; influence on O_2-induced step	511
0−1.2×10^{-2} M	x			Ni(III) catalysis;[b] effect is pH dependent	742
SO_4^{2-}					
0−0.1%		x		uncatalyzed oxidation by O_2 in tap and river water	950
0−0.149 M			x	uncatalyzed oxidation by H_2O_2	691
−		x		iron(II) catalysis; iron(III) catalysis	827
0−5.5×10^{-2} M		x		iron(II) catalysis; length of induction periode depends linear on $[SO_4^{2-}]$	826
5.0×10^{-4}−0.1 M		x		iron(III) catalysis; SO_4^{2-} complexes catalytic species	953
0−7.5×10^{-2} M		x		iron(III) catalysis; influence on O_2-induced step	511
−		x		manganese(II) catalysis; inhibiting effect smaller than in the case of iron(II) catalysis	954
0−0.195 M			x	manganese(II) catalysis	781
1.0×10^{-3}−1.0 M		x		iron(III)−manganese(II) synergism	955
$S_2O_6^{2-}$					
−			x	iron(III) catalysis; no influence on formation of the iron−sulfito complex	503
2.5×10^{-5}−5.0×10^{-4} M			x	iron(III) catalysis; no influence on O_2-induced step	511
0−5.0×10^{-3} M			x	manganese(III) catalysis; $S_2O_6^{2-}$ exhibit no reactivity toward Mn(III) in 3.5 M acid solution	781
$HCOO^-$					
0.01−0.15	x			uncatalyzed oxidation by H_2O_2; nonlinear increase of k_{obs} with increasing formic acid concentration	594
0.05−0.5 M	x			uncatalyzed oxidation by H_2O_2; reaction rate increases linear with increasing buffer concentration	691
0−3.0×10^{-4} M		x	x	iron(III) catalysis; no influence at pH ≤ 3; inhibition at pH ≥ 5	756
0−5.0×10^{-3} M		x	x	iron(III) catalysis; no influence at pH 2.5; inhibition at pH 4	511
H_3CCOO^-					
0.02−0.04 M			x	uncatalyzed oxidation by H_2O_2; in the pH range 3−5.5; in the presence of phosphate higher value for k_{obs}	698
0.04−0.18 M	x			uncatalyzed oxidation by H_2O_2; k_{obs} increases linear with increasing acetic acid concentration	594
0.05−0.5 M	x			uncatalyzed oxidation by H_2O_2; reaction rate increases linear with increasing buffer concentration	691
0−3.0×10^{-4} M		x	x	iron(III) catalysis; no influence at pH ≤ 3; inhibition at pH ≥ 5	756
0−5.0×10^{-3} M			x	iron(III) catalysis; no influence at pH 2.5 and pH 4	511
−		x		heterogeneous catalysis by aqueous suspensions of MgO; increasing buffer concentration while the ratio of $[CH_3COONa]/[CH_3COOH)]$ is constant results in a decrease of oxidation rate	924
0−0.14 M	x	x		heterogeneous catalysis by aqueous suspensions of fly ash; with increasing buffer up to 2×10^{-2} M increase in oxidation rate, at higher acetate concentration decrease in oxidation rate; at highest $[CH_3COO^-]$ oxidation rate is still higher than in the absence of a buffer	913
3.5×10^{-2}−0.28 M			x	heterogeneous catalysis by atmospheric dust at pH 5.06; no effect on reaction rate but slow initial reaction was lengthened	210

[a] Symbols are as follows: +, acceleration; −, inhibition; O, no effect. [b] $[Ni^{III}(cyclam)]$ complex.

in the case of manganese catalysis, the sulfate salt was reported to have a higher catalytic activity than the chloride salt.[958] In recent literature the catalytic activity of different salts of one transition metal has been studied e.g. for copper(II), manganese(II), and iron(III). Conklin and Hoffmann[740] found a higher sulfur(IV) oxidation rate when copper(II) chloride instead of copper(II) sulfate was used. In contrast to Bassett and Parker,[151] who reported a much higher catalytic activity for manganese(II) sulfate than for manganese(II) chloride, Huss et al.[826] observed no difference in the reaction rate when manganese(II) chloride or manganese(II) sulfate were used. A comparison of the catalytic activity of different iron(III) salts indicated that iron(III) chloride had the highest and iron(III) sulfate the lowest activity.[511] The purity of the salt is very important in such studies, since trace impurities can cause synergistic effects (see section 3.5.3) that may overrule the anion effects.

The influence of different metal salts has also been studied for the heterogeneous catalyzed oxidation of sulfur(IV) oxides. Cheng et al.[945] reported a higher catalytic activity for manganese(II) sulfate than for manganese(II) chloride aerosols. In a study of the catalytic activity of different manganese(II) and copper(II) aerosols, Berresheim and Jaeschke[239] observed the highest catalytic activity for the nitrate salts (see also Table 4.1).

The influence of Cl^- and SO_4^{2-} on the uncatalyzed and on the homogeneously catalyzed oxidation of sulfur(IV) oxides is summarized in Table 3.15. The influence of $S_2O_6^{2-}$ has only been studied in a few cases.

The influence of anions on the oxidation process of sulfur(IV) oxides can basically be accounted for in terms of (1) the anion acting as radical scavenger, (2) the anion functioning as competitive ligand at the metal center, (3) coordinated anions accelerating or inhibiting the reoxidation process of the reduced metal ion, and (4) translabilization effects by coordinated anions.

It has been suggested in the literature that anions can function as radical scavengers[181,581,589,756] and, if a free radical mechanism is operative, can inhibit the reaction rate. Cl^- for instance reacts fast with the $SO_4^{\bullet-}$ radical (eq 3.97), but the $Cl^\bullet$ product can probably also open new reaction routes. If the $SO_4^{\bullet-}$ radical is the main-chain carrier, as suggested in the case of the photooxidation of SO_3^{2-} (pH > 7),[758] high $[Cl^-]$ should inhibit the overall redox process.

$$\begin{aligned} &Cl^- + SO_4^{\bullet-} \rightarrow Cl^\bullet + SO_4^{2-} \\ &\quad k = 1.9 \times 10^8\ M^{-1}\ s^{-1} \quad (pH\ 7-8)^{599} \\ &\quad k = 2.8 \times 10^8\ M^{-1}\ s^{-1\ 959} \\ &\quad k = 3.1 \times 10^8\ M^{-1}\ s^{-1} \quad (pH\ 5.8)^{583} \\ &\quad k = 3.1 \times 10^8\ M^{-1}\ s^{-1} \quad (pH\ 6.8)^{960} \\ &\quad k = 3.7 \times 10^8\ M^{-1}\ s^{-1} \quad (pH\ 1.5)^{583} \\ &\quad k = 4.7 \times 10^8\ M^{-1}\ s^{-1} \quad (pH\ 6.6-7.2)^{961\ j} \qquad (3.97) \end{aligned}$$

In the case where the added anion competes as a ligand with sulfite (see section 2.2.1), the formation rate of the metal–sulfite complex should decrease with increasing anion concentration. A decrease in the formation rate of the iron(III)–sulfito complexes with increasing $[SO_4^{2-}]$ has indeed been observed.[511] Furthermore, the equilibrium constants of metal complexes exhibit a certain dependence on different aqueous salt solutions (see Table 2.5).

Coordinated ligands can change the redox potential of the M^{2+}/M^{3+} couple[420,448,962] and so affect the oxidation/reduction behavior of the transition metal ions. The oxidation rate of e.g. iron(II) decreases in the order $ClO_4^- > NO_3^- > Cl^- > Br^- > I^- > SO_4^{2-}$ [841,889] (see also ref 963). The strong inhibition by sulfate ions can be explained in two ways: the produced iron(II) sulfate species, $FeSO_4$, are less reactive than aquated iron(II) ions;[963] the formation of dimeric iron(II) species, $Fe^{2+}-SO_4^{2-}-Fe^{2+}$ ($[Fe^{2+}]_{total} \gg [Fe^{2+}-SO_4^{2-}-Fe^{2+}]$) can occur,[964] and these can be oxidized by oxygen. Oxidation studies of copper(I) in sea water[965] clearly indicated that the rate of the autoxidation of copper(I) decreases in the order $Cu^+ > CuCl > CuCl_2^-$ (see also ref 903). Theis and Singer[966] showed that organic acids could retard the autoxidation of iron(II) due to the formation of stable complexes. The reactivity of copper(II) complexes is substantially smaller than that of free copper(II) ions, when several organic ligand molecules are attached. This effect can be explained in terms of changes in the redox potential of the copper(II).[967] In contrast, the oxidation kinetics of aquated chromium(II) by H_2O_2 is accelerated by a factor of 2–5 in the presence of organic and inorganic anions.[968] It is suggested that an anion-bound chromium(II) species is formed, which is more easily oxidized than the hexaaqua species. Recently, the inhibiting effect of organic ligands in the iron-catalyzed autoxidation of sulfur(IV) oxides in atmospheric water droplets was suggested.[181] These authors observed, in fog water with high concentrations of organic pollutants, sulfur(IV) oxidation rates that were significantly lower than those expected for the iron-catalyzed autoxidation process. In contrast, Mohapatra[969] found for the iron(III)-catalyzed oxidation of bisulfite in the presence of 1,10-phenanthroline, that the oxidizing ability of the iron(III) species follow the order: $Fe(phen)_3^{3+} > Fe(phen)_2^{3+} > Fe^{3+}$. In addition, Richards et al.[632] observed that the reaction between hydrogen peroxide and sulfur(IV) was inhibited in cloud water samples. The inhibition was suggested to be due to the formation of hydroxymethanesulfonic acid (HMSA) via the interaction of formaldehyde with sulfite (see introduction to section 3.2).

