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ATMOSPHERIC SCIENCES REVIEW SUB GROUP
WORK GROUP 2

UNITED STATES — CANADA

MEMORANDUM OF INTENT
ON
TRANSBOUNDARY AIR POLLUTION

REPORT NO. 2F-A
NOVEMBER 1982

WORK GROUP 2

ATMOSPHERIC SCIENCES AND ANALYSIS

FINAL REPORT
TECHNICAL BASIS

Atmospheric Science Review
Sub-Group Report

Sub-Group Co-Chairmen

Jack L. Durham, United States
Douglas M. Whelpdale, Canada

Report No. 2F - A
October 15, 1982

Submitted to Work Group 2 in fulfillment of the requirements of the Memorandum of Intent on Transboundary Air Pollution signed by Canada and the United States on August 5, 1980.

March 31, 1982

Mr. Howard Ferguson
A/Regional Director General
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CANADA

Dr. Lester Machta, Director
Air Resources Laboratory
National Oceanic and Atmospheric
Administration
8060 - 13th Street, Room 613
Silver Spring, Maryland 20910
USA

Dear Mr. Ferguson and Dr. Machta:

We are pleased to transmit under cover of this letter the final report of the Atmospheric Science Review Sub-Group of Work Group 2, as provided for in the Phase III Work Plan.

Sincerely,

J. L. Durham

J. L. Durham
U.S.A. Co-Chairman
Atmospheric Science Review Sub-Group

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Atmospheric Science Review Sub-Group

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INTRODUCTION

Background

This Sub-Group report contains four contributions which are pertinent to the atmospheric chemistry and deposition aspects of the modeling being done by Work Group 2. This material was prepared and compiled for the purposes of providing some background and support for the modeling work, and of providing access to current scientific thinking and reference material in these areas.

Paper 1, on "Sulfur and Nitrogen Chemistry in Long-Range Transport Models," and Paper 2, on "The Seasonal Dependence of Atmospheric Deposition and Chemical Transformation Rates for Sulfur and Nitrogen Compounds," were prepared initially during Phase II of the MOI work at the request of Work Group 2, to review areas of the science which were thought to be inadequately treated in the MOI LRT models. Draft versions of these papers were included in Phase II Report 2-14. Following review and comment by several readers, they have been revised to the form presented here.

Two additional brief contributions have been included in this Phase III report. They are executive summaries of major contributions to the EPA Critical Assessment Document on Acid Deposition (1982): one on "Dry Deposition of Acid Substances," and another on "Precipitation Scavenging Processes. "These summaries have been included to alert the reader to the availability of current and more extensive reviews of wet and dry deposition than are presented in Paper 2 of this report (which was intended to deal only with seasonal effects), or in Chapter 5 of MOI Report 2F-A.

This collection of supporting papers is not intended to be an exhaustive, in-depth review of atmospheric chemistry and deposition. Rather it provides some information to MOI modelers in areas of particular concern. In all cases, the final responsibility for the views expressed rests with the individual authors.

It is perhaps worthwhile to clarify the relationships among the various contributions from this Sub-Group. During Phase II this Sub-Group, Atmospheric Science Review, prepared Interim Report 2-14. Papers 1 and 3 of that report are included here, in revised form, as Papers 1 and 2. Papers 2 and 4 of Report 2-14 have been incorporated into the work of the Monitoring and Data Analysis Sub-Group. During Phase III the Atmospheric Science Review Sub-Group was given the responsibility to prepare this Report 2F-A and Chapters 4 and 5 of the main Work Group 2 Report 2F. Although the summary chapters 4 (Atmospheric Chemistry) and 5 (Deposition Processes) draw on the material contained herein, there is not a direct correspondence - in that other sources were used, and the audience was expected to be less scientifically oriented than that to which this report is directed.

Paper No. 1:

SULFUR AND NITROGEN CHEMISTRY IN LONG-RANGE TRANSPORT MODELS

J. L. Durham, K. Demerjian, and H. M. Barnes,
J. Senfield, D. Grosjean, and S. Freedman

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SULFUR AND NITROGEN CHEMISTRY IN LONG-RANGE TRANSPORT MODELS

> Mark Twain: "One gets such wholesale returns of conjecture out of such trifling investment of fact."

INTRODUCTION

The purpose of this review is to present the state of knowledge of the chemistry of sulfur oxides and nitrogen oxides that is thought to be important for acid precipitation. The simple chemistry used in the long-range transport (LRT) models will be compared to the fundamental reaction schemes.

This review is organized into four principal parts:

Atmospheric Processes
- global S and N cycles
- pathways, processes influenced by human activity
- role of models

Chemistry of Oxides of Nitrogen, Organics and Oxidants
- clean tropospheric chemistry
- polluted tropospheric chemistry
- laboratory evidence of the NO_2-to-precursor relationships
- NO_x-oxidant chemistry in plumes

- computer simulation of atmospheric chemistry
- nitrite and nitrate formation

SO_2-Oxidant Chemistry in the Lower Troposphere
- gas-phase chemical reactions of SO_2
- aqueous-phase chemical reactions
- surface chemical reactions
- estimates of SO_2 oxidation

Survey of Chemical Modules

ATMOSPHERIC PROCESSES AND MODELS

Sulfur and nitrogen have important natural cycles in the environment in which they go through various oxidation and reduction reactions and translocations among the atmosphere, biosphere, hydrosphere, pedosphere, and lithosphere. Human activity (especially fossil-fuel combustion) has added a major perturbation to these natural cycles, and perhaps modified the natural translocation rates and sizes of the reservoirs. The fluxes of sulfur translocation between reservoirs have been estimated for the paths shown in Fig. 1 and are presented in Table I. The agreement among the reported values is not good, especially so for the estimates of annual anthropogenic sulfur fluxes to the atmosphere which range from 11 to 45% of the total sulfur involved in the atmospheric balance.

The fluxes of nitrogen translocation between reservoirs have been estimated for the pathways shown in Fig. 2 and are presented in Table II. The nitrogen fluxes are more poorly established than those for sulfur. Only the industrial fixation flux is known with confidence. Also, it is likely that the global cycles of sulfur, nitrogen and carbon are interactive in complex ways that may distort our understanding based on the simpler elemental cycles.

The global sulfur and nitrogen cycles and the annual fluxes between compartments provide a broad view of the processes that may lead to adverse impacts upon mankind and ecological systems. However, the global scale and annual fluxes are clearly beyond the interest in transboundary flow of pollutants between the U.S. and Canada. S- and N-oxides emissions are not uniformly distributed over the land mass of the U.S. and Canada, and the effects often have characteristic response-times that are much less than 1 year.

For areas of regional or smaller scale and times of hours to days, a reasonable way to relate source-emission areas to impact areas is to trace the pollutants' chemical transformation--atmospheric translocation pathways on a finer scale than indicated in Figs. 1 and 2.

A direct approach is through mass-conservation mathematical formulations (models) that simulate the important physico-chemical processes

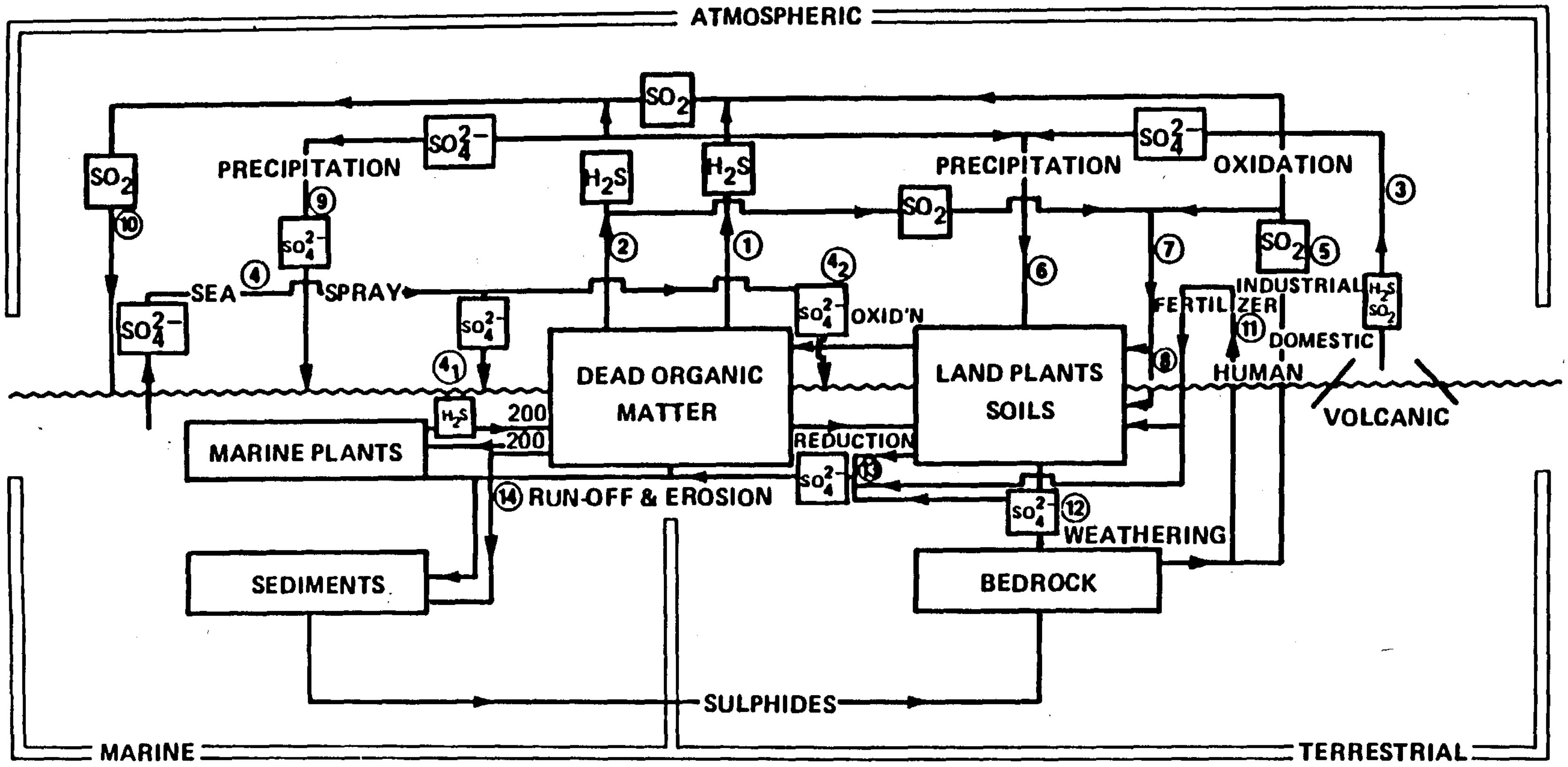


Figure 1. The global sulfur cycle, showing the major reservoirs, pathways, and forms of occurrence of sulfur. Figures enclosed in circles (e.g. 1) refer to the individual fluxes and correspond to figures in column 1, Table I.

Source: Moss (1978).

TABLE I. Estimates of Annual Fluxes (TG/year) of Environmental Sulfur*

Source of sulfur	Flux number in Figure 2-1	Eriksson (1960, 1963)	Robinson and Robbins (1968, 1970)	Kellogg et al. (1972)	Friend (1973)	Granat et al. (1976)
Biological decay (land)	1	110	68	90	58	5
Biological decay (ocean)	2	170	30		48	27
Volcanic activity	3	---	---	1.5	2	3
Sea spray (total)	4	45	44	47	44	44
To ocean	4_1	(40)	---	(43)	(40)	(40)
To land	4_2	(5)	---	(4)	(4)	(4)
Anthropogenic	5	40	70	50	65	65
Precipitation (land)	6	65	70	86	86	43
Dry deposition	7	100	20	10	20	28
Absorption (vegetation)	8	75	26	15	15	
Total sulfur involved in atmospheric balance		365	212	183	217	144
Atmospheric balance						
Land -> sea		-10	+26	+5	+8	+18
Sea -> land		5	4	4	4	17
Fertilizer	11	10	11	---	26	---
Rock weathering	12	15	14	---	26	---
Pedosphere -> river runoff	13	55	48	---	89	---
Total river runoff	14	80	73	---	136	122

Note: the numbers in parentheses for sub-pathways 4_1 and 4_2 are estimates of the decomposition of the total pathway 4.
*Sources: as cited in each column and, in part, Friend (1973, Table 4).