The sulfur-induced translabilization effect of coordinated S ligands has been studied in detail.[767,970] If other anions also induce a trans effect, ligand substitution will be accelerated resulting in a faster complex formation and subsequent decomposition. Furthermore, the decomposition of iron(III)–sulfito complexes at a given pH proceeds faster in nitric acid medium than in sulfur acid medium.[466]

For rain samples collected in Germany (pH 4.4 [acetate] = 5.2 μM, [formate] = 5.9 μM, [sulfate] = 30.5 μM, [chloride] = 12.2 μM), the distribution of different metal complexes was studied.[169] In the case of copper(II), iron(II), and manganese(II) the hexaaqua complexes dominate, whereas 90–95% of the iron(III) is present as the dihydroxo species, $[Fe(H_2O)_4(OH)_2]^+$. The contribution of metal sulfate complexes is in the range of 0.3–0.7% for copper(II), iron(II), and manganese(II), but for iron(III) < 0.1%. Complexes with organic anions like acetate and formate are only present in fractions < 0.1% for the investigated anions.[169] At higher [organic], the situation changes completely. Erel et al.[791] calculated for an atmospheric water sample (pH 3.4, [oxalate] = 13.2 μM, [acetate] = 36.8 μM, [formate] = 39.8 μM, [chloride] = 95 μM, [sulfate] = 264 μM) that more than 97% of the iron(III) is complexed by oxalate, whereas 95% of the iron(II) is in the $Fe(H_2O)_6^{2+}$ form. The remaining iron(II) is complexed by sulfate (3.2%) and acetate (1.6%).

3.5.2. Influence of Ionic Strength

The ionic strength μ can have an important influence on the rate constant k of a reaction and therefore also on the equilibrium constant K. A theoretical study on the influence of ionic strength on the reaction rate of the oxidation of sulfur(IV) oxides is reported by Clarke.[409] A compilation of literature on the effect of ionic strength on the oxidation of sulfur(IV) oxides is given in Table 3.16.

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[j] Rate constant depends on ionic strength and increases with increasing μ; given value is for $\mu = 0.1$ M; $k = 6.2 \times 10^8\ M^{-1}\ s^{-1}$ at $\mu = 0.4$ M.

Table 3.16. Influence of Ionic Strength μ on the Oxidation Rate of Sulfur(IV) Oxides

μ (M)	remarks	ref
0–1	uncatalyzed oxidation by O_3; increase of reaction rate	590
0.18–1.6	uncatalyzed oxidation by H_2O_2; influence of μ is pH dependent	570
0–0.447	uncatalyzed oxidation by H_2O_2; no influence of μ	691
0–1	uncatalyzed oxidation by H_2O_2; reaction rate depends on electrolyte used for adjusting ionic strength	698
0.1–1.0	uncatalyzed oxidation by H_2O_2; slight decrease (20%) of the reaction rate with increasing ionic strength	693
0.12–2.12	cobalt(II) oxide catalysis; slight increase of the reaction rate (ca. 25%)	643
0–0.15	iron(II) catalysis; inhibition of the reaction rate	826
0–1.0	iron(III) catalysis; enhancement of the reaction rate	953
0.1–1.0	iron(III) catalysis; inhibition of the O_2-induced step	511
0–0.2	manganese(II) catalysis; inhibition of the reaction rate	826
1×10^{-3}–1	manganese(II) catalysis; inhibition of the reaction rate	971
0–1	manganese(II) catalysis; inhibition of the reaction rate	749
1×10^{-3}–1	iron(III)–manganese(II) synergism; inhibition of the reaction rate	955

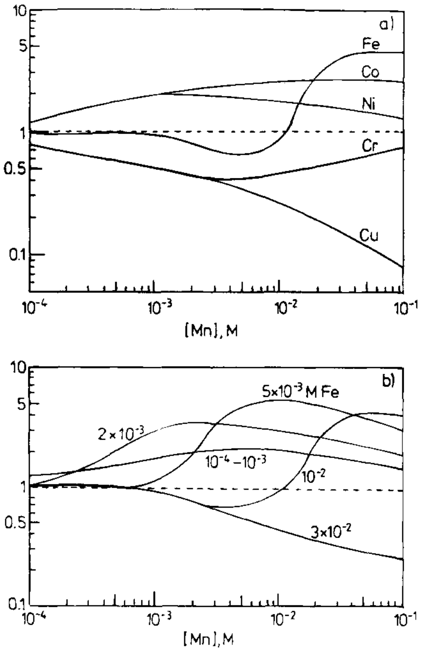


Figure 3.11. (a) Synergism coefficient S as a function of Mn concentration, 10 mM of the second catalyst, 10 mM S(IV) and pH 5; (b) synergism coefficient S for Mn–Fe system as a function of different [Fe] at 10 mM S(IV) and pH 5.[973]

3.5.3. Synergism

In atmospheric chemistry, synergistic effects probably play an important role. Positive synergism is defined as an acceleration of the transition metal-catalyzed oxidation of sulfur(IV) oxides, resulting from the action of two or more catalytically active transition metal ions. Negative synergism occurs when the catalytic activity of a transition metal ion is decreased by the presence of another metal ion. For example, the iron(III)-catalyzed oxidation of sulfur(IV) oxides is inhibited by addition of vanadium(IV) or iron(II) salts.[511,804,972] Manganese(II) exhibits a clear decrease in its catalytic activity in the presence of copper(II) (pH 5, $[Mn^{2+}] = [Cu^{2+}] \geq 5.0 \times 10^{-3}$ M)[973] (see also ref 974).

The synergistic effect (positive or negative) depends on the concentration or the concentration ratio of the involved metal ions (Figure 3.11) and can be described in a general way by the synergism coefficient S, which is defined as the ratio of the observed enhancement factor E_{obs} with both catalysts A and B present simultaneously, to the separate enhancement E_i of the individual catalyst i (ref 973 and literature cited therein).

$$S = \frac{E_{obs}}{(E_A{}^2 + E_B{}^2 - 1)^{1/2}}$$

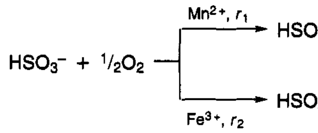
The interpretation of S can be given as

$$S > 1,\quad \text{positive synergism}$$

$$S = 1,\quad \text{no interaction}$$

$$S < 1,\quad \text{negative synergism}$$

The first study on synergistic effects in transition metal-catalyzed reactions was probably performed by Price.[975] The synergistic effect of two transition metal ions (Cu^{2+}, Fe^{2+}) during the oxidation of sulfur(IV) oxides was probably described first by Titoff.[617] In more recent literature (Table 3.17), the iron–manganese synergism is the most widely studied system for the catalyzed oxidation of sulfur(IV) oxides. The iron–manganese synergism, as well as other synergistic effects, cannot be described as the sum of the two individual reactions r_1 and r_2



(3.98)

but rather follows another mechanism

$$HSO_3{}^- + {}^1/_2O_2 \xrightarrow{Mn^{2+},\, Fe^{3+}} HSO_4{}^- \qquad (3.99)$$

and can be described for example by the following rate law:[932]

$$d[S(IV)]/dt = k\{[Mn^{2+}] + [Fe^{3+}]\}[S(IV)]^{0.85}$$

$$2.0 \times 10^{-7}\ M \leq [Fe^{3+}] \leq 1.0 \times 10^{-6}\ M$$

$$2.0 \times 10^{-7}\ M \leq [Mn^{2+}] \leq 2.0 \times 10^{-6}\ M$$

$$\mu < 1.0 \times 10^{-3}\ M$$

$$k = 1.0 \times 10^{3}\ M^{-0.85}\ s^{-1}\ (pH = 4, 25\ °C)$$

Martin and Good[955] reported a different rate law ($[S(IV)] \leq 10^{-5}$ M, pH = 3.0) for the iron–manganese synergism:

$$d[S(IV)]/[S(IV)]dt = k_1[Fe^{3+}] + k_2[Mn^{2+}] + k_3[Fe^{3+}][Mn^{2+}]$$

with $k_1 = 2600\ M^{-1}\ s^{-1}$, $k_2 = 750\ M^{-1}\ s^{-1}$, and $k_3 = 1.0 \times 10^{10}\ M^{-2}\ s^{-1}$.

Table 3.17. Selected Literature on Synergistic Effects for the Oxidation of Sulfur(IV) Oxides

catalyst	remarks	ref
Cu^{2+}/Mg^{2+}	$Mg(OH)_2$ inhibits in alkaline solution	976
Fe^{3+}/Cu^{2+}	influence of Fe^{2+} and Cu^+	845
Fe^{2+}/Mn^{2+}	Fe^{2+} is oxidized into the catalytic active Fe^{3+}	745
Mn^{2+}/Cu^{2+}	no synergism by Cu^{2+} in acidic solution	745
Fe^{3+}/Cu^{2+}	influence on $SO_4^{2-}/S_2O_6^{2-}$ ratio; reaction rate increases with increasing $[Cu^{2+}]$	516
Fe^{3+}/Mn^{2+} Fe^{3+}/Ni^{2+} Fe^{3+}/Cr^{3+}	no synergism observed	516
Fe^{3+}/Mn^{2+}	no synergism in the presence of succinic acid	619
Fe^{3+}/Mn^{2+}	synergistic effect	977
Fe^{3+}/Co^{2+} Fe^{3+}/Cu^{2+} Mn^{2+}/Co^{2+}	no synergism observed	578
Fe^{3+}/Mn^{2+}	influence of pH, $[Fe^{3+}]$, $[Mn^{2+}]$	578
Fe^{2+}/Cu^{2+}	no synergism observed	828
Mn^{2+}/Fe^{3+} Mn^{2+}/Co^{2+} Mn^{2+}/Ni^{2+} Mn^{2+}/Cu^{2+}	influence of the concentration of the second metal ion	973
Fe^{3+}/Mn^{2+}	influence of pH, anions	978
Fe^{3+}/Mn^{2+}	pH dependence of rate constant; highest rate at pH 4	332
Fe^{3+}/Mn^{2+} Fe^{3+}/Cu^{2+}	synergistic effect	974
Mn^{2+}/Cu^{2+}	inhibition by Cu^{2+}	974
Mn^{2+}/Ni^{2+}	synergistic effect	832
Fe^{3+}/Mn^{2+}	influence of SO_4^{2-} and ionic strength	955
Fe^{3+}/Mn^{2+} $Fe^{3+}/Mn^{2+}/Pb^{2+}$	synergistic effect	932
Fe^{3+}/Mn^{2+}	no influence of Mn^{3+}	750
Fe^{3+}/Mn^{2+} Fe^{3+}/Co^{2+} Fe^{3+}/Ni^{2+} Fe^{3+}/Cr^{3+}	synergistic effect on the oxygen-induced step	511

Clarke and Radojevic[614] found no evidence for a synergistic effect between manganese and iron in rain water samples. In contrast, Tanaka et al.[332] reported that the sulfur(IV) oxidation rate in rain water depends on both the iron(III) and the manganese(II) concentrations.

Synergism in the transition metal-catalyzed oxidation of sulfur(IV) oxides can result from two effects. On the one hand, the transition metal ions act as individual catalysts which results in an oxidation rate that is not necessarily the sum of the individual rates (see Discussion above). On the other hand, in view of a redox cycle (see section 3.3.6), the synergism can also be due to a faster reoxidation of the reduced metal ion. Synergistic effects in the case of metal ion oxidation processes has widely been reported.[833,842,843,867,868]

Table 3.18. Reaction Order for O_2 for the Oxidation of Sulfur(IV) Oxides

catalyst	order for O_2	conditions	ref
	(a) Homogeneous Catalysis[a]		
Fe^{6+}	0	c_{O_2}: 0−0.26 mM	778
Fe^{3+}	0	p_{O_2}: 1.0−7.5 atm	827
	0	c_{O_2}: 0.26−1.25 mM	905
	0	c_{O_2}: 0.26−1.25 mM	752
Fe^{2+}	0	c_{O_2}: <10 mM	755
	1	c_{O_2}: 10−90 mM	755
	1	p_{O_2}: 1.0−7.5 atm	827
Mn^{2+}	0	c_{O_2}: 0.3−0.8 mM	831
	0	c_{O_2}: 0.3−90 mM	755
	0	c_{O_2}: 0.26−0.43 mM	981
	1[b]		982
Co^{2+}	0	c_{O_2}: 0.1−0.4 mM	983
	0	c_{O_2}: 0.25−1.25 mM	984
	0[c]	p_{O_2}: 0.05−0.93 atm	985
	0	c_{O_2}: 3.4−22 μM	760
	0	c_{O_2}: 0.3−0.8 mM	748
	1	c_{O_2}: 0−0.9 mM	986
	1	c_{O_2}: 0.6−2.4 mM	987
	1	c_{O_2}: $>6 \times 10^{-4}$ M	618
	1[b,d]	c_{O_2}: 0.25−1.25 mM	984
	1	c_{O_2}: >0.375 mM	988
	1	p_{O_2}: 0.1−1 atm	979
	1	p_{O_2}: 12.5−99%	989
	1	p_{O_2}: 1.1−7 atm	990
	2	c_{O_2}: $<6 \times 10^{-4}$ M	618
	2[b,e]	c_{O_2}: 0.25−1.25 mM	984
	2[c]	p_{O_2}: 0.2−1 atm	991
	2	p_{O_2}: <0.8 atm	990
	2	c_{O_2}: <0.375 mM	988
	2	c_{O_2}: 0.1−0.6 mM	992
	2	c_{O_2}: 0.2−0.8 mM	993
Cu^{2+}	0	c_{O_2}: $<3 \times 10^{-3}$ M	994
	(b) Heterogeneous Catalysis		
CoO	1	c_{O_2}: 20−80%	643
Fe_2O_3	0	p_{O_2}: 0−11 Torr	934
	0.5	p_{O_2}: 38−75 Torr	927
MgO	0	c_{O_2}: 0.26−1.25 mM	924
MnO_2	0	p_{O_2}: 0−11 Torr	934
Ni_2O_3	1	c_{O_2}: 0.26−1.25 mM	782
	(c) Uncatalyzed		
	0[f]	c_{O_2}: >0.8 mg L^{-1}	641
	0	c_{O_2}: 0.02−0.5 mM	995
	0[g]	p_{O_2}: 120−700 mmHg	980
	0	p_{O_2}: 0.11−1 atm	591
	0	c_{O_2}: 0.26−1.25 mM	570
	0	c_{O_2}: 0.26−0.43 mM	981
	0	c_{O_2}: 0.26−1.25 mM	850
	0.5[h]	c_{O_2}: 0.21−0.98 mM	906
	1	p_{O_2}: 0.02−1 atm	642
	1	c_{O_2}: 20−80%	643
	1	c_{O_2}: 0.26−1.25 mM	559

[a] Under homogeneous conditions if not mentioned otherwise. [b] Under heterogeneous conditions. [c] Under both homogeneous and heterogeneous conditions. [d] $[CoSO_4] = 1.0 \times 10^{-6}$ M. [e] $[CoSO_4] \geq 1.0 \times 10^{-5}$ M. [f] At $[O_2] < 0.8$ mg L^{-1} oxygen concentration is rate controlling; pH 6.5−7.7. [g] O_2 dependence in the range 20 mmHg $< p_{O_2} <$ 100 mmHg. [h] In sea water.

3.5.4. Influence of Oxygen

The important role of oxygen during the overall redox process for the transition metal-catalyzed oxidation of sulfur(IV) oxides was discussed in section 3.3.4. The homogeneously catalyzed oxidation (see section 3.3) in general proceeds in the presence as well as in the absence of oxygen (Ar- or N_2-saturated solutions).[387,649,777] In the case of cobalt(II)[760,979] and manganese(II) catalysts,[831] the oxidation of sulfur(IV) was only observed as long as oxygen was still present in the solution. In the case of heterogeneous catalysis (see section 3.4) (CoO, CuO, SiO_2), Prasad et al.[242,643] observed nearly no oxidation of sulfur(IV)

Table 3.19. The Effect of $[O_2]$ on the Chain Length of the Uncatalyzed Oxidation of Sulfur(IV) Oxides[818]

	chain length	
initial $[O_2]$ (M)	pH 4.0	pH 9.0
1.02×10^{-3}	68 ± 11	7509 ± 1455
7.5×10^{-4}	67 ± 12	6733 ± 1159
6.8×10^{-4}	85 ± 15	5770 ± 1581
2.6×10^{-4}	87 ± 14	4407 ± 395

in the absence of oxygen. For the uncatalyzed oxidation (see section 3.2.1) of sulfur(IV) oxides, Fedorova et al.[980] observed first an enhancement of the reaction rate with increasing O_2 partial pressure, which then becomes independent of $[O_2]$ at $P_{O_2} = 120$ mmHg (see also Table 3.18). It was suggested that reaction 3.19 is no longer rate-determining at high $[O_2]$.[980]

$$SO_3^{\bullet -} + O_2 \rightarrow SO_5^{\bullet -} \qquad (3.19)$$

Kraft and van Eldik[792] reported an additional step in the presence of oxygen for the iron(III)-catalyzed oxidation of sulfur(IV) oxides, which was recently studied in more detail[511,751,752] (see also Figure 3.8).

The effect of oxygen on the chain length of the uncatalyzed oxidation of sulfur(IV) oxides was studied recently by pulse radiolysis.[818] At the studied pH values (4.0 and 9.0), the chain length was independent of $[O_2]$ within the experimental error (Table 3.19), whereas it depended linearly on the sulfur(IV) concentration.