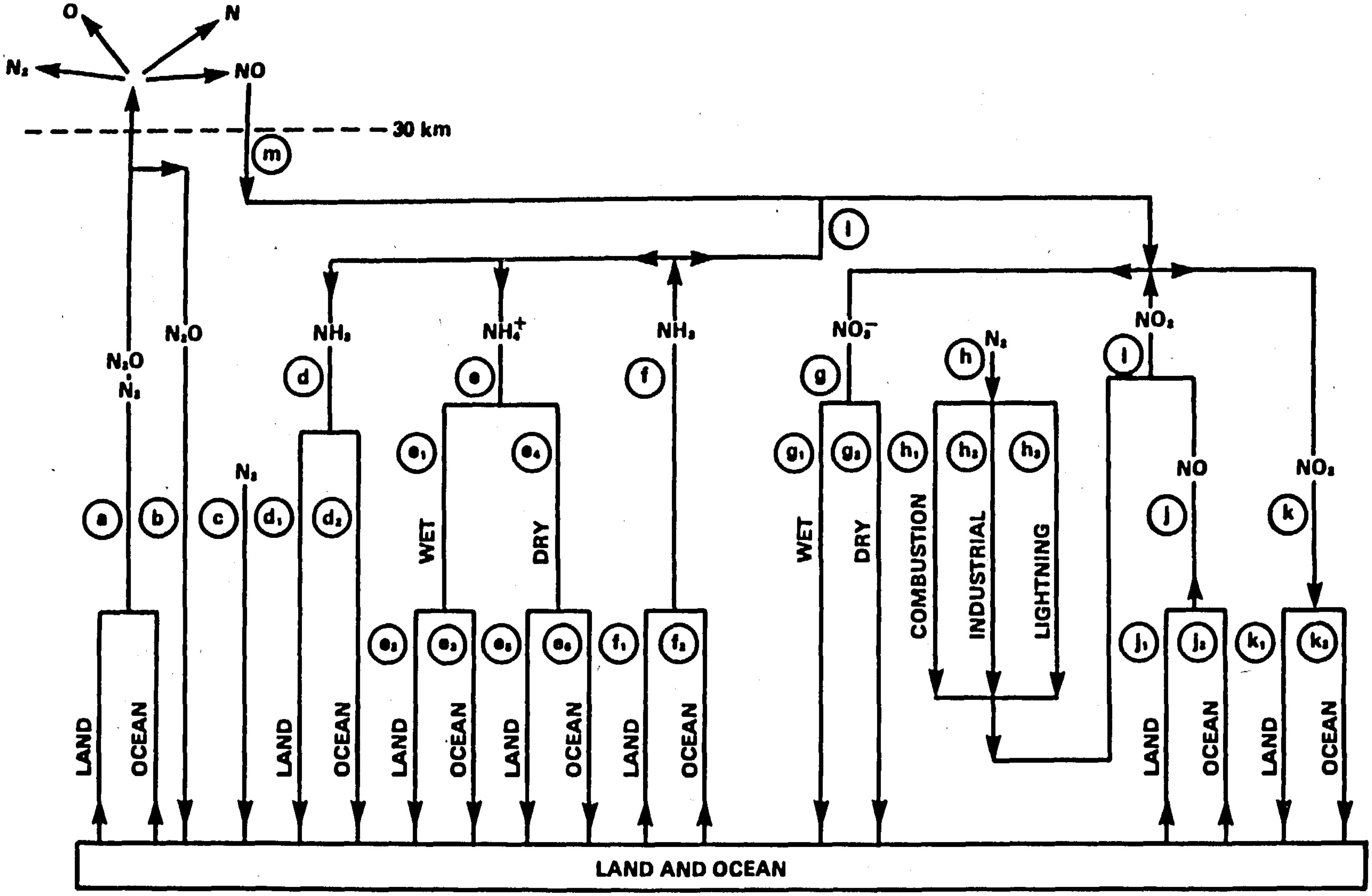


Figure 2. Global environmental nitrogen circulation pathways.

TABLE II. ESTIMATES OF GLOBAL FLUXES (T_g N/yr) OF N-OXIDES AND RELATED COMPOUNDS

	Pathway	Delwiche (1970)	Burns and Hardy (1975)	Söderlund and Svensson (1976)	Robinson and Robbins (1975)	Liu et al. (1977)	CAST (1976)	Sze and Rice (1976)	Chameides (1977)	Crutzen and Ehhalt (1977)
a.	Biological denitrification (land and sea)	83 (N_2, N_2O)	190 (N_2) 20 (N_2O)	96-191 (N_2) 36-149 (N_2O)	341 (N_2O)	270 (N_2, N_2O)	171-200 (N_2, N_2O)	260 (N_2, N_2O)		
	a_1. Land		13 (N_2O)	16-69 (N_2O)			7 (N_2O)			12-80 (N_2O)
	a_2. Ocean		7 (N_2O)	20-80 (N_2O)						40-90 (N_2O)
b.	Deposition of N_2O to land				320					
c.	Biological N_2-fixation (land and sea)	54	175	169-269	117	240		260		
d.	Total gaseous NH_3 dry deposition			67-134	679					
	d_1. Land			57-114						
	d_2. Ocean			10-20						
e.	Total NH_4^+ deposition			43-102	190					
	e_1. Total wet			38-85	150					
	e_2. Land			30-60						
	e_3. Ocean			8-25						
	e_4. Total dry			5-17	40					
	e_5. Land			4-12						
	e_6. Ocean			1-5						
f.	Total gaseous NH_3 emissions		165	113-244	866					
	f_1. Land			113-244						
	f_2. Ocean			0						
g.	Total particulate NO_3^- deposition		60	18-51	95					
	g_1. Wet			0.3-3	75					
	g_2. Dry			18-46	20					
h.	Total N_2 atmospheric fixation	38	60							
	h_1. Combustion	18	20	19	} 15	18	21			
	h_2. Industrial	12	30	36		36				
	h_3. Lightning	8	10			9			30-40	8-40
i.	Total NO_2 formed in atmosphere		20		95					
j.	Total NO natural emissions				212					
	j_1. Land			21-89						
	j_2. Ocean									
k.	Total NO_2 deposition		49	43-116	132					
	k_1. Land		31	32-83						
	k_2. Ocean		18	11-33						
l.	$NH_3 \rightarrow NO$		30	3-8						
m.	NO stratosphere → troposphere		5	0.3	2					

that occur between the point of emission and deposition, which are shown in Fig. 3. Significant acidification in the atmosphere occurs between the time and points of pollutant emission and removal. The quantities of strong acids (H_2SO_4, HNO_3) in the atmosphere are increased significantly by the oxidation of SO_2 and NO_2 through direct photochemical production of gas-phase strong oxidizing free radicals, production of stable gaseous oxidants, and aqueous-phase oxidation reactions. Other strong acids such as HCl and H_3PO_4 are either emitted into the atmosphere directly, or formed by acid displacement reactions of H_2SO_4 and HNO_3 with inorganic salts of Cl^- and PO_4^{3-}. The most important inorganic species that govern the acidic nature of dry and wet precipitation are:

cations: H^+, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}
anions : OH^-, SO_4^{2-}, NO_3^-, Cl^-, PO_4^{3-}, SO_3^{2-}, CO_3^{2-}.

The long-range transport (LRT) models used by Work Group 2 (see Table III) account for the formation of H_2SO_4 through a simple, linear rate law, which is:

$$\frac{d[H_2SO_4]}{dt} = \frac{d[SO_4^{2-}]}{dt}$$
$$= k_S[SO_2].$$

The rate constant k_S includes the combined rate constants SO_2 oxidation for all major pathways. For this linear representation of the H_2SO_4 formation rate to be reasonable, some necessary conditions are:

a. each of the major SO_2 oxidation processes must have a first-order dependence on SO_2 concentration,

b. each of the major SO_2 oxidation processes must be linear in dependence on SO_2 concentration, and each of the pseudo-first order rate constants must not change over the period that they are assumed to be constant. For some of the LRT models identified in Table III,

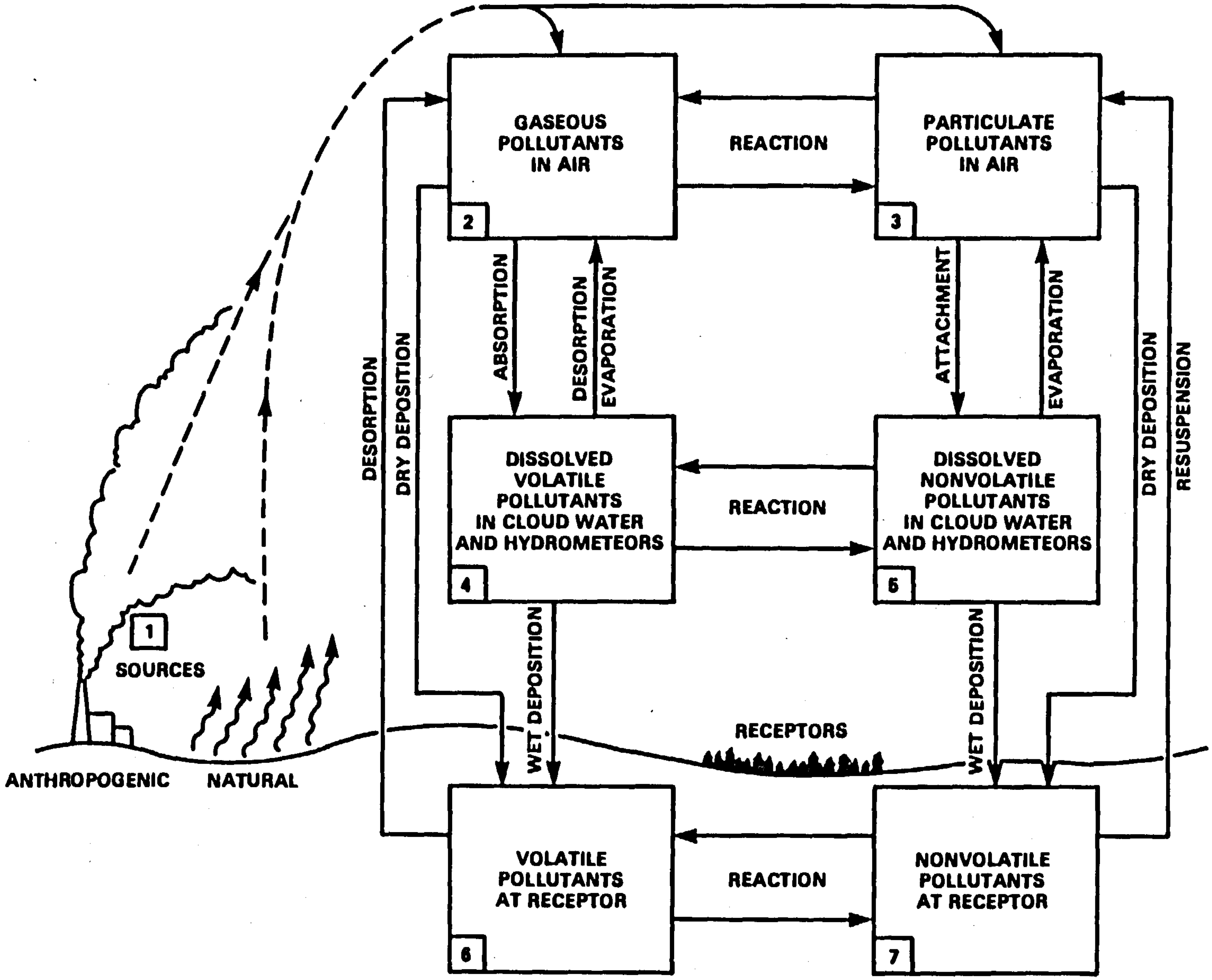


Figure 3. Simplified schematic of pollutant pathways between sources and receptors. Source: MAP3S/RAINE Program Design—Basis Document (1980).

this period is one time step (typically 6 hours), after which k_S is modified. For those that use a constant oxidation rate, the period is the duration of complete scenerio, which may be many days long.

At present, the LRT models identified in Table III make no attempt to account for the acidification due to HNO_3 and organic acids, nor the basification due to NH_3 and basic minerals.

In the review that follows, it will be demonstrated that the major SO_2 oxidation reactions are first order in SO_2, which satisfies condition "a." However, these reactions are not linear, and when the rates are expressed as pseudo-first order, their rate constants vary significantly over time steps of ≥ 6 hours. Thus, for all important SO_2 oxidation reactions, condition "b" is violated.

CHEMISTRY OF THE OXIDES OF NITROGEN AND THE PRODUCTION OF OXIDANTS

In this section, the following topics are reviewed: oxidant and free radical production in the clean and polluted lower troposphere, laboratory evidence of the NO_2-to-precursor relationships, computer simulation of the atmospheric chemistry of these chemicals, and nitrite and nitrate formation.

Clean Tropospheric Chemistry

The chemistry of the clean troposphere and its mathematical simulation have been studied extensively by Levy (1971), Wofsy et al. (1972), Crutzen (1974), Fishman and Crutzen (1977), Chameides and Walker (1973, 1976) and Stewart et al. (1977).

The photochemistry of the unpolluted troposphere develops around a chain reaction sequence involving NO, CH_4, CO and O_3. The photochemical reaction chain sequence in the troposphere is initiated by hydroxyl radicals (HO) formed from the interaction of $O(^1D)$, the product of photolysis of ozone in the short end portion of the solar spectrum, with water.

TABLE III. Approaches to Treatment of Chemical Transformation in the LRT Models

Model	Chemical transformation[a]
AES	SO_2: constant oxidation rate (1% h^{-1})
ASTRAP	SO_2: diurnal and seasonal varying oxidation rate; summer (0.2 to 5.5% h^{-1}, average of 2.0% h^{-1}) winter (0.1 to 1.5% h^{-1}, average of 0.5% h^{-1})
CAPITA	SO_2: seasonal varying oxidation rate; winter (constant 0.6% h^{-1}) summer (constant 1.2% h^{-1})
ENAMAP	SO_2: constant oxidation rate (1% h^{-1})
MEP	SO_2: seasonal and diurnal oxidation rate (mean, 1% h^{-1})
OME	SO_2: constant oxidation rate (1% h^{-1})
RCDM	SO_2: constant oxidation rate (1% h^{-1})
UMACID	SO_2: seasonal and diurnal varying oxidation rate; summer (day 2.8% h^{-1}, night 0.2% h^{-1}) winter (day 1.4% h^{-1}, night 0.1% h^{-1})

[a] H_2SO_4 formation rate ($\mu g\ m^{-3}\ h^{-1}$) = SO_2 transformation rate = $0.01\ k_S(\%h^{-1})[SO_2](\mu g\ m^{-3})$

(HO) formed from the interaction of $O(^1D)$, the product of photolysis of ozone in the short end portion of the solar spectrum, with water.

$$O_3 + h\nu(\leq 310 \text{ nm}) \longrightarrow O(^1D) + O_2 \tag{1}$$
$$O(^1D) + H_2O \longrightarrow 2HO \tag{2}$$

The HO produced reacts with CH_4 and CO present in the clean troposhere, resulting in the generation of peroxyl radical species, HO_2, CH_3O_2.

$$HO + CH_4 \longrightarrow CH_3 + H_2O \tag{3}$$
$$HO + CO \longrightarrow H + CO_2 \tag{4}$$
$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M \tag{5}$$
$$H + O_2 + M \longrightarrow HO_2 + M \tag{6}$$

The peroxyl radicals, in turn, participate in a chain propagating sequence which converts nitric oxide (NO) to nitrogen dioxide (NO_2) and in the process produces additional hydroxyl and peroxyl radical species.

$$CH_3O_2 + NO \longrightarrow CH_3O + NO_2 \tag{7}$$
$$HO_2 + NO \longrightarrow HO + NO_2 \tag{8}$$
$$CH_3O + O_2 \longrightarrow HO_2 + H_2CO \tag{9}$$
$$H_2CO + h\nu(\leq 370 \text{ nm}) \longrightarrow H + HCO \tag{10}$$
$$HCO + O_2 \longrightarrow HO_2 + CO \tag{11}$$

The major chain terminating steps include:

$$HO + NO_2 + M \longrightarrow HONO_2 + M, \tag{12}$$
$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2. \tag{13}$$

The reaction sequence for O_3 production involves converting NO to NO_2 at a rate sufficiently high to maintain a NO_2/NO ratio to sustain the observed background levels of O_3.

$$H_2O_2 + HO \longrightarrow H_2O + HO_2 \tag{14}$$
$$HO_2 + NO \longrightarrow NO_2 + HO \tag{8}$$
$$NO_2 + h\nu \longrightarrow NO + O \tag{15}$$

$$O + O_2 + M \longrightarrow O_3 + M \quad (16)$$
$$NO + O_3 \longrightarrow NO_2 + O_2 \quad (17)$$
$$HO + CO \longrightarrow H + CO_2 \quad (4)$$

In general, reactions (15) through (17) govern the ozone concentration levels present in the sunlight irradiated well-mixed atmosphere at any instant and to a first approximation the steady state relationship, Leighton (1961).