In the presence of oxygen the oxidation of sulfur(IV) oxides proceeded faster than in the absence of oxygen.[744,792,833] In contrast, most of the authors observed a zero-order dependence on oxygen for homogeneous catalysis (homogeneous conditions), whereas the reaction order is usually 1 or 2 under heterogeneous conditions (Table 3.18). The homogeneous iron(II)-catalyzed reaction is independent of the $[O_2]$ at low $[O_2]$, but shows a dependence at high $[O_2]$.[755] Because of this, Huss et al.[755] suggested an oxygen-dependent reaction step in the overall reaction mechanism that is negligible at low $[O_2]$ (see also ref 980). Alper[990] reported for homogeneous catalysis by cobalt(II) that the reaction was second order in O_2 at $p_{O_2} < 0.8$ atm, and first order in O_2 at $p_{O_2} \geq 11$ atm. Sawicki and Barron[984] found that the cobalt(II)-catalyzed oxidation process involved a zero-order reaction in O_2 under homogeneous conditions and a first- or second-order reaction in O_2 under heterogeneous conditions (see Table 3.18). In contrast, Bengtsson and Bjerle[985] observed for both homogeneous and heterogeneous reaction conditions a zero-order reaction in O_2. Sawicki and Barron[981] explained the different $[O_2]$ dependence by assuming that the heterogeneous conditions provide a mechanism for the regeneration of the catalyst cobalt(III) (see section 3.3.6), due to the constant supply of oxygen to the system. In the homogeneous system, there is no further supply of oxygen. Thus, after initiating the chain reaction and the consumption of oxygen, cobalt(III) is not regenerated in the homogeneous system any longer. Hoffmann and Boyce[996] pointed out that the zero order in $[O_2]$ found in many of the studies may be an experimental artifact.

During the oxidation of sulfur(IV) oxides, oxygen is consumed.[547,641,751,752,850,981,987,997,998] For the cobalt(II)-catalyzed autoxidation of sulfur(IV) oxides (reactions 3.100–3.102), the oxygen consumption can be

$$Co^{2+} + SO_3^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{complex} \qquad \text{fast} \quad (3.100)$$

$$\text{complex} + O_2 \xrightarrow{k_2} SO_5^{2-} + Co^{2+} \qquad \text{slow} \quad (3.101)$$

$$SO_5^{2-} + SO_3^{2-} \xrightarrow{k_3} 2SO_4^{2-} \qquad \text{fast} \quad (3.102)$$

described e.g. by the following rate law[987] (compare also with rate laws given in refs 985, 986, and 998):

$$-\frac{d[O_2]}{dt} = \frac{k_1k_2[Co^{2+}][SO_3^{2-}][O_2]}{k_1[SO_3^{2-}] + k_{-1} + k_2[O_2]}$$

For the uncatalyzed autoxidation in buffered solution, Braga and Connick[981] found the following rate law for the oxygen consumption (pH 4.7, $[S(IV)] \gg [O_2]$):

$$-\frac{d[O_2]}{dt} = \frac{k[HSO_3^-]^{3/2}[O_2]^0}{[H^+]}$$

Examples for the oxygen consumption during the transition metal-catalyzed oxidation of sulfur(IV) oxides are given in Figure 3.12. Stoichiometric measurements for the oxygen consumption during iron(III) catalysis (Figure 3.13a) demonstrate a linear dependence of the $[O_2]$ consumed on the initial $[S(IV)]$ employed (ratio 1:2), as well as a slight increase in the consumption of oxygen with increasing $[Fe(II)]$ (Figure 3.13b). Figure 3.13 clearly indicates that oxygen is mainly consumed during the overall oxidation of sulfite to sulfate (reaction 3.103) and that very little is really used for the autoxidation of iron(II) to iron(III) under the selected reaction conditions ($[S(IV)] \gg [O_2]$). Thus, iron(II) is only oxidized indirectly via sulfur oxide radicals (see section 3.3.4). The stoichiometry in reaction 3.103 is in line with other results

$$HSO_3^- + {}^1/_2O_2 \rightarrow SO_4^{2-} + H^+ \qquad (3.103)$$

reported in the literature.[777,812]

Recently, Brandt et al.[752] reported evidence for the kinetic correlation of the oxygen consumption and the decomposition of the iron(III)–sulfito complexes during the iron(III)-catalyzed autoxidation of sulfur(IV) oxides. The rate constants obtained for the oxygen consumption were exactly a factor of 2 smaller than those values found for the decomposition reaction. This was related to the stoichiometry of the oxygen consumption (Figure 3.13a).

For the influence of oxygen on the product distribution see section 3.5.6.

3.5.5. Influence of pH

The pH dependence of the uncatalyzed oxidation of sulfur(IV) oxides has been mentioned in section 3.2. In the case of the transition metal-catalyzed

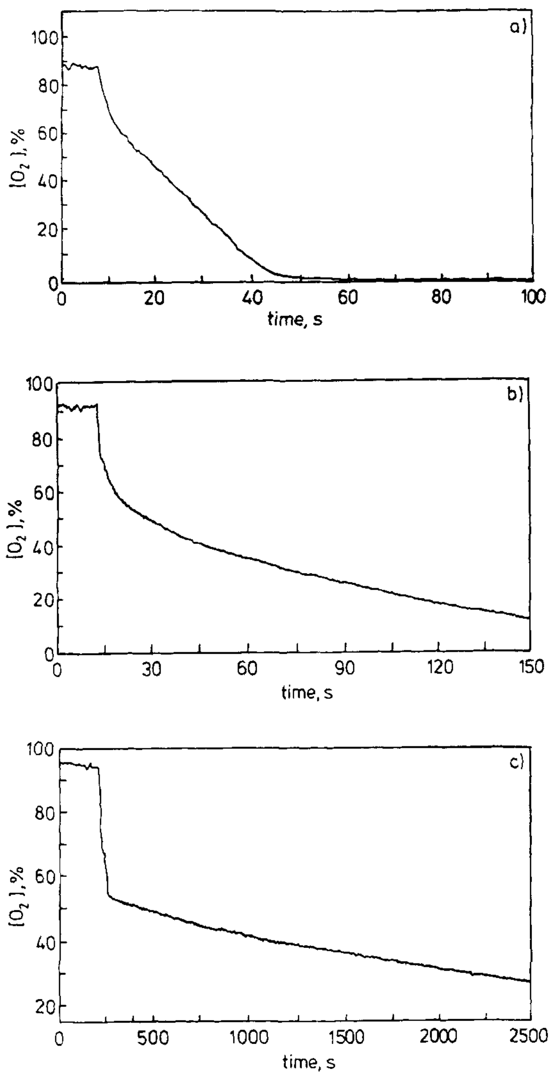


Figure 3.12. Oxygen consumption during the transition metal-catalyzed oxidation of sulfur(IV) oxides: (a) iron(II) catalysis, (b) manganese(II) catalysis, (c) cobalt(II) catalysis; conditions: [M(II)] = 5.0×10^{-4} M, [S(IV)] = 5.0×10^{-3} M, [O_2] = 7.5×10^{-4} M, $\mu = 0.5$ M, $T = 25$ °C, pH = 2.5.[511]

oxidation process, the reaction mechanism and the oxidation rate are influenced by the pH dependent distribution of the metal ions [see Figure 2.5 for iron(III)] and of the sulfur(IV) species (see Figure 2.2). The different metal and sulfur(IV) species exhibit different reactivities. For instance, HSO_3^- is ca. 20–40 times less reactive than SO_3^{2-} [596,649] (see also ref 597). Ali et al.[847] reported for the oxidation of S(IV) by a cobalt(III) complex the reactivity order $SO_3^{2-} > HSO_3^- > SO_2{\cdot}H_2O$, where SO_3^{2-} is 16 times more reactive than HSO_3^-, and HSO_3^- is 53 times more reactive than $SO_2{\cdot}H_2O$. Furthermore, the pH affects the stability of the produced transition metal complexes. Where the copper(II)–sulfito complex is only stable in acidic solution, the iron(III)–sulfito complex decomposes slower in alkaline than in acidic medium.[999]

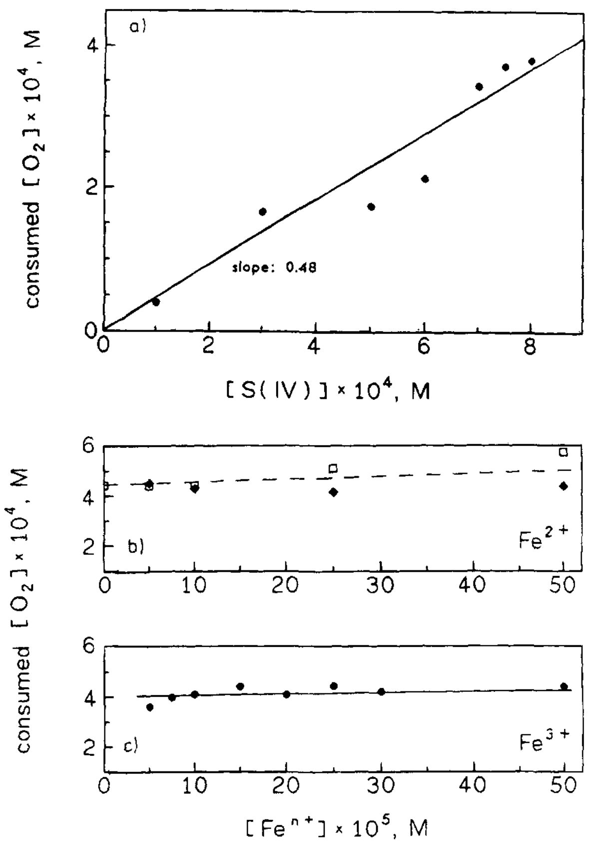


Figure 3.13. Oxygen consumption during the iron(III)-catalyzed oxidation of sulfur(IV) oxides: (a) S(IV) dependence, (b) influence of Fe(II), (c) influence of iron(III). Conditions: (a) [Fe(III)] = 5.0×10^{-4} M, [O_2] = 7.5×10^{-4} M, $\mu = 0.5$ M, $T = 25$ °C, pH = 2.5; (b and c) [S(IV)] = 7.5×10^{-4} M, [O_2] = 7.5×10^{-4} M, $\mu = 0.5$ M, $T = 25$ °C, pH = 2.5, for iron(II) initial [Fe(III)] = 5.0×10^{-4} M (open squares), [Fe^{n+}] = 5.0×10^{-4} M (closed rhombs), respectively.[572]

Table 3.20. pH-Dependent Chain Length during the Oxidation of Sulfur(IV) Oxides

pH	chain length	remarks	ref
≤2.9	1–2	iron(III) catalysis	1000
4.0	76	uncatalyzed oxidation by radiolysis	605,818
9.0	3470	uncatalyzed oxidation by radiolysis	806
9.0	6100	uncatalyzed oxidation by radiolysis	605,818

As mentioned in section 3.3, it is suggested in the literature that the pH has a strong influence on the overall reaction mechanism. For pH 0–3, Martin et al.[756] suggested a nonradical mechanism for the iron(III)-catalyzed oxidation of sulfur(IV) oxides, whereas a radical mechanism was proposed for the pH range 4–7 (see also ref 755, p 4232). In contrast, Brandt et al.[752] observed an inhibiting effect of radical scavengers on the iron(III)-catalyzed reaction at pH 2.5. There is some evidence in the literature for a pH-dependent chain length during the oxidation of sulfur(IV) oxides (Tables 3.19 and 3.20). According to data of Zhang and Edwards,[815] the chain length of the vanadium- and cobalt-catalyzed decomposition of the HSO_5^- anion seems to be independent of pH.

For the heterogeneously catalyzed oxidation of sulfur(IV) oxides by soot particles the reaction pathway is pH dependent. At an initial lower pH (≤4), iron(III) species are the catalyst, whereas at an initial higher pH (5.2–5.5), iron(II) is the catalytic active species.[912]

It is impossible to formulate a rate law over a wide pH range due to the pH-dependent distribution of the metal and sulfur(IV) species. The following rate laws for iron(III) catalysis[756] clearly indicate a change in

Table 3.21. pH-Dependent Reaction Orders for Different Species, Involved in the Iron- and Manganese-Catalyzed Oxidation of Sulfur(IV) Oxides

species	pH	reaction order[a]	ref
Fe^{3+}	0−3	1	756
	4	2	756
	5−7	0 or 2[b]	756
Fe^{2+}	1.67	0.94	826
	2.14	1.2	826
Mn^{2+}	0−3	2	578
	1−4	2	826
S(IV)	0−3	1 (Fe^{3+})	578
	0−7	1 (Fe^{3+})	756
	1−4	≤1[c] (Fe^{2+})	826
		1 (Fe^{3+})	1001
	≤4	1 (Fe^{3+})	1002
	≥5	2 (Fe^{3+})	1001
	5−8	2 (Fe^{3+})	1002

[a] In brackets: metal ion used as catalyst. [b] Only dissolved Fe(III) is catalytically active; see text. [c] pH and ionic strength affect reaction order.

the reaction order for some species for different pH ranges (rate in M s^{-1}):

$$\text{pH } 0-3 \qquad -d[S(IV)]/dt = 6.0[Fe^{3+}][S(IV)][H^+]$$

$$\text{pH } 4 \qquad -d[S(IV)]/dt = 1.0 \times 10^9[Fe^{3+}]^2[S(IV)]$$

$$\text{pH } 5-6 \qquad -d[S(IV)]/dt = 1.0 \times 10^{-3}[S(IV)]$$

$$\text{pH } 7 \qquad -d[S(IV)]/dt = 1.0 \times 10^{-4}[S(IV)]$$

(rate laws valid for $[Fe^{3+}] > 1.0 \times 10^{-7}$ M, $[S(IV)] < 1.0 \times 10^{-5}$ M, $\mu_{(pH4-7)} < 1.0 \times 10^{-2}$ M, and T = 25 °C)

In slightly acidic to neutral pH (5−7) the reaction is zero order in total iron(III) concentration since colloidal iron is a much weaker catalyst than dissolved iron (see also refs 905 and 906) and it is supposed that traces of iron are usually present[756] (see also sections 3.2 and 3.4).

It should be noted, that the pH-dependent reaction order for the individual species is an area of contradicting results (Table 3.21).

The pH dependence of the transition metal-catalyzed oxidation of sulfur(IV) oxides has been studied by many groups (Table 3.22). For iron(III) catalysis only a few studies are available for pH > 5, since at pH > 4 precipitation of iron hydroxides occurs.

The reaction rate of the transition metal-catalyzed oxidation process in general exhibits a bell-shaped pH dependence with a maximum rate around pH 2−4.[511,749,779,905,932,978,1002]

3.5.6. Products

The analysis and the distribution of the products formed during the transition metal-catalyzed oxidation of sulfur(IV) oxides can give further information on the reaction mechanism. Ion chromatography[1003,1004] can be used as a sensitive technique for this purpose.[387,340,511,733,1005,1006]

The reaction products of the oxidation of sulfur(IV) oxides are SO_4^{2-} and $S_2O_6^{2-}$ (see Table 3.23). Although $S_2O_6^{2-}$ is thermodynamically unstable with respect to disproportionation, it is kinetically stable with respect to disproportionation and oxidation at room temperature[1015] (see also ref 596). Lew and Powell[1016] observed a slow disproportionation at room temperature in acidic solution ($k_{obs} = 4.2 \times 10^{-5}$ s^{-1} in 7.15 M H_2SO_4). The rate of this reaction increases with increasing acidity. Ion chromatographic studies revealed no evidence for the oxidation of $S_2O_6^{2-}$ in the presence of iron(III) and oxygen during 2 h; air-saturated $S_2O_6^{2-}$ solutions are stable for more than 2 weeks.[511] Siskos et al.[781] observed no reaction between $S_2O_6^{2-}$ and manganese(III) in 3.5 M acid during 2 h.

The product formation not only depends on the presence or absence of metal ions, it also depends on other reaction parameters like initial concentrations, presence of anions, and the pH of the solution. One

Table 3.22. Selected Literature on the pH Dependence of the Transition Metal-Catalyzed Oxidation of Sulfur(IV) Oxides

metal	pH range	remarks	ref
Co^{3+} [a]	2−8	slight increase of the reaction rate with increasing pH in the range 2−5; strong increase at pH > 5.5	847
CoO	2.5−6.5	surface catalysis; minimum reaction rate at pH 4	643
CuO	4.2−5.3	surface catalysis; nearly no pH dependence for reaction rate	242
Cu^{2+}, Cu^{3+} [b]	4−12	maximum reaction rate for sulfite-induced Cu^{2+} oxidation at pH 8−9	649
Fe^{2+}	0−3	no significant pH effect in the range 0.5−2	828
	3−7	in the presence of small $[H_2O_2]$; reaction rate increases with increasing pH	697
Fe^{3+}	1−3	maximum reaction rate at pH 2−2.5	387
	1.6−3	maximum decomposition rate of iron−sulfito complex at pH 2−2.2	466
	2−6	maximum reaction rate at pH 4	978
	2.6−6.2	with decreasing pH decline in chain length	1000
	3−5	no significant pH effect in the range 3.5−4.5	905
	3−8	change in reaction order	1002
α-Fe_2O_3	2−10.5	surface catalysis; maximum quantum yield at pH 5.7	777
Mn^{2+}	2.5−7.5	no significant pH effect in the range 3−6	779
	3−6	no significant pH effect in the range 3.5−5	905
	3−7	no significant pH effect in the range 3.5−6	978
Mn^{3+} [c]	4−8.5	minimum reaction rate at pH 6.5	753
Ni^{3+} [d]	0−1.9	reaction rate is accelerated with decreasing pH	742
Fe^{3+}, Mn^{2+}	2−6	maximum reaction rate at pH 4	978
	3−5	maximum reaction rate at pH 4	932

[a] Co(III)−dipicolinate complex. [b] Cu(II)− and Cu(III)−tetraglycine. [c] Mn(III)−(acetylacetonato) complex. [d] Ni(III)−(cyclam) complex.