The equation,

$$\frac{(NO_2)k_{15}}{(NO)k_{17}} = (O_3),$$

provides an accurate estimate of ozone given the ratio of $(NO_2)/(NO)$ and k_{15}/k_{17}. The photolytic rate constant k_{15} is directly related to the integrated actinic solar flux over the wavelength range 290-430 nm.

The paths for ozone destruction in the clean troposphere include the reactions sequence

$$HO_2 + O_3 \longrightarrow HO + 2O_2, \quad (18)$$
$$HO + O_3 \longrightarrow HO_2 + O_2. \quad (19)$$

Hydroxyl radical abundances predicted by the tropospheric photochemical models, 10^5 to 10^6 molecules cm^{-3}, are in qualitative agreement with recent measurements by Davis et al. (1976), Perner et al. (1976), and Campbell et al. (1979) and inferred HO levels based on measured trace gas abundances in the troposphere by Singh (1977).

Polluted Tropospheric Chemistry

Solar radiation triggers a series of reactions in the atmosphere between gaseous organic molecules and nitrogen oxides, producing a wide variety of secondary pollutants. The totality of primary and secondary pollutants involved in these photochemical reactions is known as photochemical smog. To understand the chemistry of the formation of oxidants in the polluted lower troposphere, it is necessary to consider the interactions that take place between the oxides of nitrogen and organic constituents. Several reviews of polluted atmospheric chemistry are available (Leighton, 1961; Stern, 1977; Seinfeld, 1975; Heiklen, 1976), as are detailed discussions of reaction mechanisms (Demerjian et al., 1974; Carter et al., 1979; Baldwin et al., 1977; Whitten and Hogo, 1977; Falls and Seinfeld, 1978), and rate constants (Baulch et al., 1980). In this section the chemistry of the oxides of nitrogen and organics in the lower polluted troposphere is briefly reviewed. The above-cited references should be consulted for more detail.

Most of the chemistry that occurs in a sunlight-irradiated polluted atmosphere involves the interaction of a variety of molecules, excited molecules and molecular fragments. These species include: hydrocarbons; organics such as aldehydes and ketones; the unexcited and first excited electronic states of the oxygen atom, triplet-P oxygen atoms [$O(^3P)$], and singlet-D oxygen atoms [$O(^1D)$]; ozone (O_3); nitrogen dioxide (NO_2); nitric oxide (NO); symmetrical nitrogen trioxide (NO_3); dinitrogen pentoxide (N_2O_5); hydroxyl radicals (HO); hydroperoxyl radical (HO_2); alkylperoxyl radicals (RO_2); acylperoxyl radicals $RC(O)O_2$; and less important species. In the formulas, R represents a methyl (CH_3), ethyl (C_2H_5), or another, more complex hydrocarbon radical. The paths by which these intermediates are formed and destroyed are important keys in explaining the chemical changes that occur in the polluted atmosphere.

The major portion of the total oxides of nitrogen emitted by combustion sources is nitric oxide (NO). The rate at which NO is converted to nitrogen dioxide (NO_2) through oxidation by molecular oxygen in air:

$$2NO + O_2 \longrightarrow 2NO_2, \qquad (20)$$

is proportional to the square of the nitric oxide concentration since two molecules of NO are required for the oxidation; it is, therefore, very sensitive to changes in nitric oxide concentration. Reaction 20 can be important in the vicinity of high NO emission sources in converting up to 25% of the total NO_x to NO_2 during the initial stages of dilution with air when the concentration of NO is still quite high. Reaction 20 is much too slow, however, to account for the high conversion rates of nitric oxide to nitrogen dioxide observed in the atmosphere under typical ambient concentrations.

Since sunlight triggers the phenomenon of photochemical smog formulation, it is important to recognize those constituents that will absorb light energy. In some cases, these constituents decompose or become activated for reaction. Nitrogen dioxide, a dominant sunlight absorber in the urban atmosphere, photodissociates upon absorbing wavelengths of light <430 nm. This photolytic reaction results in the formation of the ground state, triple-P oxygen atom, and a nitric oxide molecule. The efficiency of this process is wavelength-dependent:

$$NO_2 + \text{sunlight (290-430 nm)} \longrightarrow O(^3P) + NO. \qquad (21)$$

The highly reactive triplet-P oxygen atom predominantly reacts with oxygen molecules in the air, resulting in the formation of ozone.

$$O(^3P) + O_2 + M \longrightarrow O_3 + M. \qquad (22)$$

In this equation M represents a nitrogen, oxygen, or other third molecule that absorbs the excess vibrational energy released, thereby stabilizing the ozone produced. For many conditions common in polluted atmospheres when NO is present at high concentrations, ozone molecules regenerate nitrogen dioxide by reaction with nitric oxide:

$$O_3 + NO \longrightarrow NO_2 + O_2. \qquad (23)$$

To a much lesser extent, ozone can react with nitrogen dioxide to form the transient species, nitrogen trioxide:

$$O_3 + NO_2 \longrightarrow NO_3 + O_2. \qquad (24)$$

The nitrogen trioxide can further react with nitrogen dioxide to form dinitrogen pentoxide, the reactive anhydride of nitric acid,

$$NO_3 + NO_2 \longrightarrow N_2O_5 \qquad (25)$$

Dinitrogen pentoxide which is in equilibrium with nitrogen trioxide and nitrogen dioxide can dissociate or react with water to form nitric acid ($HONO_2$):

$$N_2O_2 \longrightarrow NO_3 + NO_2, \tag{26}$$

$$N_2O_5 + H_2O \longrightarrow 2HONO_2. \tag{27}$$

Additional reactive pathways that can take place between oxygen atoms and NO_2 and NO include:

$$NO_2 + O(^3P) \longrightarrow NO + O_2, \tag{28}$$

$$NO_2 + O(^3P) + M \longrightarrow NO_3 + M, \tag{29}$$

$$NO + O(^3P) + M \longrightarrow NO_2 + M. \tag{30}$$

Also, NO and NO_3 can react to regenerate NO_2:

$$NO_3 + NO \longrightarrow 2NO_2 \tag{31}$$

Nitrous acid is produced by:

$$NO + NO_2 + H_2O \longrightarrow 2HONO, \tag{32}$$

and may react bimolecularly to regenerate the original reactants:

$$HONO + HONO \longrightarrow NO + NO_2 + H_2O. \tag{33}$$

The unexcited and first excited electronic state of the oxygen atom are produced by ozone photolysis in sunlight:

$$O_3 + \text{sunlight} \begin{array}{ll} (290\text{-}350\ \text{nm}) \longrightarrow O_2 + O(^1D) \text{ or } O(^3P) & (34a) \\ (450\text{-}700\ \text{nm}) \longrightarrow O_2 + O(^3P) & (34b) \end{array}$$

The singlet-D oxygen [$O(^1D)$] atom is much more reactive than the ground state triplet-P oxygen [$O(^3P)$] atom. For example, it reacts efficiently during collision with a water molecule to form an important transient species in the atmosphere, the hydroxyl radical:

$$O(^1D) + H_2O \longrightarrow 2HO \tag{35}$$

This radical is also formed through the photodecomposition of nitrous acid (HONO):

$$HONO + \text{sunlight (290-400 nm)} \longrightarrow HO + NO. \tag{36}$$

The hydroxyl radical can react with nitric oxide to give back nitrous acid:

$$HO + NO + M \longrightarrow HONO + M, \tag{37}$$

or form nitric acid by reacting with nitrogen dioxide:

$$HO + NO_2 + M \longrightarrow HONO_2 + M. \tag{38}$$

It has been shown that the reaction sequence 20 through 38 cannot explain the rapid conversion of NO to NO_2 observed in the ambient atmosphere (Leighton, 1961; Altshuller and Bufalini, 1965; Demerjian et al., 1974). In fact, if these reactions alone occurred, the original supply of nitrogen dioxide in our atmosphere would be only slightly depleted under irradiation with sunlight, and a small and near constant level of ozone would be created in a few minutes. The key to the observed nitric oxide to nitrogen dioxide conversion lies in a sequence of reactions between the transient species present and other reactive molecules such as the hydrocarbons and aldehydes present in the polluted atmosphere.

In the presence of hydrocarbons, the number of reactions greatly increases. Thus, the hydroxyl radicals produced by reactions 35 and 36 can react with a hydrocarbon (paraffin, olefin, aromatic, or any compound having C-H bonds):

$$OH + \text{Hydrocarbon} \longrightarrow R + H_2O. \tag{39}$$

Reaction 39 produces an alkyl radical (R) which contains a free electron. This radical quickly picks up an oxygen molecule from the air to form a peroxyl radical RO_2:

$$R + O_2 \xrightarrow{M} RO_2. \tag{40}$$

Typically, the next reaction in the series converts NO to NO_2 and produces an alkoxyl radical, RO:

$$RO_2 + NO \longrightarrow RO + NO_2. \tag{41}$$

A hydrogen abstraction by molecular oxygen may then produce a hydroperoxyl radical, HO_2. The rest of such an RO radical typical forms a carbonyl compound, OHC:

$$RO + O_2 \longrightarrow OHC + HO_2. \tag{42}$$

Finally, the hydroperoxyl radical (HO_2) can react with a second NO to form NO_2 to complete the cycle:

$$HO_2 + NO \longrightarrow OH + NO_2. \tag{43}$$

Although this description is very simplified, these series of reactions contain the essential features of NO to NO_2 oxidation and subsequent ozone formation.

The initial source of radicals is very important; although the rate and yield of oxidant formation depend on many other factors, the length of the induction period before accumulation of oxidant depends strongly on the initial concentration of radicals. (The length of the induction period is important primarily in constant light intensity smog chambers. Diurnally varying radiation tends to lessen the importance considerably.) In smog chambers and possibly in the ambient atmosphere, the photolysis of nitrous acid, reaction 36, may be the most important initial source of radicals. Nitrous acid has been detected in smog chambers in concentrations sufficient to explain the observed induction time for smog chemistry, but the concentrations necessary to initiate smog chemistry in the atmosphere are below the limits measured by most modern instruments.

Another important source of radicals in the atmosphere is the photolysis of aldehydes:

$$RCHO + h\nu \longrightarrow HCO + R. \qquad (44)$$

Aldehydes are emitted from many sources, including automobiles. They are also formed by the reaction of ozone with olefins and through reaction 42.

During the course of the overall smog formation process, the free radical pool is maintained by several sources, but the dominant one appears to be photolysis of the aldehydes formed from the initial hydrocarbons. Since the reactions of free radicals with NO form a cyclic process, any additional source of radicals will add to the pool and increase the cycle rate. Conversely, any reaction that removes free radicals will slow the cycle rate. For example, a primary radical sink and a primary sink for oxides of nitrogen is reaction 38 to form nitric acid.

The hydrocarbon classes important in the chemistry of the polluted troposphere are alkanes, alkenes, and aromatics. In addition, the oxygenated hydrocarbons, such as aldehydes, ketones, esters, ethers, and alcohols are also important. A great variety of chemical reactions take place among these organic species and the free radicals cited above. The reactions of typical hydrocarbon species are now discussed briefly. Throughout the discussion, references to more extensive coverages are given.

The most important atmospheric reaction involving alkanes is with the HO radical. For n-butane, for example, the reaction is

$$CH_3CH_2CH_2CH_3 + HO \longrightarrow CH_3CH_2CH_2CH_2 + H_2O, \qquad (45a)$$

and

$$\longrightarrow CH_3CH_2CHCH_3 + H_2O. \qquad (45b)$$

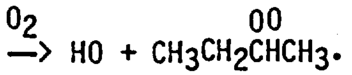
The alkyl radicals will rapidly add O_2 to form the corresponding peroxyalkyl radicals, e.g.,

$$CH_3CH_2CH_2CH_2 + O_2 + M \longrightarrow CH_3CH_2CH_2CH_2O_2 + M, \tag{46}$$

(subsequently the third body M will not be indicated). A reaction of substantially lesser importance is with oxygen atoms,

$$CH_3CH_2CH_2CH_3 + O(3P) \xrightarrow{O_2} HO + CH_3CH_2CH_2CH_2O_2, \tag{47a}$$

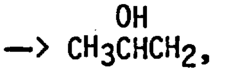
and



$$\xrightarrow{O_2} HO + CH_3CH_2\overset{OO}{C}HCH_3. \tag{47b}$$

The importance of both the HO and $O(^3P)$ reactions with alkanes is the generation of the peroxyalkyl radical RO_2, which plays a substantial role in the conversion of NO to NO_2. Rate constants for alkane reactions are summarized by Baulch et al. (1980). The atmospheric chemical reactions involving olefins have been widely studied (Demerjian et al., 1974; Carter et al., 1979; Niki, 1978). The most important reactions in which olefins participate are with HO radicals, ozone, and atomic oxygen, in that order. The reaction of HO with an olefin, such as propylene, may proceed by addition of OH to the double bond or by abstraction of an H-atom from the olefin. For propylene, for example, the reaction paths with HO are:

$$CH_3CH = CH_2 + HO \longrightarrow CH_3CHCH_2OH, \tag{48a}$$

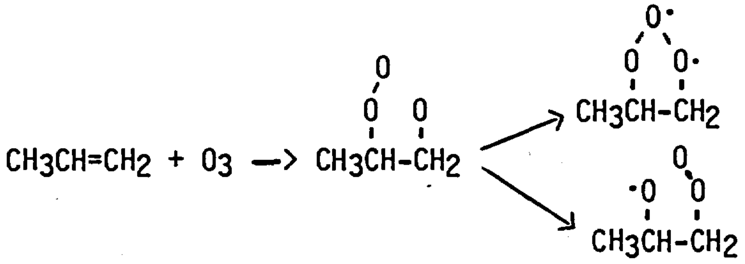


$$\longrightarrow CH_3\overset{OH}{C}HCH_2, \tag{48b}$$

$$\longrightarrow CH_2CH = CH_2 + H_2O. \tag{48c}$$

In each case the free radical product will quickly react with O_2 to produce a peroxyalkyl radical that is capable of converting NO to NO_2.

Ozone-olefin reactions are a source of free radicals and stable products in air pollution chemistry. The initial attack of O_3 on an olefin produces an unstable intermediate, which may decompose by several pathways (Niki, 1978; O'Neal and Blumstein, 1973). For propylene, for example, the initial step in the reaction with O_3 is believed to be:



(59)

Subsequent decomposition of the products leads to a variety of free radicals and stable products, including aldehydes and ketones (Herron and Huie, 1977; Niki et al., 1977). The mechanisms of ozone-olefin reactions are still under considerable study, although most of the potential paths have been delineated.

The reaction of olefins with atomic oxygen plays a minor role in olefin consumption and radical and product formation. Again, for propylene the reaction is:

$$CH_3CH{=}CH_2 + O(^3P) \longrightarrow CH_3CH_2 + HCO, \qquad (60a)$$

or

$$\longrightarrow CH_3CO + CH_3, \qquad (60b)$$

or

$$\longrightarrow CH_3CH_2CHO. \qquad (60c)$$

The mechanism of photooxidation of aromatic species in the atmosphere is perhaps the area of greatest uncertainty in atmospheric hydrocarbon chemistry. The principal reaction of aromatics is with the hydroxyl radical (Hendry, 1978; Perry et al., 1977). For aromatic-OH reactions, the initial step can be either addition to or abstraction from the aromatic ring. The free radical addition products may then react, most likely with either O_2 or NO_2, leading to the cresols or nitrotoluenes, respectively. The abstraction route probably leads to benzaldehyde or ring fragmentation. The mechanism of aromatic-hydroxyl radical reactions is yet to be clarified.

Aldehydes, both aliphatic and aromatic, occur as primary and secondary pollutants and are direct precursors of free radicals in the atmosphere (Lloyd, 1978). Consequently, aldehyde chemistry represents an important subject area in atmospheric chemistry. Although aldehydes are the main oxygenated hydrocarbons generally considered with respect to their role in atmospheric chemistry, other classes of oxygenated hydrocarbons, such as ketones, esters, ethers and alcohols, are present and participate to a somewhat lesser extent. Major secondary sources of aldehydes include the reactions of ozone and OH radicals with hydrocarbons, and radical decomposition products. In addition, aromatic aldehydes can be formed as an ultimate consequence of the reaction of OH with aromatics, e.g., benzaldehyde. The aldehydic hydrogen-carbon bond in aldehydes is relatively weak (CH bond strength is 86 kcal mol^{-1}). Consequently, this hydrogen atom will be susceptible under atmospheric conditions to attack by radical species, such as $O(^3P)$, $O(^1D)$, HO, and HO_2. Of these HO is by far the most dominant. Hydroxyl radicals are generally thought to abstract an H-atom from aldehydes--chiefly the aldehydic H-atoms, i.e.,

$$HO + RCHO \longrightarrow H_2O + RCO. \tag{61}$$

If one assumes an atmospheric concentration of 10^6 HO radicals cm^{-3}, the rates of decay of HCHO and CH_3CHO by reaction with OH are approximately 4.2% and 5.8% h^{-1}, respectively (Lloyd, 1978).

The photodissociation of aldehydes is an important radical generation mechanism in the formation of photochemical air pollution. The reactions that are most significant can be generalized in terms of a radical and a molecular route:

$$RCHO + h\nu \longrightarrow R + HCO, \tag{62a}$$

and

$$\longrightarrow RH + CO. \tag{62b}$$

(Reaction 62a was previously given as reaction 44.) The radical route is the more important one from the point of view of atmospheric chemistry. Considerable attention has been given to formaldehyde photolysis in recent years. There appears to be general agreement that the primary paths are:

$$HCHO + h\nu \longrightarrow H + HCO, \tag{63a}$$

and

$$\longrightarrow H_2 + CO. \tag{63b}$$

To compare the rates of photolysis with the depletion of formaldehyde by HO reaction, one can calculate a photolysis rate of approximately 13% h^{-1} for a solar zenith angle of 20 degrees using the value of the photodissociation rate given by Horowitz and Calvert (1978).

The interaction with NO and NO_2 of the organic free radicals produced by hydrocarbon oxidation represents an extremely important aspect of the chemistry of the oxides of nitrogen in the polluted atmosphere. The radicals can be classed according to:

R	alkyl
RO	alkoxyl
ROO	peroxyalkyl
$R\overset{\overset{O}{\Vert}}{C}$	acyl
$R\overset{\overset{O}{\Vert}}{C}O$	acylate
$R\overset{\overset{O}{\Vert}}{C}OO$	peroxyacyl

In air it can be assumed that combination with O_2 is the sole fate of alkyl (R) and acyl (RCO) radicals and that the reaction is essentially instantaneous. Consequently, in reactions with alkyl or acyl radicals as products, these products are often written as the corresponding peroxy radicals. Also, acylate radicals will decompose rapidly to give an alkylradical and CO_2. Therefore, only alkoxyl, peroxyalkyl, and peroxyacyl radicals need to be considered explicitly in terms of NO_x chemistry.

Table IV shows the various reaction combinations that are important between these radicals and NO and NO_2.

The reactions of HO with NO_2 and NO are reasonably well-understood and have been previously listed as reactions 37 and 38. Rate constants for these two reactions are available (Baulch et al., 1980; Tsang et al., 1977).

The rate constant for the reaction of HO_2 and NO has recently been determined by direct means and is substantially larger than previously calculated indirectly (Howard and Evenson, 1977). The HO_2-NO reaction, as noted earlier, is a key reaction in the atmospheric conversion of NO to NO_2.

The reaction of HO_2 and NO_2 has the following two possible mechanisms (Howard, 1977). Reaction 64b is not considered to be important in atmospheric chemistry:

$$HO_2 + NO_2 \longrightarrow HO_2NO_2, \qquad (64a)$$

and

$$HO_2 + NO_2 \longrightarrow HONO + O_2. \qquad (64b)$$

In addition, the peroxynitric acid formed in reaction 64a thermally decomposes as follows (Graham et al., 1977):

$$HO_2NO_2 \longrightarrow HO_2 + NO_2. \qquad (65)$$

At the present time it appears that, at the temperatures prevalent in summer smog episodes (>20°C), peroxynitric acid does not represent an appreciable sink for NO_2 because of the rapid thermal decomposition reaction 65. At lower temperatures HO_2NO_2 will achieve higher concentrations and its importance as a sink for NO_2 increases.

The reactions of RO, RO_2 and RCO_3 with NO and NO_2 represent key reactions in the conversion of NO to NO_2 and the formation of organic nitrites and nitrates.

TABLE IV. Reactions of Alkoxyl, Alkyperoxyl and Acylperoxyl Radicals with NO and NO_2

	NO		NO_2	
Free radical	Reaction	Reference	Reaction	Reference
OH	$OH + NO \rightarrow HONO$	Hampson and Garvin, 1978	$OH + NO_2 \rightarrow HONO_2$	Tsang et al., 1977
HO_2	$HO_2 + NO \rightarrow NO_2 + OH$	Howard and Evenson, 1977	$HO_2 + NO_2 \rightarrow HONO + O_2$ $\rightarrow HO_2NO_2$ $(HO_2NO_2 \rightarrow HO_2 + NO_2)$	Howard, 1977 Graham et al., 1977
RO	$RO + NO \rightarrow RONO$ $(RONO + h\nu \rightarrow RO + NO)$	Batt et al., 1977	$RO + NO_2 \rightarrow RONO_2$ $\rightarrow RCHO + HONO$	Wiebe et al., 1973
RO_2	$RO_2 + NO \rightarrow NO_2 + RO$ $\rightarrow RONO_2$	Adachi and Basco 1979a, 1979b	$RO_2 + NO_2 \rightarrow RO_2NO_2$ $(RO_2NO_2 \rightarrow RO_2 + NO_2)$	Sander and Watson, 1980 Adachi and Basco, 1979c
RCO_3	$RCO_3 + NO \rightarrow NO_2 + RCO_2$	Cox and Roffey, 1977 Hendry and Kenley, 1977	$RCO_3 + NO_2 \rightarrow RCO_3NO_2$ $(RCO_3NO_2 \rightarrow RO_3 + NO_2)$	Cox and Roffey, 1977 Hendry and Kenley, 1977

The main alkoxyl radical reactions with NO and NO_2 are:

$$RO + NO \longrightarrow RONO \qquad (66a)$$

or

$$\longrightarrow RCHO + HNO \qquad (66b)$$

and

$$RO + NO_2 \longrightarrow RONO_2 \qquad (67a)$$

or

$$\longrightarrow RCHO + HONO. \qquad (67b)$$

The reaction of alkylperoxyl radicals with NO is generally assumed to proceed by the oxidation of NO to NO_2 with formation of an alkoxyl radical:

$$RO_2 + NO \longrightarrow NO_2 + RO. \qquad (41)$$

Reaction 41 is believed to be an important route for the oxidation of NO to NO_2 in the atmosphere (the alkoxyl radical may react further to produce HO_2, which also converts NO to NO_2).

It has been postulated that longer chain peroxyalkyl radicals ($n > 4$) from alkane photooxidation will add to NO to form an excited complex that can be stabilized to produce an alkyl nitrate (Darnall et al., 1976):

$$RO_2 + NO \longrightarrow RONO_2. \qquad (68)$$

The peroxyalkyl-NO_2 reaction proceeds principally by

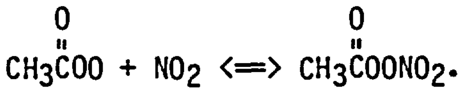
$$RO_2 + NO_2 \longrightarrow RO_2NO_2. \qquad (69)$$

The peroxynitrate may thermally decompose according to

$$RO_2NO_2 \longrightarrow RO_2 + NO_2. \qquad (70)$$

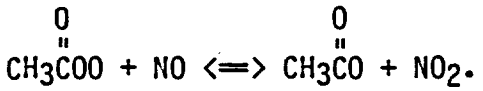
Measured rate constants for the RO_2-NO_2 reaction and the RO_2NO_2 decomposition are not currently available.

Peroxyacyl nitrates have been recognized as important components of photochemical air pollution (U.S. EPA, 1978). Peroxyacetyl nitrate (PAN) exists in equilibrium with the peroxyacyl radical and NO_2:



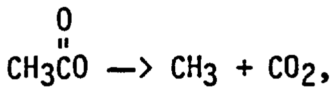
$$CH_3\overset{O}{\overset{\|}{C}}OO + NO_2 \Longleftrightarrow CH_3\overset{O}{\overset{\|}{C}}OONO_2. \tag{71}$$

There exists a competition between NO and NO_2 for the peroxyacyl radical through:



$$CH_3\overset{O}{\overset{\|}{C}}OO + NO \Longleftrightarrow CH_3\overset{O}{\overset{\|}{C}}O + NO_2. \tag{72}$$

The acetyl radical will rapidly decompose as follows:



$$CH_3\overset{O}{\overset{\|}{C}}O \longrightarrow CH_3 + CO_2, \tag{73}$$

followed by:

$$CH_3 + O_2 \longrightarrow CH_3O_2, \tag{40}$$

$$CH_3O_2 + NO \longrightarrow CH_3O + NO_2, \tag{41}$$

$$CH_3O + O_2 \longrightarrow HCHO + HO_2, \tag{42}$$

$$HO_2 + NO \longrightarrow OH + NO_2. \tag{43}$$

Thus, PAN chemistry is intimately interwoven in the NO to NO_2 conversion process. Rate constants for reactions 71 and 72 have recently been reported by two groups of investigators (Cox and Roffey, 1977; Hendry and Kenley, 1977).

The chemistry of the oxides of nitrogen in a hydrocarbon-containing atmosphere can be summarized as follows: the major observed phenomenon in the system is conversion of NO to NO_2 and formation of a variety of nitrogen-containing species, such as nitrites and nitrates. The conversion of NO to NO_2 is accompanied by accumulation of O_3. NO_2 serves both as initiator and terminator of the chain reactions that result in conversion of NO to NO_2 and buildup of O_3. Termination of the chain reactions leads to nitric acid and organic nitrates. The nature of the system can be explained by considering its behavior as a function of the initial concentrations of NO_x and hydrocarbon in the irradiation of a static system, as well as the ratio of two reactants, i.e., the $[HC]/[NO_x]$ ratio.

At low $[HC]/[NO_x]$ ratios (usually ratios of less than about 1 to 2/1) the rate at which NO is converted to NO_2 is influenced by the availability of organic compounds. Therefore, the effects of reducing organic compounds are to slow the conversion of NO to NO_2, thereby lowering the NO_2/NO ratio. When this occurs, a larger proportion of the NO that is converted to NO_2 occurs through the reaction with ozone. This, then, has the overall effect of reducing the ozone buildup. If the oxidation of NO by organics is delayed sufficiently so that the sun has passed its zenith before significant amounts of NO_2 are created, photodissociation of NO_2 will be diminished and less ozone will accumulate on that date. At moderately high $[HC]/[NO_x]$ ratios (usually greater than about 5 to 8/1), the greater availability of organic radicals means that all of these radicals are not consumed as rapidly in reactions with NO, and more reactions between the radicals and NO_2 are able to occur. Thus, the amount of ozone formed and accumulated begins to become limited by the availability of NO_x, and becomes less sensitive to additional organic precursors. At very high $[HC]/[NO_x]$ ratios (greater than about 20 to 30/1), ozone cannot accumulate because either the ozone is consumed by reaction with hydrocarbons, NO_x becomes unavailable due to reactions with free radicals, and radical-radical termination reactions occur which reduce oxygen atom and, hence, ultimate ozone concentration.