Table 3.23. Formation of SO_4^{2-} and $S_2O_6^{2-}$ during the Oxidation of Sulfur(IV) Oxides

metal ion	SO_4^{2-}	$S_2O_6^{2-}$	remarks	ref
	+	+	pulse radiolysis of deoxygenated aqueous S(IV) solutions; SO_4^{2-}:$S_2O_6^{2-}$ ratio depends on pH	798
	+	+	photolysis of aqueous sulfite solutions; no influence of light but strong influence of pH on yield of $S_2O_6^{2-}$	1007
	+	+ (−)	photolysis of aqueous sulfite solutions; SO_4^{2-}:$S_2O_6^{2-}$ = 2:1 in the absence of O_2; in the presence of O_2 no formation of $S_2O_6^{2-}$	758
	+	−	oxidation of S(IV) by HSO_5^- in the absence of O_2	810
	+	+ (−)	oxidation of S(IV) by $S_2O_8^{2-}$; if S(IV) in excess higher yield of $S_2O_6^{2-}$; addition of pyridine, dioxane, or fluoride results also in higher [$S_2O_6^{2-}$]; no effect by addition of HCO_3^-, SO_4^{2-} or PO_4^{3-}	1008
	+	+	oxidation of S(IV) by $S_2O_8^{2-}$; amount of formed $S_2O_6^{2-}$ depends on pH; in acidic medium higher yield of $S_2O_6^{2-}$ than in basic medium	596
	+	−	oxidation of S(IV) by $S_2O_8^{2-}$	597
	+	−	oxidation of S(IV) by ONOOH in the pH range 2−6	691
	+	+	oxidation of S(IV) by NO_2; presence of oxygen reduces amount of formed $S_2O_6^{2-}$; in absence of oxygen ratio of [SO_4^{2-}]:[$S_2O_6^{2-}$] = 1.8	736
	+	−	oxidation of S(IV) by H_2O_2; [$S_2O_6^{2-}$] ≈ 0.4%; no effect by addition of pyridine	1008
Co^{2+}	+	+	in presence of $CoCl_2$ greater amount of $S_2O_6^{2-}$ formed than in the presence of $CoSO_4$	151
	+	−	no formation of $S_2O_6^{2-}$ after 30 min; presence of oxygen; pH 2.5	511
Co^{II}TSP[a]	+	−	in the presence of O_2 under neutral and alkaline pH conditions	1009
Co^{3+} [b]	+ (−)	+	SO_4^{2-}:$S_2O_6^{2-}$ ratio depends on Co^{3+}:S(IV) ratio; at high [S(IV)] no formation of SO_4^{2-}	1010
Cr^{3+}	+	−	no formation of $S_2O_6^{2-}$ after 30 min; presence of oxygen; pH 2.5	511
Cu^{2+}	+	+	SO_4^{2-}:$S_2O_6^{2-}$ ratio depends on Cu^{2+}:S(IV) ratio	1008
	+	+ (−)	different complexes studied (labile and inert; see text)	787
	+	−	absence of O_2	649
	+	−	absence of O_2	740
	+	−	no formation of $S_2O_6^{2-}$ after 30 min; presence of oxygen; pH 2.5	511
Cu^{II}TSP[a]	+	−	in the presence of O_2 under neutral and alkaline pH conditions	1009
Fe^{2+}	+	−	yield of $S_2O_6^{2-}$ less than 1%; presence of O_2; pH 0.9−3	828
Fe^{II}TSP[a]	+	−	in the presence of O_2 under neutral and alkaline pH conditions	1009
Fe^{3+}	+	+		999
	+	+	addition of HCl decreases amount of $S_2O_6^{2-}$ formed, whereas addition of H_2SO_4 has nearly no influence	151
	+	+	yield of $S_2O_6^{2-}$ independent of Fe^{3+}:S(IV) ratio	774
	+	+	in the presence of Cu^{2+} only small quantities of $S_2O_6^{2-}$	845
	+	−	redox titration with $K_2Cr_2O_7$; pH 1.0	1011
	+	+	addition of copper(II) decreases amount of $S_2O_6^{2-}$ formed	1012
	+	+	amount of formed $S_2O_6^{2-}$ depends on Fe^{3+}:S(IV) ratio, present anions, [O_2]; SO_4^{2-} inhibits formation of $S_2O_6^{2-}$	387
	+	+	lower SO_4^{2-}:$S_2O_6^{2-}$ ratio as by the Mn^{2+} catalysis with the same metal ion concentration	974
	+ (−)	+	addition of Cu^{2+} decreases amount of $S_2O_6^{2-}$ formed; depending on Fe^{3+}:S(IV) ratio nearly quantitative formation of $S_2O_6^{2-}$	1013
	+ (−)	+	depending on Fe^{3+}:S(IV) ratio nearly quantitative formation of $S_2O_6^{2-}$; addition of Cu^{2+} or Cl^- results in a decrease of amount of $S_2O_6^{2-}$ formed; no $S_2O_6^{2-}$ formation in presence of 1 M NaCl	516
	+	+	amount of formed $S_2O_6^{2-}$ depends on Fe^{3+}:S(IV) ratio and pH; no influence of [O_2]	511
	+	+ (−)	addition of Co^{2+}, Cr^{3+}, Mn^{2+}, or Ni^{2+} decreases amount of formed $S_2O_6^{2-}$; in presence of Cu^{2+} no formation of $S_2O_6^{2-}$; presence of oxygen, pH 2.5	511
α-Fe_2O_3	+	+ (−)	in N_2-saturated solutions up to 28% $S_2O_6^{2-}$; no $S_2O_6^{2-}$ formation in air saturated solutions	777
Mn	+	+	in water from flue gas desulfurization processes; mainly Mn present (~50 mg L^{-1}) (other metals: Fe ≈ 0.15 mg L^{-1}, Co ≈ 0.08 mg L^{-1}, Cu < 0.01 m L^{-1})	1014
Mn^{2+}	+	+ (−)	amount of $S_2O_6^{2-}$ formed is reduced to about one-tenth of that obtained in the absence of manganese salts	151
	+	+	higher SO_4^{2-}:$S_2O_6^{2-}$ ratio as by Fe^{3+} catalysis with same metal ion concentration	974
	+	+	in buffered solution; pH 2.44; leached mineral suspension; presence of O_2 and Fe([Fe] ≪ [Mn])	1006
	+	−	no formation of $S_2O_6^{2-}$ after 30 min; presence of oxygen; pH 2.5	511
Mn^{II}TSP[a]	+	−	in the presence of O_2 under neutral and alkaline pH conditions	1009
Mn^{3+}	+	+	different complexes studied (labile and inert; see text)	787
	+ (−)	+		781
Mn^{3+} [c]	+	−	no formation of $S_2O_6^{2-}$ under either aerobic or anaerobic conditions	753
Ni^{2+}	+	+	in the presence of $NiCl_2$ greater amount of $S_2O_6^{2-}$ formed than in the presence of $NiSO_4$	151
	+	−	no formation of $S_2O_6^{2-}$ after 30 min; presence of oxygen; pH 2.5	511
Ni^{II}TSP[a]	+	−	in the presence of O_2 under neutral and alkaline pH conditions	1009
Ni^{3+} [d]	+	−	in the presence of O_2; product formation followed spectroscopically; $S_2O_6^{2-}$ < 2%	746

[a] TSP = 4,4′,4″,4‴-tetrasulfophthalate cyanine. [b] [Co^{III}(dodecatungsto)] complex. [c] [Mn^{III}(acetylacetonato)] complex. [d] [Ni^{III}(cyclam)] complex.

of the earliest detailed studies on the formation of $S_2O_6^{2-}$ was performed by Meyer.[783] The presence of metal ions seemed to result in higher $S_2O_6^{2-}$ yields. Sato and Okabe[1012] observed a higher concentration of $S_2O_6^{2-}$ in the case of copper(II) catalysis than for the uncatalyzed autoxidation reaction. The concentration of $S_2O_6^{2-}$ also dependent on the transition metal ion used as catalyst.[1017,1018] Cavicchi[1018] reported the following quantities of $S_2O_6^{2-}$ formed during the oxidation of sulfur(IV) oxides: Mn(IV) 49%, Fe(III) 39%, Co(III) 15%, Ni(III) 9%. The use of different manganese oxides also resulted in dif-

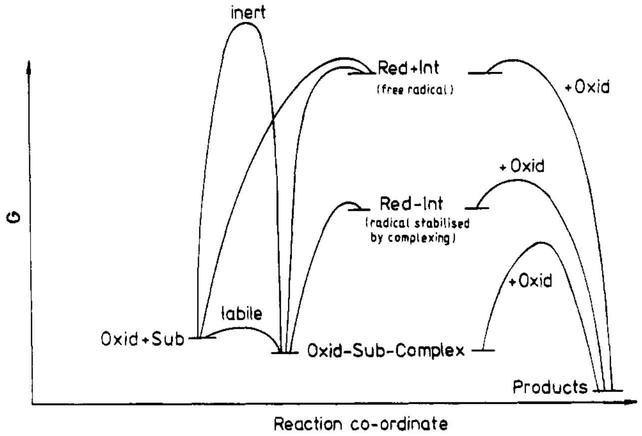


Figure 3.14. Paths in the oxidation of nonmetallic substrates by metal complexes. Oxid = metal complex oxidizing agent. Red = reduced form of the metal complex. Sub = nonmetallic reducing substrate. Int = intermediate, a free radical if Oxid is a 1 equiv oxidant. Oxid–Sub complex = complex between oxidizing agent and reducing substrate. Reaction by this route does not involve the formation of free radicals or other relatively high-energy intermediates.[1019]

ferent yields of $S_2O_6^{2-}$:[151] β-Mn_2O_3 94%, α-Mn_2O_3 77%.