Identification of the nitrogen-containing products in atmospheric reactions has been under investigation for a number of years (Gay and Bufalini, 1971; Spicer and Miller, 1976; Pitts, 1977). In general, the most important gaseous nitrogen-containing products in the NO_x-organic system are nitric acid and PAN. As noted, reactions of NO and NO_2 with free radicals produce, in addition to nitrous, nitric, and peroxynitric acids, a variety of organic nitrogen-containing species (Table IV). There currently exist important areas of uncertainty with regard to the formation of nitrogen-containing products in atmospheric reactions. The extent of formation and decomposition of peroxynitrates, RO_2NO_2, is unknown, and rate constants for the key reactions in the series, RO_2 + NO, are yet to be determined.

Laboratory Evidence of the NO_2-to-Precursor Relationships

In the previous section, the nature of chemical reactions involving oxides of nitrogen and hydrocarbons in the atmosphere was discussed. These reactions have traditionally been studied experimentally in laboratory vessels called smog chambers. These chambers characteristically employ radiation sources that closely approximate the UV portion of the solar spectrum as observed at the earth's surface and clean, chemically inert interior surfaces. It is believed that the chemical processes that take place in smog chambers are similar to those that take place in the atmosphere.

The presence of surfaces in a smog chamber may, however, be a source of difficulty in interpreting chamber results because of possible surface-catalyzed reactions or absorption of species on the walls. In addition, most chamber experiments have been conducted by initially injecting fixed amounts of reactants rather than simulating the continuous time-varying injection and dilution of reactants that characterize the ambient situation. Nevertheless, the behavior of irradiated mixtures of oxides of nitrogen and hydrocarbons in smog chambers has served as the foundation for our understanding of atmospheric chemical mechanisms.

Considerable effort has been devoted to the development of chemical reaction mechanisms that are capable of describing the processes observed in smog chambers (Demerjian et al., 1974; Carter et al., 1979; Baldwin et al., 1977; Whitten and Hogo, 1977; Falls and Seinfeld, 1978). Smog chambers have been used extensively to determine how concentrations of NO_x and other photochemical products respond to changes in the initial composition of nitrogen oxides and organics. The ozone/photochemical criteria document (U.S. EPA, 1978) discusses smog chamber evidence concerning the relationship between ozone/oxidant and the photochemical precursors. This section focuses on how NO_2 concentrations respond to changes in the input levels of organics and nitrogen oxides.

Several researchers have used smog chambers to investigate the dependence of nitrogen dioxide concentrations on the levels of precursor inputs:

- The University of North Carolina (UNC) study using an 11,000 cubic-foot (311 m^3) outdoor Teflon chamber, a simulated urban hydrocarbon mix, and 12-hour irradiations (Jeffries et al., 1975)

- The Bureau of Mines study, using a 100 cubic-foot (2.8 m^3) aluminum-glass chamber, auto-exhaust hydrocarbons, and six-hour irradiations (Dimitriades, 1972, 1977)

- The General Motors study, using a 300 cubic-foot (8.5 m^3) stainless steel-glass chamber, a simulated Los Angeles hydrocarbon mix, and six-hour irradiations (Heuss, 1975)

- The Health, Education and Welfare (HEW) study using a 335 cubic-foot (9.5 m^3) chamber, auto-exhaust hydrocarbons, and up to 10-hour irradiation time (Korth et al., 1964).

- The HEW study using a 335 cubic-foot (9.5 m^3) chamber, toluene and m-xylene, and 6-hour irradiations (Altshuller et al., 1970).

Trijonis (1978a, 1978b) has recently reviewed the results of these studies, as summarized in Table V. As indicated in Table V, the various chamber studies basically agree concerning the dependence of maximum NO_2 and average NO_2 on NO_x input. With other factors held constant, maximum NO_2 and average NO_2 tend to be proportional to initial NO_x. The minor deviations away from proportionality that sometimes occur tend to be in the direction of a slightly less than proportional relationship, i.e., a 50% reduction in NO_x input sometimes produces slightly less than a 50% reduction in NO_2.

There is less agreement among the chamber studies concerning the dependence of NO_2 on initial hydrocarbon concentrations. With respect to maximum NO_2, the Bureau of Mines study indicates essentially no dependence on hydrocarbons. However, two other studies suggest that hydrocarbon reductions decrease maximum NO_2 concentrations. The UNC results indicate that 50% hydrocarbon control tends to decrease maximum NO_2 by about 10 to 20%. The General Motors studies imply that 50% hydrocarbon control reduces maximum NO_2 by about 25%.

TABLE V. Summary of Conclusions from Smog Chamber Experiments

	MAXIMAL NO_2		AVERAGE NO_2	
CHAMBER STUDY	Dependence on NO_x	Dependence on HC	Dependence on NO_x	Dependence on HC
University of North Carolina (Jefferies et al., 1975)	Proportional or slightly less than proportional	50% HC reduction reduces maximal NO_2 by 10 to 20%	Proportional or slightly less than proportional	Uncertain, 50% HC reduction may decrease average NO_2 by 20% or may increase average NO_2
Bureau of Mines (Dimitriades, 1972, 1977)	Proportional	No effect	Proportional	50% HC reduction increases average NO_2 by 10 to 30%
General Motors (Heuss, 1975)	Slightly less than porportional	50% HC reduction reduces maximal NO_2 by 25%	Proportional to slightly less than proportional	No effect
HEW, Auto Exhaust (Korth et al., 1964)	-------------	-------------	Proportional	No consistent effect
HEW, Toluene (Altschuller et al., 1970)	-------------	-------------	Proportional	No effect

With respect to average NO_2, the Bureau of Mines study indicates that hydrocarbon reductions would tend to increase NO_2 dosage. This result is consistent with the theoretical argument of Stephens (1973) who hypothesized that hydrocarbon reduction would increase average NO_2 because these reductions would delay and suppress the chemical reactions that consume NO_2 after it reaches a peak. However, the General Motors chamber study and the two HEW studies indicate that hydrocarbons produce no consistent effects on average NO_2 concentrations. The UNC experiments imply that a 50% reduction in hydrocarbons produces about a 20% decrease in average NO_2. There is some question about the UNC conclusion, however, because the UNC chamber runs were of a 10-hour duration and the NO_2 levels at the end of the experiments were greater when hydrocarbons were reduced. The extra NO_2 remaining after the 10-hour period could cause an increase in 24-hour average NO_2, even though average NO_2 was reduced during the first 10 hours.

Considering the results of all the chamber studies, Trijonis suggested a consensus based on existing chamber results which would appear to be as follows: 50% hydrocarbon reduction would have little effect on average NO_2 concentrations (a change of ± 10%) but would yield moderate decreases in maximal NO_2 (a reduction of about 10 to 20%). It should be noted that these conclusions are meant to apply to one basic type of ambient situation--the situation of well-mixed urban air.

Some additional support for these conclusions was provided recently by studies of actual ambient data on NO_x and hydrocarbon levels from a number of cities in the U.S. Using empirical modeling and historical trend analysis, Trijonis (1978a, 1978b) concluded that the ambient data were generally consistent with the consensus of chamber results. The exact form of the NO_2/precursor relationship, however, was found to vary somewhat from one location to another, presumably depending on local hydrocarbon/NO_x ratios, on the details of the hydrocarbon mix, and on specific meteorological conditions.

Reference is made also to another body of data due to Pitts et al. (1977) (collected for a different purpose) which also contains potential information on the relationship between NO_x and its precursors. However, the data have not been analyzed to date for its pertinence to the NO_x/precursor question.

NO_x-Oxidant Chemistry in Plumes

The atmospheric chemistry involving oxides of nitrogen in plumes from major fuel burning installations is essentially that described earlier. However, the relatively high concentrations of NO and NO_2 in such plumes compared with those in the ambient urban atmosphere leads to certain chemical phenomena particularly characteristic of plumes. For example, ambient ozone is quickly scavenged in the plume by the large quantities of NO through reaction 23. Because the rate of the NO-O_3 reaction is fast relative to that of dilution of the plume the rate of conversion of NO to NO_2 is controlled by the rate at which ambient O_3 is entrained into the plume by turbulent mixing (Kewley, 1978; Shu et al., 1978; Hegg et al., 1976; White, 1977). There is some nitric acid produced in power plant plumes during the daylight hours through the oxidation of nitric oxide (reaction 20) and the subsequent photodissociation of NO_2 (reaction 21), then followed by the combination of NO_2 with NO_3 and H_2O (reactions 29 and 27). The generation of nitrous acid is also probable since the stack gases will contain NO, NO_2, and H_2O (reaction 32). Since nitrous acid will photodissociate to given hydroxyl radicals (reaction 36), more nitric acid can be produced by reaction 38. Thus, although the free radical concentration is expected to be low in power plant plumes, some NO_x will be converted to nitric acid. In addition, after sufficiently long travel times during which ambient hydrocarbons have been mixed with the plume constituents, the usual free radical reactions described earlier occur, possibly leading to O_3 production.

There are several studies in which measurements have been made of the concentrations of pollutants in power plant plumes (Hegg et al., 1976; White et al., 1976; Davis et al., 1974). The most difficult current problem is predicting the rate at which NO is converted to NO_2 in such a plume.

Computer Simulation of Atmospheric Chemistry

A key problem underlying the development and evaluation of kinetic mechanisms for atmospheric chemistry is determining the sensitivity of the concentration predictions to those uncertain aspects of the reaction scheme.

Such a determination can serve as a valuable guide for future experimental studies and for identifying those parameters that, when varied within accepted bounds, will be most influential on the predictions of the mechanism.

Although the qualitative aspects of the chemistry of the polluted troposphere appear to be reasonably well understood, there are many important details that still need to be investigated before a complete quantitative understanding of the photochemical smog system is possible. Several groups (Demerjian et al., 1974; Carter et al., 1979; Baldwin et al., 1977; Whitten and Hogo, 1977; Falls and Seinfeld, 1978) have formulated chemical reaction mechanisms for polluted tropospheric chemistry. Some of these are based on specific surrogate hydrocarbon chemistries; in others, attempts have been made to simulate the complex ambient atmospheric system by representing the general features of the hydrocarbon chemistry. All mechanisms contain aspects of uncertainty, whether in unknown rate constants, in the importance of competing reaction paths, or in the manner of representing the reaction of a generalized species. The measure of the accuracy of a mechanism is usually based on the extent of agreement between predicted concentration profiles and those generated experimentally in smog chambers. But here also, the inherent uncertainty of the experimental data base must be taken into consideration when comparing predictions to observations.

The chemistry of the inorganic portion of the photochemical smog mechanism is, by and large, well understood. Uncertainties remaining include:

- photolysis rates,
- alkane-HO product distributions,
- olefin-HO and olefin-O_3 product distributions,
- aromatic chemistry,
- alkoxyl radical reactions, and
- RO_x/NO_x reactions.

Uncertainty in the model prediction can result from inappropriate specification of photolysis rate constants. In the case of computer simulations of smog chamber data, photolysis rate constants relative to the reported value for NO_2 are frequently used. A recent review of theoretical estimates of photolytic rate constants in the lower troposphere by Demerjian, Schere and Peterson (1980) indicates that for species such as NO_2, HONO, H_2O_2, O_3, and formaldehyde, extensive experimental determinations of absorption cross sections and quantum yields are fairly reliable. However, since cross section and quantum yield data for higher aldehydes, alkyl nitrites and other carbonyl compounds are much less well characterized, these photolysis rate constants are subject to a large uncertainty. Of course, even if absorption cross sections and quantum yields could be determined accurately for all photo-sensitive species, uncertainties in atmospheric photolysis rate constants would still exist, as meteorological conditions, clouds, dust, and aerosols cause unknown variances in actinic irradiance.

Whereas rate constants in the inorganic portion of the mechanism are known fairly well, many more uncertainties, both in reaction rate constants and products, are associated with the organic reaction steps. Still to be determined are product distributions and reaction rate constants for the initial steps of the reactions of OH and hydrocarbon species, the largest uncertainties lying in the routes of the various radical species produced. For example, although rate constants for alkane-OH reactions are well established, the ratio of internal to external abstraction for all alkanes is not known. Addition to O_2 to form peroxyalkyl (RO_2) radicals can be considered as the sole fate of the alkyl radicals first produced in alkane-OH reactions, but after the formation of alkoxyl radicals through the conversion of NO to NO_2, the reaction mechanism becomes uncertain. Alkoxyl radicals can decompose, react with O_2, isomerize, or react with NO or NO_2, with the importance and rate of each reaction path depending on the nature of the alkoxyl group. Even for the most studied of the alkane-hydroxyl radical reactions, the relative rates between decomposition, isomerization, and reaction with O_2, NO, and NO_2 for alkoxyl radicals have not been measured, but must be estimated (Baldwin et al., 1977).

Less well understood than alkane reaction mechanisms are olefin oxidation processes, primarily by HO. Olefin-hydroxyl radical reactions may proceed by addition or abstraction. For smaller olefins, the addition path predominates. However, the abstraction fraction increases with the size of the olefin. Along the addition path for terminally bonded olefins, there is uncertainty as to the ratio of internal to external addition. Similar to alkyl radicals, the hydroxy-alkyl radicals formed in the initial HO addition to olefins are thought to immediately add O_2 to form hydroxy-peroxyalkyl radicals and thereafter react with NO to give NO_2 and hydroxy-alkoxyl species. The fate of the hydroxy-alkoxyl radicals is subject to speculation, although the analogous alkoxyl reaction paths of decomposition, isomerization, and reaction with NO, NO_2 and O_2 are most likely possibilities.

The inherent uncertainty of the decomposition, reaction with O_2, and isomerization of the alkoxyl and hydroxy-alkoxyl radicals class can be presented by the generalized reaction step:

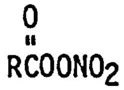
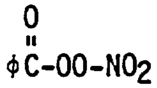
$$RO \longrightarrow \alpha HO_2 + (1 - \alpha)RO_2 + \beta HCHO + \gamma RCHO. \qquad (74)$$

From the earlier discussions of alkoxyl radical behavior, RO always gives rise to either HO_2 or RO_2 in any of the decomposition, isomerization, or O_2 reaction pathways. Hence, the stoichiometric coefficients representing the fraction of HO_2 and RO_2 found in the lumped RO reaction should sum to one. Since the lumped RO species represents a large class of different-sized radicals and because splits between reaction paths for even specific radicals are not known, α can have a value in the range of 0 to 1. Many RO reaction routes produce aldehydes. Thus, $0 \leq \beta \leq 1$ and $0 \leq \gamma \leq 1$. Since the composition of the RO radical pool is continually changing during the course of a photooxidation, the actual values of α, β, and γ are functions of time. Thus, the selection of constant values of these coefficients introduces uncertainty.

A comprehensive sensitivity/uncertainty analysis of photochemical smog mechanisms has been carried out by Falls et al. (1979). In this study the effects of rate constant and mechanistic uncertainties on predicted concentrations are illustrated.

NITRITE AND NITRATE FORMATION

The oxides of nitrogen are converted eventually to nitrites and nitrates by the reactions previously given. In particular, the following gaseous nitrites and nitrates have been identified:

$HONO$	nitrous acid
$HONO_2$	nitric acid
HO_2NO_2	peroxynitric acid
$RONO$	alkyl nitrite
$RONO_2$	alkyl nitrate
 $R\overset{\overset{O}{\parallel}}{C}OONO_2$	peroxyacylnitrate (PAN)
RO_2NO_2	peroxyalkyl nitrate
 $\phi\overset{\overset{O}{\parallel}}{C}\text{-OO-}NO_2$	peroxybenzoyl nitrate (PBZN)

In addition to these gaseous species, particulate nitrites and nitrates may be formed. The object of this section is to present estimates of the importance of the various nitrites and nitrates. In most cases, estimates are necessary because ambient measurements of the concentration level of all but a very few of the species are lacking.

Typical ambient concentration levels of the gaseous nitrogen-containing species listed above can be estimated from simulations of smog chamber experiments using chemical mechanisms representing the hydrocarbon-NO_x chemistry. Table VI lists calculated concentrations of $HONO$, $HONO_2$, HO_2NO_2, $RONO$, $RONO_2$, $RC(O)OONO_2$, and RO_2NO_2 for smog chamber experiment EC-237 carried out at the Statewide Air Pollution Research Center of the University of California, Riverside, using the chemical mechanism of Falls and Seinfeld (1978). The conditions of the experiment are given in the footnote of Table VI. The simulated and predicted concentrations of the major measured species, such as NO, NO_2 O_3, PAN, and hydrocarbons, agreed well.

The concentrations of HONO, HO_2NO_2, and RONO are predicted to be small relative to those of NO and NO_2. Each of these species has decomposition reactions,

$$HONO + h\nu \longrightarrow OH + NO, \tag{36}$$

$$HO_2NO_2 \longrightarrow HO_2 + NO_2, \tag{65}$$

$$RONO + h\nu \longrightarrow RO + NO, \tag{75}$$

that, at the temperatures and solar intensities prevalent in the experiment and in the summer atmosphere, are fast enough to insure that the concentrations of each of the three species are low. At lower solar intensities than those in the experiment, HONO and RONO can be expected to reach higher concentrations, and at lower temperatures, such as those in the stratosphere, HO_2NO_2 may accumulate.

Under daytime conditions the reactions that govern the concentration of HONO are 36 and 37. At night, however, the only apparent destruction route for HONO is reaction 33. Depending on the relative importance of reactions 37, 32, and 33, HONO may reach substantial concentrations under night-time conditions. A lower limit on the night-time concentration of HONO can be estimated from the equilibrium HONO concentration based on reactions 32 and 33.

$$[HONO] = \left[\frac{k_{13}[NO][NO_2][H_2O]}{k_{14}}\right]^{1/2} \tag{76}$$

At $[NO] = [NO_2] = 0.1$ ppm, $[H_2O] = 2.4 \times 10^4$ ppm (50% relative humidity), the equilibrium HONO concentration calculated from equation 76 is 1.9×10^{-2} ppm. Nitrous acid has been recently observed in the atmosphere just before sunrise in Jülich, Germany, at concentrations as high as 0.8 ppb (Platt and Perner, 1979).

TABLE VI. Predicted Nitrite and Nitrate Concentrations in Simulation of Experiment EC-237 of the Statewide Air Pollution Research Center of the University of California, Riverside, using the Chemical Mechanism of Falls and Seinfeld (1978)

	Concentration, ppm		
	60 min	180 min	300 min
HONO	0.0061	0.00040	0.00036
$HONO_2$	0.067	0.22	0.29
HO_2NO_2	0.00083	0.0019	0.0025
RONO	0.0030	0.00054	0.000080
$RONO_2$	0.0041	0 .0070	0.0072
$R\overset{\overset{O}{\|}}{C}OONO_2$	0.025	0.089	0.13
RO_2NO_2	0.034	0.075	0.098

Conditions of the experiment: T = 303°K, $k_2 = 0.3\ min^{-1}$, $[NO_2]_o = 0.106$, $[NO]_o = 0.377$, $[H_2O] = 2.4 \times 10^4$, $[CO] = 0.96$, $[Aldehydes]_o = 0.0012$, $[Alkanes]_o = 2.488$, $[Non\text{-}ethylene\ Olefins]_o = 0.15$, $[C_2H_4]_o = 0.875$, $[Aromatics]_o = 0.177$, $[HONO]_o$ (assumed) = 0.1 (all concentrations in ppm). Dilution rate = $2.93 \times 10^{-4}\ min^{-1}$.

Like HONO, HO_2NO_2 and RONO, PAN undergoes both formation and decomposition steps (reaction 71). Unlike these former species, however, the balance between the formation and decomposition reactions is such that PAN may achieve appreciable concentration levels relative to those of NO and NO_2. Because the decomposition reaction for PAN is strongly temperature dependent, the steady state PAN concentration is highly dependent on the temperature. As temperature increases the role of PAN as an NO_2 sink decreases markedly; at low temperatures, on the other hand, steady state PAN concentrations can reach rather substantial levels.

Little is known about the existence and importance of peroxynitrates other than HO_2NO_2 and PAN. It is presumed in the mechanism on which the results of Table VI are based that RO_2NO_2 thermally decomposes at a rate between those for HO_2NO_2 and PAN. Assessment of the importance of RO_2NO_2 as a sink for NO_x will depend on measurement of the rates of reactions 69 and 70.

In contrast to the other species of Table VI, nitric acid and alkyl nitrates apparently do not undergo appreciable decomposition reactions. Thus, these two species potentially serve as important atmospheric sinks for NO_2. Both nitric acid and alkyl nitrates may remain in the gas phase or react with other atmospheric constituents, such as ammonia, to produce low vapor pressure species that have a tendency to condense on existing particles or homogeneously nucleate to form particles.

Figure 4 depicts the potential paths by which particulate nitrate species may be formed from NO and NO_2. Path 1 involves the formation of gaseous nitric acid by reactions 27 and 38. Nitric acid concentrations resulting from these two reactions for the simulated smog chamber experiment have been given in Table VI. Comparisons of the individual rates of reactions 27 and 38 indicate that reaction 38 is the predominant route for gas-phase nitric acid formation under typical daytime conditions. Nitric acid vapor, once formed, may then react with NH_3, a ubiquitous atmospheric constituent with both natural and anthropogenic sources, to produce ammonium nitrate, NH_4NO_3 (path 2), which at standard temperature and pressure, exists as a solid. Alternatively, the nitric acid vapor may be absorbed directly onto a particle (path 3), although thermodynamic and kinetic considerations favor reaction with NH_3 to form NH_4NO_3 as the path of conversion of gaseous nitric acid to nitrate in particulate form (Bradner et al., 1962; Morris and Niki, 1971; Stelson et al., 1979). Path 4 involves the direct absorption of NO and NO_2 into an atmospheric particle, a route that is likely for certain aqueous particles, particularly when accompanied by the absorption of ammonia (path 5) (Orel and Seinfeld, 1977). Path 6 depicts the formation of organic nitrates through reactions such as 67a, followed by absorption of these nitrates into particles. At present little is known about the existence or importance of mechanisms such as that depicted by Path 6.

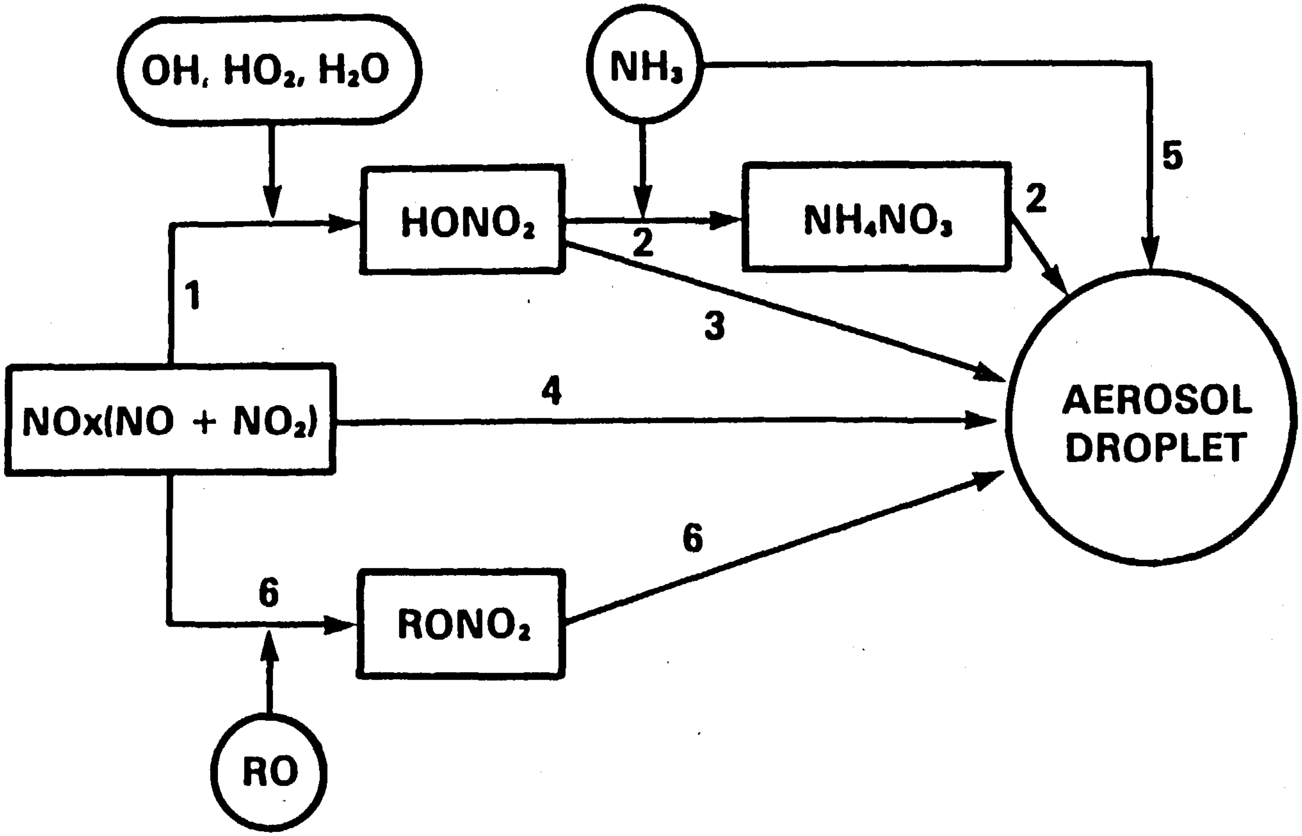


Figure 4. Paths of nitrate formation in the atmosphere.
Source: Orel and Seinfield (1977).

There have been a limited number of measurements of nitric acid and particulate nitrate concentrations in ambient air, and of these measurements many have identified the particulate nitrate as NH_4NO_3, suggesting that the aerosol may consist of solid NH_4NO_3 or NH_4^+ and NO_3^- in solution in approximate stoichiometric balance. It is difficult to estimate the relative importance of the paths in Figure 4 for several reasons. First, the rate of reaction of nitric acid and ammonia is not well known, although the forward reaction is probably rapid, and in fact, can be presumed to be in equilibrium with the dissociation of solid ammonium nitrate (Bradner et al., 1962; Morris and Niki, 1971; Stelson et al., 1979).

$$NH_{3(g)} + HONO_{2(g)} \Longleftrightarrow NH_4NO_{3(s)} \qquad (77)$$

Second, the rate of absorption of NO and NO_2 into existing particles depends on the composition and size of each particle and cannot generally be predicted a priori. In either case it is apparent that the presence of NH_3 is required, either to form NH_4NO_3 or to neutralize the acidity of a liquid droplet in which NO and NO_2 dissolve.

The current state of understanding of atmospheric inorganic nitrate formation can be summarized as follows. The principal gas-phase nitrate forming reaction is reaction 38. The nitric acid vapor formed in reaction 38 probably reacts rapidly with ammonia to form small particles of solid ammonium nitrate such that the equilibrium of reaction 77 is established. In competition with the nitric acid/ammonium nitrate path is the path consisting of direct absorption of NO and NO_2 into aqueous droplets. The relative rates of these two paths cannot be determined in general. Although measurements of particulate organic nitrate levels have been reported (Grosjean, 1979), the mechanisms of formation of organic aerosol nitrates have not been fully identified.

SO_2-OXIDANT CHEMISTRY IN THE LOWER TROPOSPHERE

The chemical transformation of sulfur dioxide in the atmosphere has been studied extensively over the past 20 years. Recent reviews (Calvert et al., 1978; Middleton et al., 1980; and Moller, 1980), which consider analysis of laboratory and field data as well as theoretical studies, indicated that SO_2 oxidation may proceed through both gas and liquid phase reactions. The oxidation of SO_2 in the atmosphere is of considerable importance, in that it represents a major pathway for particle production through the formation of sulfates. Homogeneous gas phase reactions are by far the most extensively studied and best understood quantitatively.

Gas-Phase Chemical Reactions of SO_2

The homogeneous gas-phase chemistry of oxidation in the clean and polluted troposphere is reviewed in this section. The status of our knowledge is presented for the elementary oxidation reactions of SO_2 and the importance of volatile organic and nitrogen oxides as generators of free radical oxidizers. This review will show that the photochemical oxidation of SO_2 is potentially a significant pathway for tropospheric sulfate formation. The three most important oxidizers of SO_2 are: (1) hydroxyl radical HO; (2) peroxyl radical, HO_2; and (3) methoxyl radical, CH_3O_2. At this time, only the reaction rate constant for HO is well established. The pathways of formation of the oxidizer radicals for the unpolluted troposphere can be explained in terms of the photochemistry of the NO-HC-CO-O_3 system. In polluted atmospheres, volatile organics and oxides of nitrogen act together to produce additional radicals and accelerate overall radical production. There is also evidence that a dark reaction among O_3, alkenes, and SO_2 is effective in oxidizing SO_2.