According to Vepřek-Šiška et al.,[787] the substitution reactivity of the complex [inert or labile (see ref 788)] is the main factor that influences product formation during the oxidation of sulfur(IV) oxides (see Figure 3.14). Labile complexes result in SO_4^{2-} and $S_2O_6^{2-}$ as oxidation products, whereas inert complexes only result in the formation of SO_4^{2-}. The latter complexes form S-bonded metal–sulfito complexes (see Table 3.7), whereas labile complexes can provide two coordination sites in the cis position. Thus, the sulfite ion can bind via two O atoms to the metal center, which is the steric basis for the formation of the S–S bond and in $S_2O_6^{2-}$.[787] When the labile $Fe(H_2O)_6^{3+}$ complex is used as catalyst, the formation of both SO_4^{2-} and $S_2O_6^{2-}$ can be expected. Faust et al.[777] observed the formation of $S_2O_6^{2-}$ only in the absence of oxygen (see Table 3.23), whereas Kraft[387] detected both products in the absence as well as in the presence of oxygen. Sarala and Stanbury[1020] assumed that $S_2O_6^{2-}$ is only produced via inner-sphere reactions.

It has been discussed in the literature that the formation of dithionate during the transition metal-catalyzed oxidation of sulfur(IV) oxides depends on the redox potential of the oxidant.[781,957,1019]

The product distribution depends on the pH of the reaction solution. An increase in the amount of $S_2O_6^{2-}$ formed has been observed with increasing pH.[387,999,1017] Bassett and Henry[1017] observed the formation of $S_2O_6^{2-}$ only under acidic conditions. The highest formation rate of $S_2O_6^{2-}$ was obtained for the uncatalyzed oxidation in the pH range 2.8–3.5; no $S_2O_6^{2-}$ formation was observed at pH > 6.[1012] In the case of iron(III) catalysis, the formation of $S_2O_6^{2-}$ was observed at pH > 2, whereas no $S_2O_6^{2-}$ formation was detected at pH > 5.7.[1012] In the presence of EDTA, $S_2O_6^{2-}$ was also formed in the pH range 5–8.[1021]

The effect of oxygen on the formation of dithionate is uncertain. In the case of iron(III) catalysis, Kraft[387] found a higher quantity of $S_2O_6^{2-}$ in the presence of oxygen than in its absence, whereas Brandt[511] observed no effect of oxygen. Using α-Fe_2O_3 as catalyst, Faust et al.[777] found dithionate as one oxidation product in N_2-saturated solutions and no dithionate in air-saturated solutions. Oxygen seems to have an inhibiting effect on the formation of dithionate for the uncatalyzed oxidation. The photolysis of aqueous sulfite solutions results in the absence of oxygen, in a $SO_4^{2-}/S_2O_6^{2-}$ ratio of 2:1, whereas no dithionate was formed in the presence of oxygen.[758] Littlejohn et al.[736] observed a $SO_4^{2-}/S_2O_6^{2-}$ ratio of 1.8:1 for the oxidation of sulfur(IV) by nitrogen dioxide in the absence of oxygen. In the presence of oxygen less dithionate is formed.

Different reaction mechanisms have been suggested for the formation of $S_2O_6^{2-}$. In earlier work, Meyer[783] postulated the decomposition of a manganese–sulfito complex as source for $S_2O_6^{2-}$:

$$2MnO_2 + 3H_2SO_3 \rightarrow Mn_2(SO_3)_3 + 3H_2O + O \qquad (3.104)$$

$$Mn_2(SO_3)_3 \rightarrow MnSO_3 + MnS_2O_6 \qquad (3.105)$$

$$MnSO_3 + O \rightarrow MnSO_4 \qquad (3.106)$$

Carlyle and Zeck[774] postulated that the reaction of the iron(III) sulfito complex with the sulfite radical is the source for $S_2O_6^{2-}$:

$$\begin{array}{c} FeSO_3^+ + SO_3^{-\bullet} + H_2O \rightleftharpoons Fe(OH)_2SO_3 + SO_2 \\ \downarrow \\ Fe^{2+} + S_2O_6^{2-} + H_2O \qquad (3.107) \end{array}$$

Kraft and van Eldik[792] suggested that $S_2O_6^{2-}$ is mainly formed via decomposition of the 1:3 iron(III)–sulfito complex (see sections 3.3.1 and 3.3.2), since an increase in [S(IV)] at constant [Fe(III)] resulted in an increase in the concentration of $S_2O_6^{2-}$. In view of a free radical mechanism another source for the formation of $S_2O_6^{2-}$ is the recombination of $SO_3^{\bullet-}$ and $SO_5^{\bullet-}$ radicals:

$$SO_3^{\bullet-} + SO_3^{\bullet-} \rightarrow S_2O_6^{2-} \qquad (3.28)$$

$$SO_3^{\bullet-} + SO_5^{\bullet-} \rightarrow S_2O_6^{2-} + O_2 \qquad (3.29)$$

$$SO_5^{\bullet-} + SO_5^{\bullet-} \rightarrow S_2O_6^{2-} + 2O_2 \qquad (3.30)$$

Reaction 3.28 takes place only in acidic solution. In alkaline media the recombination of the $SO_3^{\bullet-}$ radicals results only in the formation of sulfate[798] via reactions 3.108 and 3.109, since the redox potential

$$SO_3^{\bullet-} + SO_3^{\bullet-} \rightarrow SO_3 + SO_3^{2-} \qquad (3.108)$$

$$SO_3 + H_2O \rightarrow SO_4^{2-} + 2H^+ \qquad (3.109)$$

of the intermediately formed SO_3 (0.43 V) is lower than that of $SO_3^{\bullet-}$ (0.72 V; see also Table 3.5). $SO_3^{\bullet-}$ is therefore unstable with respect to disproportionation to SO_3^{2-} and SO_3.[647]

4. Concluding Remarks

Since the middle of the 19th century the catalytic activity of transition metal ions in the oxidation of

Table 4.1. Catalytic Activity of Different Transition Metals toward the Oxidation of Sulfur(IV) Oxides

transition metals	ref
(a) Homogeneous Catalysis	
$Mn^{2+} > Cu^{2+} > Fe^{3+} > Co^{2+}$	985
$Co^{2+} > Cu^{2+}$	1023
$Mn^{2+} > Cu^{2+} > Fe^{2+} > Co^{2+}$ (pH < 5)	1024
$Fe^{3+} > Cu^{2+} > Mn^{2+} > Co^{2+}$	200
$Mn^{2+} > Fe^{2+} > Fe^{3+}$ (pH 2–3)	745
$Fe^{2+} \approx Co^{2+} > Mn^{2+} \approx Cu^{+}, Cu^{2+} \gg Fe^{3+} \approx Co^{3+} \gg Ni^{2+}$ (pH 8.5)	739
$Fe^{2+} > Mn^{2+} > Fe^{3+}$ (pH 1–4)	826
$Co^{2+} > Fe^{2+} > Mn^{2+} > V^{4+}$ (pH 9.2[a])	1009
$Fe^{3+} > Mn^{2+} > Co^{2+} > Ni^{2+}$ (pH 5[b])	973
$Mn^{2+} > Fe^{3+} > Co^{2+} > Ni^{2+}$ (pH 5[c])	973
$Mn^{2+} > Co^{2+} > Fe^{3+} > Ni^{2+}$ (pH 5[d])	973
$Mn^{2+} > Fe^{3+} > Cu^{2+}$	974
$Fe^{2+} > Fe^{3+} > Mn^{2+} \approx Co^{2+} > Ni^{2+}$ (pH 5.3[e])	697
$Fe^{3+} > Mn^{2+} > Cu^{2+}$ (pH 3–4, 5)	905
$Fe^{2+} > Mn^{2+} > Cr^{3+} > Cu^{2+} > Co^{2+} > Ni^{2+}$ (pH 2.5)	511
(b) Heterogeneous Catalysis	
$MnSO_4 > MnCl_2 > CuSO_4$	945
$MnCl_2 > CuCl_2 \gg NaCl$	238
$MgO > Fe_2O_3 > Al_2O_3 > MnO_2 > PbO$	934
$MnO_2 > PbO > CuO > Fe_2O_3$	1025
$Mn(NO_3)_2 > MnCl_2 > Cu(NO_3)_2 > MnSO_4 > CuSO_4 > CuCl_2$	239
γ-FeO(OH) > α-Fe_2O_3 > γ-Fe_2O_3 > δ-FeO(OH) > β-FeO(OH)	944
$CuO > Co_2O_3 > CoO > SiO_2$	242
$MgO > CdO > SiO_2$ (pH 5.3)	924

[a] Metals as phthalocyanine complexes. [b] [Catalyst] ≤ 1×10^{-3} M. [c] [Catalyst] = 1×10^{-2} M. [d] [Catalyst] = 1×10^{-1} M. [e] In the presence of H_2O_2 ($[H_2O_2] < [M^{n+}]$).

sulfurous acid has been known.[1022] Meyer[958] studied for the first time in detail the effectivity of different transition metal ions in the oxidation of sulfur(IV) oxides. In more recent literature, the catalytic activity of transition metal ions in the oxidation of sulfur(IV) oxides is judged in different ways (Table 4.1), which is probably related to different selected reaction conditions (e.g. pH, temperature, ionic strength, presence of anions; see section 3.5). For a comparison of the catalytic activity, one should keep in mind that if the metal ions are present in different oxidation states, e.g. +2 and +3, the metal ion with the lower oxidation state must first be oxidized into the higher oxidation state in order to show catalytic activity (see section 3.3.3).