The elementary chemical reactions of SO_2 in air have been the subject of intense investigation. Studies prior to 1970 have been critically reviewed by Bufalini (1971), and more recently by Calvert et al. (1978). The review of Calvert et al. (1978) systematically examined the rate constants and significance of SO_2 elementary reactions known to occur in the troposphere; identified as generally unimportant reactions were: photodissociation, photoexcitation, reaction with singlet delta oxygen [$O_2({}'\Delta g)$], reaction with triplet oxygen atom [$O(^3P)$], reaction with ozone (O_3), reaction with nitrogen oxides (NO_2, NO_3, N_2O_5), reaction with tert-butylperoxyl radical [$(CH_3)_3CO_2$], and reaction with acetyl-peroxyl radical (CH_3COO_2). The only SO_2 reactions in the troposphere that were identified as important were those due to hydroxyl radical (HO), peroxyl radical (HO_2), and methoxyl radical (CH_3O_2). The rate constants recommended by Calvert et al. (1978) for these three reactions are given in Table VII. More recent work is in conflict with the rate constants for HO_2 and CH_3O_2 that have been recommended by Calvert et al. (1978). Graham et al. (1979) and Burrows et al. (1979) have reported rate constants for the HO_2 reaction that are much lower than that recommended by Calvert et al. (1978); these more recent results are shown in Table VII. Also, Sander and Watson (1981) have reported a rate constant for the CH_3O_2 reaction that is much lower than that recommended by Calvert et al. (1978); that value is given in Table VII. The reasons for the discrepancies for these two rate constants are unknown, and there is no basis to recommend preferred values.

Although the dark reaction of $SO_2 + O_3$ is too slow to be important in the troposphere, the addition of alkenes greatly enhances the oxidation rate. The experimental work of Cox and Penkett (1971a,b, 1972) and McNelis et al. (1975) has been reviewed and reevaluated by Calvert et al. (1978). The reaction system is too complex to discuss here, but Calvert et al. (1978) report results of their calculations for total alkenes = 0.10 ppm, $[O_3] = 0.15$ ppm, and $[SO_2] = 0.05$ ppm; they estimated that the disappearance rate of SO_2 is 0.23 and 0.12% h^{-1} at 50 and 100% relative humidity (25°C), respectively. The reaction mechanism for the O_3 + alkene + SO_2 system is not known, but studies by Niki et al. (1977) and Su et al. (1980) indicate that the reactive species may be the biradical, formed by the decomposition of the original molozanide.

The status of our knowledge of the gas-phase tropospheric oxidation reactions is:

1. Three reactions have been identified as being potentially important.
   a. HO radical. The rate constant appears to be well established.
   b. HO_2 radical. The rate constant is not well established.
   c. CH_3O_2 radical. The rate constant is not well established.

2. The $SO_2 + O_3$ + alkenes reaction may be an important dark reaction.

TABLE VII. Rate Constants for Hydroxyl, Peroxyl, and Methoxyl Radicals

Reaction	Second order rate constant, $cm^3 mole^{-1} s^{-1}$	Source
$HO + SO_2 \rightarrow HOSO_2 \rightarrow H_2SO_4$	$(1.1 \pm 0.3) \times 10^{-12}$	Calvert et al. (1978)
$HO_2 + SO_2 \rightarrow HO + SO_3 \rightarrow H_2SO_4$	$>(8.7 \pm 1.3) \times 10^{-16}$	Calvert et al. (1978)
	$<1 \times 10^{-18}$	Graham et al. (1979)
	$\leq 2 \times 10^{-17}$	Burrows et al. (1979)
$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3 \rightarrow H_2SO_4$	$(5.3 \pm 2.5) \times 10^{-15}$	Calvert et al. (1978)
	5×10^{-17}	Sander and Watson (1981)

In its simplest form the photochemical oxidation cycle in polluted atmospheres (which has been previously discussed) is governed by the following basic features. Free radical attack on atmospheric VOCs is initialized by a select group of compounds which are for the most part activated by sunlight. Formaldehyde and nitrous acid, in particular, show high potential as free radical initiators during the early morning sunrise period. After initial free radical attack, the VOCs decompose through paths resulting in the production of peroxyl radical species (HO_2, RO_2, $R'O_2$, etc.) and partially oxidized products which in themselves may be photoactive radical-producing compounds. The peroxyl radicals react with NO, converting it to NO_2, and in the process produce hydroxyl/alkoxyl radical species (OH, RO, R'O, etc.). Alkoxyl radicals can be further oxidized, forming additional peroxyl radicals and partially oxidized products, thereby completing the inner cyclical loop reaction chain process illustrated in Figure 5; or they may attack, as would be the major path for hydroxyl radical, the VOC pool present in the polluted atmosphere, thereby completing the outer loop reaction chain process. The resultant effect in either case is the conversion of NO to NO_2 with a commensurate oxidation of reactive organic carbon.

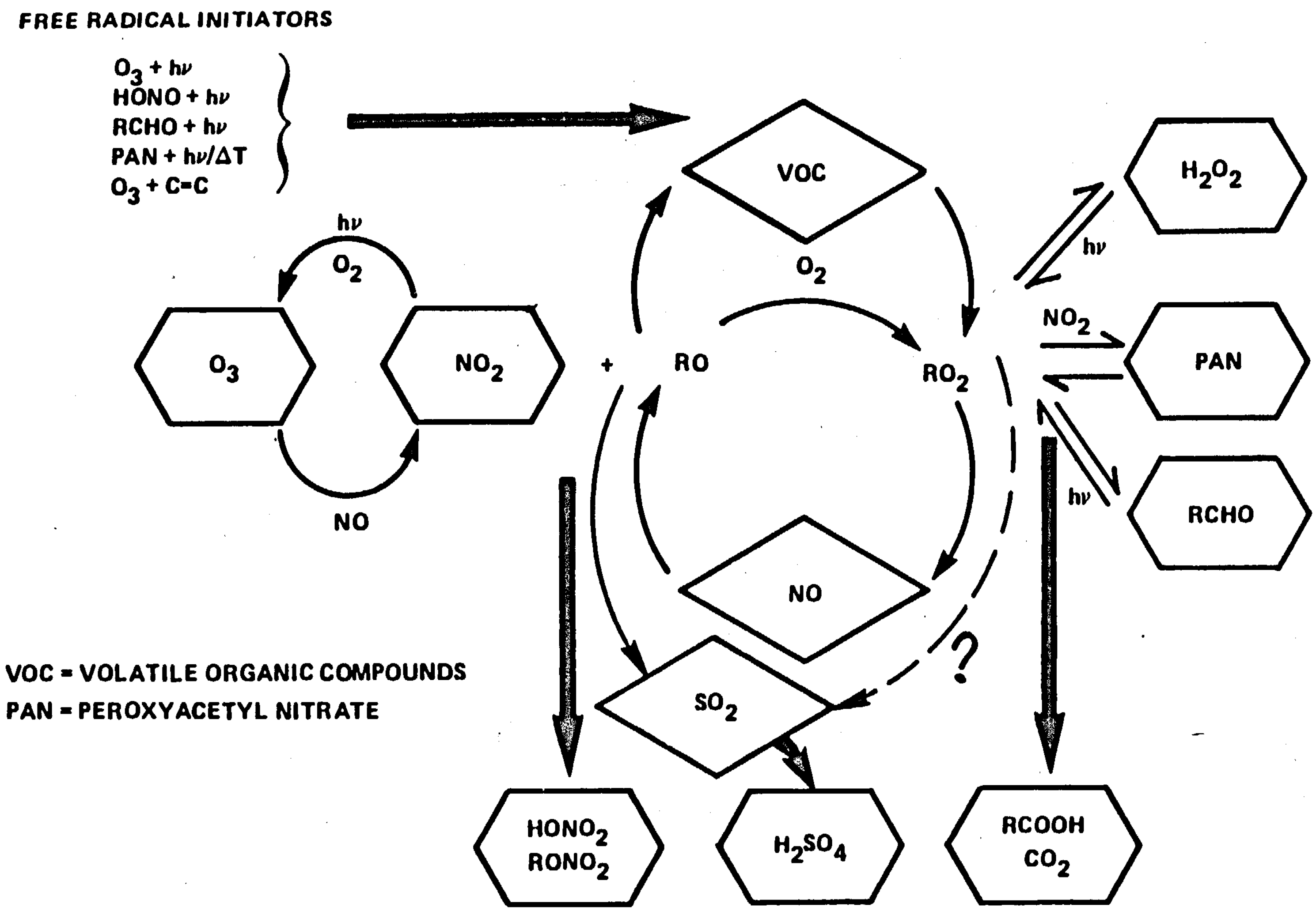


Figure 5. Schematic of the polluted atmospheric photooxidation cycle.

The complex mixture of organic compounds present in the polluted atmosphere react at different rates depending upon their molecular structure, the result being varying yields of free radical species, ozone, NO_2, PAN and other partially oxidized organic products as a function of VOC composition and VOC-NO_x levels.

Hydroxyl radical (HO) reactions seem to be the dominant gas-phase mechanism by which hydrocarbons, nitrogen dioxide and sulfur dioxide are consumed in the atmosphere (Niki et al., 1972; Demerjian et al., 1974; Calvert et al., 1978). Interestingly enough, this highly reactive transient species, quite contrary to its organic free radical counterparts, does not show appreciable change in concentration with atmospheric VOC and NO_x variation, a result readily explainable upon review of the free radical production and consumption sources. In the case of hydroxyl radicals, ambient concentration conditions which enhance its production tend to also consume the radical at an equivalent rate. The result is a faster cycling in the VOC-NO_x oxidation chain (that is, increased chain lengths) but very little perturbation in the HO steady state concentration. In contrast, organic free radicals, mainly peroxyl species, are consumed by alternate pathways which are less competitive and result in increased steady state concentration.

Applying this basic knowledge of the photochemistry of the lower atmosphere, Calvert et al. (1978) determined theoretical rates of SO_2 oxidation via attack of various free radical species whose concentrations were estimated from computer simulations of the chemical reaction mechanisms (using the rate constants given in Table VII) for clean and polluted atmospheres.

Based on limited rate constant data for the SO_2-free radical reactions, Calvert determined that the hydroxyl radical dominated the rate of SO_2 oxidation in the clean troposphere, while in polluted atmospheres the rate of SO_2 oxidation showed equivalent contributions from hydroxyl, hydroperoxyl (HO_2), and methylperoxyl (CH_3O_2) radicals. Figure 6 depicts the estimated time dependent rates of SO_2 oxidation by free radical species in a polluted air mass. Recent laboratory measurements suggest that the rate of reaction of SO_2 with HO_2 and CH_3O_2 may not be as great as estimated by Calvert et al. (1978). Typical rates of SO_2 oxidation were predicted to be of the order of

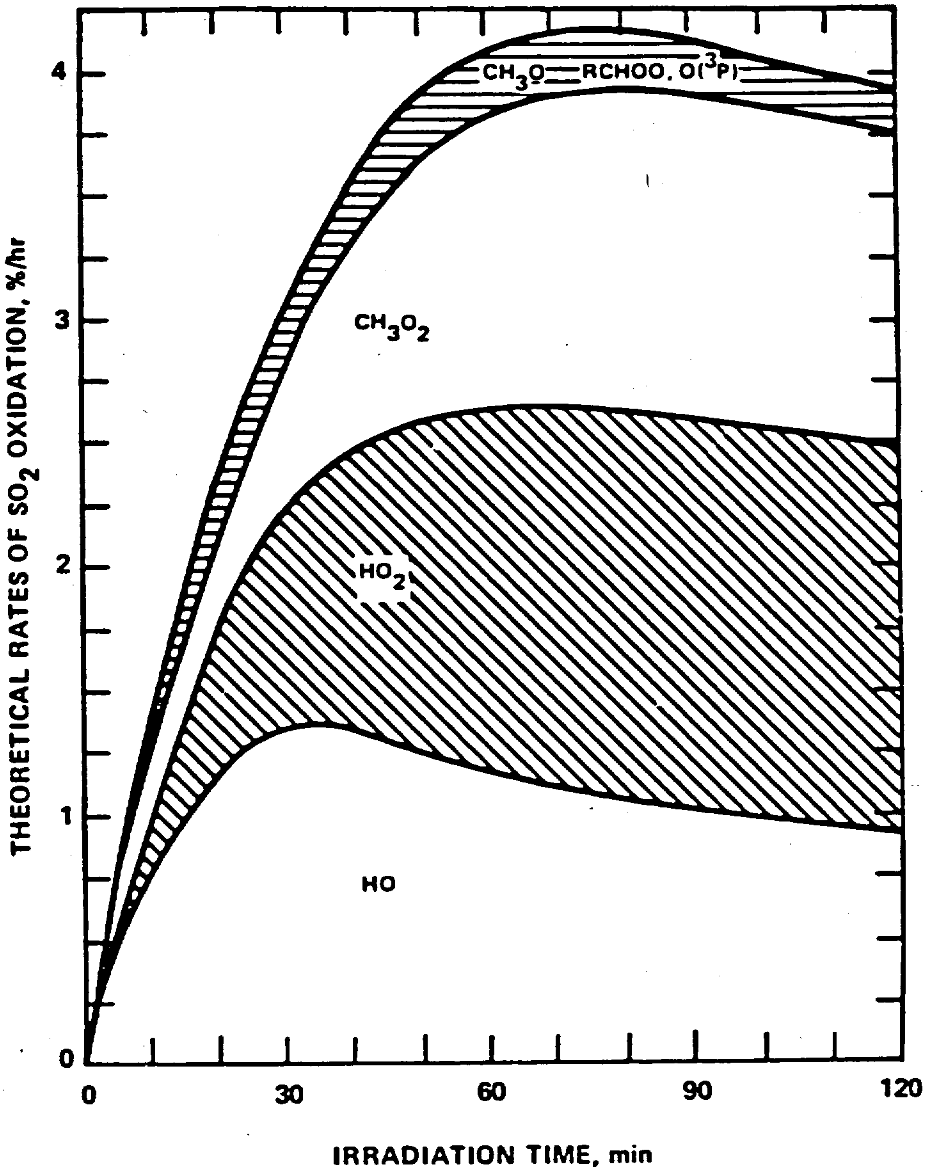


Figure 6. The theoretical rate of reaction (percent per hour) of various free-radical species with SO_2 is shown for a simulated sunlight-irradiated (solar zenith angle of 40°) polluted atmosphere. The initial concentrations (in ppm) were as follows: SO_2, 0.05; NO, 0.15; NO_2, 0.05; CO, 10; CH_4, 1.5; CH_2O, 0; CH_3CHO, 0. The relative humidity was 50 percent, and the temperature was 25° C.