Iron and manganese are the most effective catalysts in the oxidation of sulfur(IV) oxides in aqueous solution.[151–153,511,922] As mentioned before, the catalytic activity of transition metal ions depends on the pH (see ref 1026, Table 3.2, and Figure 3.2). According to Graedel et al.,[157] the contribution of iron(III) and manganese(II) on the oxidation of sulfur(IV) oxides at pH 4 is 6–8% ($[Fe(III)] = 2 \times 10^{-5}$ M) and 22–29% ($[Mn(II) = 2 \times 10^{-6}$ M), respectively. In contrast, Cocks and McElroy[563] report a 10 times higher oxidation rate for the iron(III)-catalyzed pathway compared to manganese(II) catalysis at pH 4 ($[Fe(III)] = 1.1 \times 10^{-6}$ M, $[Mn(II)] = 2 \times 10^{-7}$ M). According to Warneck,[1027] the catalytic activity of both iron(III) and manganese(II) are almost equal at pH 4. Iron(III) has been reported to be 2 times more effective than manganese(II) at pH 5.[153] Investigations on rain water samples indicate that the pH and the iron concentration are the major factors controlling the oxidation of sulfur(IV) oxides in rain water.[171] In contrast, Penkett et al.[172] claimed that manganese is the dominant catalyst in rain droplets, whereas iron is unimportant as a catalyst.

In order to comment on the relative contribution of iron and manganese in atmospheric oxidation of sulfur(IV) oxides, it should be taken into account that under atmospheric conditions ($4 \leq pH \leq 6$) a higher rate constant for the overall oxidation process has been observed for the manganese catalysis, but the atmospheric concentration of iron is in general ca. 10 times higher than that of manganese (Tables 1.7 and 1.10). The higher iron concentration in the atmosphere is certainly due to the higher emission quantities of iron compared to other transition metals (see Table 1.6). Unfortunately, less data on the emitted quantities of iron are available. Nevertheless, in view of its importance compared to other oxidation pathways, the transition metal-catalyzed autoxidation of sulfur(IV) oxides seems to be a local phenomenon (see Figure 1.5), which is more or less restricted to the industrialized regions. There is a certain metal background concentration also in rural areas (see Table 1.7) and the influence of metal ions (especially the synergistic effect) on the "uncatalyzed" oxidation of sulfur(IV) oxides still remains uncertain (see section 3.2).

A comparison of rate constants for the transition metal-catalyzed oxidation of sulfur(IV) oxides is only partly possible, since the reported rate constants are sometimes based on different mechanisms, or the studies have been performed with different metal salts (see section 3.5.1). As shown in sections 3.3 and 3.4, the transition metal-catalyzed oxidation of sulfur(IV) oxides follows complex reaction mechanisms which are probably very sensitive to the individual reaction conditions. We do not present a comparative summary of rate laws and rate constants. This has been done by e.g. Freiberg,[152] Hoffmann and Calvert,[153] Hegg and Hobbs,[574] and Hoffmann and Jacob.[758]

The above discussion clearly indicates that it is impossible to decide which transition metal ion is the most important catalyst during the catalytic oxidation of sulfur(IV) oxides. Furthermore, the catalytic activity of a transition metal ion measured in the laboratory under known reaction conditions cannot be extrapolated to atmospheric conditions, since the overall reaction process is very sensitive to miscellaneous effects (see section 3.5) and the presence of other oxidants like H_2O_2, O_3, NO_x or various radicals (see section 3.2). The effect of organic compounds in atmospheric water (for an overview see refs 369 and 1028) on the atmospheric concentration of sulfur(IV), as well as on the overall oxidation process, is still uncertain. Formaldehyde, for instance, reacts with HSO_3^- to form hydroxymethanesulfonate in acidic water (see introduction to section 3.2). Organic acids are strong complexing agents that can reduce the catalytic activity of the transition metals (see e.g. ref 181) either by complexing the ion or occupying active adsorption sites.

In summary, the role of transition metals (ions as well as metal oxides and hydroxides) in the atmospheric oxidation of sulfur(IV) oxides is probably as important as the alternative oxidation routes, since each individual route does not exist on its own in an atmospheric water droplet. Thus, atmospheric water droplets can be seen as a "reaction chamber" in which all redox reactions occur simultaneously and influence each other. The contributions of the ndividual routes to the overall reaction process depends on the meterological and atmospheric conditions (see Figure 3.3 and also ref 1029). The chemistry in a raindrop is not as important as the chemistry in cloud or fog droplets and in the water shell of aerosols, because the lifetime of the rain drop is too short. Furthermore, model calculations[1030] indicate that the alkaline water shell of sea salt aerosols represents an ideal medium for the oxidation of atmospheric SO_2 especially by ozone. Thus, the scavenging effectivity of rain drops toward atmospheric compounds also influences the composition of rain water. Here it is interesting to note that snow contained higher precipitation-weighted mean concentrations of nitrate than did rain water in the winter, whereas the opposite occurred for sulfate.[1031]

Acknowledgments. The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, Bundesministerium für Forschung und Technologie, and the Commission of the European Community (STEP Programme). We acknowledge useful discussions with Michael Schmülling and the help of Carlos Dücker-Benfer in obtaining relevant literature.

Note Added in Proof

The review covers literature up to June/July 1994. In the Table A.1 the most recent literature, as far as available, up to December 1994 is included. The literature is cited in the order of the sections of the review.

Table A.1

section/subject	remarks	ref
(1) emissions, conversions, atmospheric concentrations	air pollution problems and strategies in Europe	1032
	expected reductions of sulfur emissions (from base year 1980) for several european countries for 2000, 2005, and 2010	1033
	SO_2 emission trends in Germany 1975–1992	1034
	SO_2 and NO_x emission trends in Denmark 1975–1992	1035
	emitted amounts of S in former USSR	1036
	emission of SO_2 from Italian volcanoes	1037
	emitted amounts of NO_x in several countries; values for 1980, 1987, and 1992	1038
	natural NO_x emissions from equatorial rain forests	1039
	oxidation of DMS in the troposphere	1040
	atmospheric concentrations of NO_3^- and HNO_3 in the Rocky Mountains; concentration trends 1985–1988	1041
	atmospheric NO_2 concentrations in Wales, UK	1042
	atmospheric concentrations of SO_x and NO_x during 1979–1988 and 1985–1988, respectively, in northeastern Poland	1043
transition metals	atmospheric concentrations of transition metals, long-term trends	1044
	concentration of some transition metals in North Sea aerosols; solubilities into sea water and rain water	1045
	concentration of some transition metals in airborne particles from the southeastern coast of Turkey	1046
aerosols	water uptake by aerosol particles	1047
	influence of S compounds on the aerosol formation in the marine boundary layer	1048
deposition	discussion of physical, biological and chemical processes that control SO_2 deposition fluxes	1049
	wet deposition of S in former USSR	1036
	wet deposition of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} in northeastern Poland	1043
acid precipitation atmospheric water droplets	chemical composition of acid precipitation in India	1050
	chemical composition of rain water in northeastern Poland	1043
	chemical composition of rain water over India; neutralization of acidity by alkaline components	1051
	chemical composition of cloud water	1052
	chemical composition of snow water	1053
	chemical composition of snow water in India	1054
	chemical composition of bulk deposition in Norway during 1989–1990; influence of long-range transport	1055
	enrichment of organic compounds in fog water	1056
(2) SO_2	absorption of SO_2 into falling water droplets	1057
(3) O_3	removal of O_3 by radicals; role of NO_x in O_3 removal	1058
	formation of formic acid and formaldehyde via the reaction of O_3 with unsaturated VOCs	1059
	modeling of the effect of O_3 depletion in the stratosphere on the sulfuric acid production in the troposphere	1060
NO_y	reactions of N_2O_5 and HNO_2 with NaCl	1061
	uptake of N_2O_5 onto sulfuric acid aerosols	1062
S(IV) oxidation	SO_2 conversion rates in the Kuwait oil fire smoke plume	1063
	SO_2 oxidation in winter clouds; role of H_2O_2 and Fe(III)/Mn(II) in the oxidation pathways	1064
	acidity differences between large and small cloud droplets may result in different rates of sulfur(IV) oxidation by O_3	1065
	increase of sulfuric acid production in the troposphere due to increase of $[OH^\bullet]$ as a consequence of O_3 depletion in the stratosphere	1060
	light-induced oxidation of HMSA (hydroxymethanesulfonate) and other S(IV) aldehyde adducts	1066
	oxidation of S(IV) by Cr(VI) ($HCrO_4^-$) in perchloric media	1067
	oxidation of S(IV) over activated carbon catalysts; influence of surface functional groups	1068
	iron(III) catalysis; influence of different radical scavengers	1069
	copper(II) catalysis	1070
	transition metal catalysis; redox cycle of transition metal ion	1071
	oxidation of S(IV) by photooxidants and iron in the presence of copper	1072
HSO_5^-	decomposition of HSO_5^- induced by Mn^{2+}	1073
$SO_3^{\bullet-}$, $SO_4^{\bullet-}$, $SO_5^{\bullet-}$	rate constants, e.g. recombination	1074
	formation of $SO_3^{\bullet-}$ and $OH^\bullet$ radicals during S(IV) reactions	1075
	oxidation of Fe(II) by $SO_5^{\bullet-}$, $HSO_5^{\bullet-}$, reaction rates depend on [S(IV)]	1076

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CR940111E