Note: The rate constants for HO_2 and CH_3O_2 radical reactions with SO_2 are not well established. See Table VII and its discussion.

Source: Calvert et al. (1978).

1.5% h^{-1} and 4.0% h^{-1} for clean and polluted atmospheres, respectively, during July at mid-northern latitudes. The major difference in rates are a result of higher concentration levels of free radicals in the hydrocarbon rich polluted atmospheres. In a similar manner, Altshuller (1979) predicted the rates of homogeneous oxidation of sulfur dioxide to sulfate in the clean troposphere using concentration predictions of the pertinent free radicals from a two dimensional global model by Fishman and Crutzen (1978). A sample result from this study showing the latitudinal and seasonal dependence of the rate of SO_2 oxidation is presented in Figure 7; the variability in rate being predominantly due to availability of UV solar intensity which drives the free-radical production process. The solar radiation dependence of SO_2 conversion rate has also been observed in field measurements within power plants plumes (Husar et al., 1978), but should be viewed cautiously in light of the complicating factors introduced by the dispersion and local chemistry of the primary source emissions.

The most important impact on SO_2 homogeneous gas phase reactions has come from recent experimental determinations of the reaction rate constants of SO_2 with HO_2 (Graham et al., 1979; Burrows et al., 1979) and SO_2 with CH_3O_2 (Sander and Watson, 1981). As a result of these recent determinations, HO_2 and CH_3O_2 must be considered as questionable contributing sources to oxidation of SO_2 in the atmosphere. Therefore, in the theoretical estimates of SO_2 oxidation rates, by Calvert et al. (1978), and by Altshuller (1979), only the hydroxyl radical portion of the contribution is now accepted as established, in view of these recent experimental rate constant determinations. This results in maximum established SO_2 oxidation rates of the order of 1.5% h^{-1} for both clean and polluted atmosphere during July at midnorthern latitudes, a factor of 2.5 less than previous theoretical estimates for polluted atmospheres. The revised rate is equivalent to a diurnally averaged rate of the order 0.4% h^{-1}. Field measurements on the rates of SO_2 oxidation indicate that maximum SO_2 oxidation rates of the order of 10% h^{-1} are typical of many atmospheric pollution scenarios. Our present knowledge of homogeneous SO_2 gas-phase reactions does not sufficiently account for the rates observed. Smog chamber studies have demonstrated that some species other than HO radical oxidizes SO_2 (Kuhlman et al., 1978; McNelis et al., 1975). Alternate

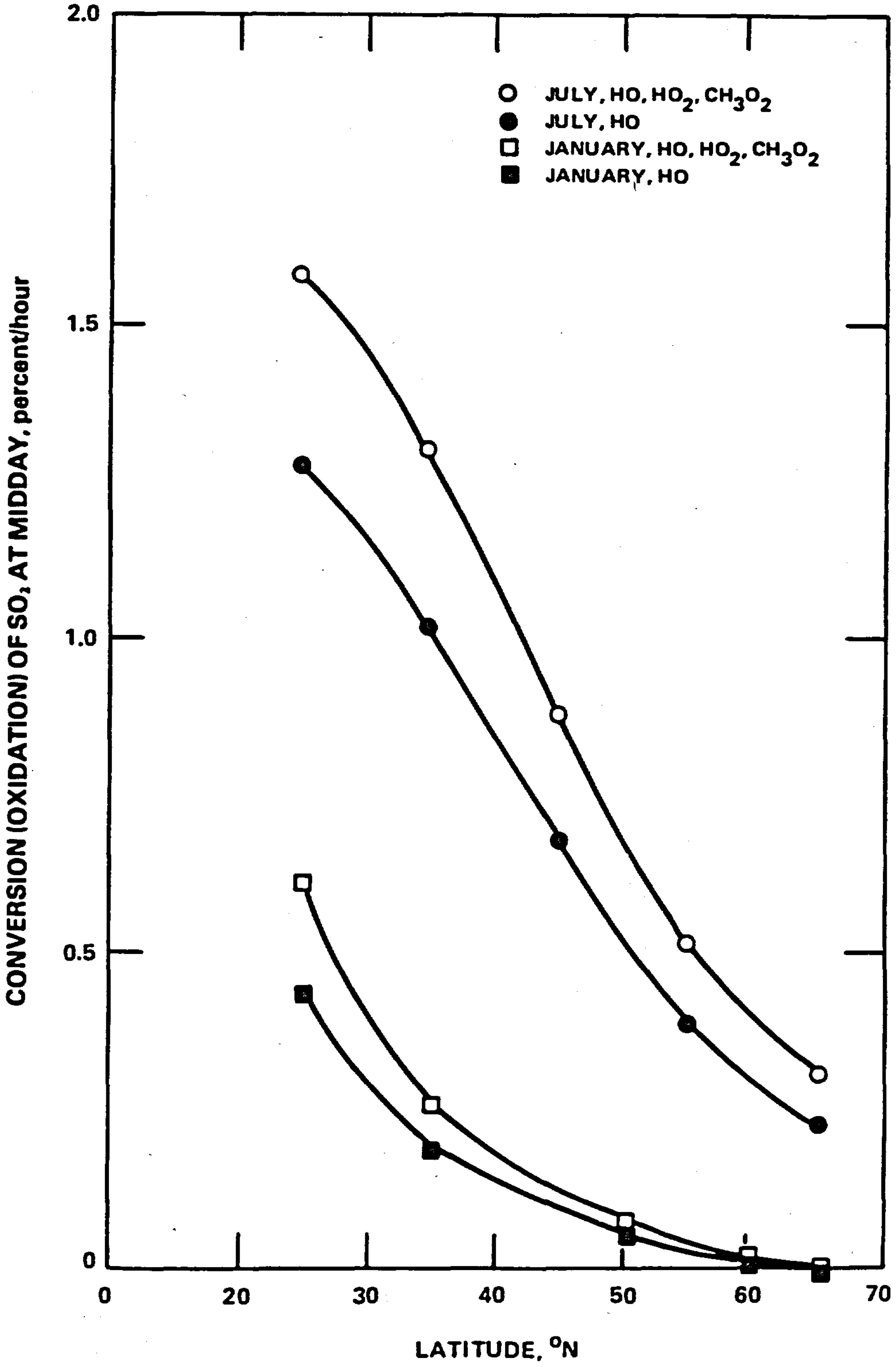


Figure 7. Percentage conversion at mid-day of sulfur dioxide to sulfate by HO and by HO, HO_2, and CH_3O_2 radicals as a function of degrees N latitude in summer and winter.

Source: Altshuller (1979).

homogeneous gas reaction oxidation pathways are being studied (Su et al., 1980), but certainly the role of heterogeneous and liquid phase SO_2 oxidation pathways should not be overlooked in attempts to resolve this discrepancy.

Summary. The status of our knowledge of SO_2 gas-phase oxidation in the troposphere is:

1. HO radicals appear to dominate the gas-phase oxidation of SO_2 in the clean trosophere. A typical rate is on the order of 1.5% h^{-1} at noon during July at mid-northern latitudes.

2. HO radical accounts for about 1.2% h^{-1} of the SO_2 oxidation in the polluted troposphere. The combined contribution of HO_2 and CH_3O_2 radical reactions may result in a greater oxidation rate of SO_2, but their rate constants are not well established.

Solution-Phase Chemical Reactions of Sulfur Dioxide

The knowledge of the reactions of the aqueous $SO_2 \cdot H_2O$-HSO_3^- and SO_3^{2-} system is important to understanding the processes of H_2SO_4 formation in tropospheric particles, mists, fogs and rain. This section reviews the oxidation reaction of dissolved SO_2 species, including the auto-oxidation, metal-ion catalyzed oxidation, carbon catalyzed oxidation, and reactions with the dissolved oxidants NO_2, O_3, and H_2O_2.

The state of knowledge of aqueous oxidation rates of dissolved SO_2, HSO_3^-, and SO_3^{2-} is inadequate for simple systems and is extremely poor (or non-existent) for complex systems that include dissolved nitrogen and carbon compounds. Unfortunately, most of the studies are not definitive because the investigators: (1) did not provide sufficient descriptions of experimental procedure (especially the purification of the water and reagents), (2) did not select a proper reactor design to eliminate mass transfer limitations, and (3) worked at concentration levels that were orders of magnitude greater than possible for ambient atmospheric aqueous systems. Trace quantities (at the part-per-billion level) of catalytic metal ions are capable of enhancing the reaction velocities by orders of magnitude over the auto-oxidation rate, while similar trace quantities of organics inhibit the rate. The characteristics of the chemical reactor govern the range of the half-life that can be investigated and may influence the observed rate of oxidation. Two-phase air-water reactors (e.g., bubblers and supported droplets) may have reaction characteristics that are dependent upon: (1) the mass transfer rate of the reactants through the air-water interface, and (2) the mixing rates within the gas and water phases (Carberry, 1976; Freiberg and Schwartz, 1981). Unless an adequate characterization of the two-phase reactor was performed, it is not recommended that the implied elementary rate constant be accepted. Supported droplets may suffer from an additional problem: radical chains are efficiently terminated at liquid-solid interfaces, thereby reducing the observed rate. Therefore, supported droplet measurements are not defensible unless it is established that the oxidation is not a free-radical mechanism. Notable reviews of the oxidation of dissolved SO_2 and its hydration products in simple systems have been published (Schroeter, 1963; Hegg and Hobbs, 1978).

This review will show that:

1. The auto-oxidation (uncatalyzed) reaction is very slow compared to the other reactions.
2. Mn(II) and Fe(III) are significant catalysts for the oxidation. The kinetic rate expression is in doubt for the Mn(II) reaction, but that for Fe(III) is in agreement among several independent investigators.
3. The catalytic effectiveness of these ions is unknown: Cu(II), V(V), V(IV), Ni(II), Zn(II), and Pb(II).
4. Elemental carbon (soot) with a water film is a potentially effective oxidation catalyst.
5. Dissolved HNO_2 and O_3 oxidation rates are known and appear to be too low to be effective.
6. The kinetics of the dissolved H_2O_2 oxidation of dissolved SO_2 species are known and appear to be effective for forming sulfate in particles, mists, fogs and rain.

The simple S(IV)-O_2 auto-oxidation has been the subject of numerous investigations, most of which are listed in Table VIII. The mechanism for the auto-oxidation is not firmly established. However, the behavior of the system is best explained as a modification to the scheme of Bäckström (1934), taking into account the recent results of Schmidkunz (1963) and Hayon et al. (1972):

Chain initiation,

$SO_3^{2-} + M+ \longrightarrow SO_3^- + M$ (78)

(M^+ = trace concentration of metal ion or reactive wall);

Chain propagation,

$SO_3^- + O_2 \longrightarrow SO_5^-$ (79)

$SO_5^- + SO_3^{2-} \longrightarrow SO_4^- + SO_4^{2-}$; (80)

Oxidation,

$SO_4^- + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_3^-$; (81)

Termination,

$SO_4^- +$ inhibitor $\longrightarrow$ (82)

radical + radical $\longrightarrow$. (83)

Brimblecombe and Spedding (1974b) propose an alternative scheme that does not include the SO_4^- radical-ion; in their scheme, equation (80) is replaced by:

$SO_5^- + SO_3^{2-} \longrightarrow SO_3^- + SO_5^{2-}$, (84)

$SO_5^{2+} + SO_3^{2-} \longrightarrow 2\ SO_4^{2-}$, (85)

and equation (82) is absent.

Hegg and Hobbs (1978) have discussed most of the investigations identified in Table VIII, and they summarized the rate expressions, rate constants, and important features of the studies. The observations can be classified into three types of rate expressions:

TABLE VIII. Investigations of SO_2-O_2 Aqueous Systems

Investigators	Type of System	Comment*
Bigelow (1898)	Bubbler	1,2,3
Titoff (1903)	Bulk	2,3
Lumiere and Seyewetz (1905)	Bulk	2,3
Milbaur and Pazourek (1921)	Bulk	2,3
Reinders and Vles (1925)	2-phase bulk	2,3
Haber and Wansbrough-Jones (1932)	Bulk	2,3
Vol'fkovick and Belopol'skii (1932)	Bulk	2,3
Backstrom (1934)	Theoretical	
Fuller and Crist (1941)	Bubbler	1
Riccoboni et al. (1949)	Bulk	2,3
Abel (1951)	Theoretical	
Winkelmann (1955)	Bulk	2
van den Heuvel and Mason (1963)	Supported droplet	1,3
Schroeter (1963)	Bubbler	1
Schwab and Strohmeyer (1965)	Bulk	2
Rand and Gale (1967)	Bulk	2,3
Scott and Hobbs (1967)	Theoretical	
McKay (1971)	Theoretical	
Miller and de Pena (1972)	Supported droplets	1
Brimblecombe and Spedding (1974a)	Bubbler	1
Beilke et al. (1975)	Supported droplet	1,3
Horike (1976)	Bubbler	1,3
Larson (1976)	Bubbler	1
Huss et al. (1978)	Bulk	1,3
Larson et al. (1978)	Bubbler	1

*1. Incompletely characterized 2-phase system; results may not be reliable.
2. Purity of water is uncertain; results cannot be considered to be reliable.
3. Rate expression not reported.

1. The type first reported by Fuller and Crist (1941),

$$\frac{d[SO_4{}^{2-}]}{dt} = (k_{86a} + k_{86b}[H^+])^{0\ 5}\ [SO_3{}^{2-}] \qquad (86)$$

2. The type first reported by Winkelmann (1955),

$$\frac{d[SO_4{}^{2-}]}{dt} = k_{87}\ [SO_3{}^{2-}] \qquad (87)$$

3. The type observed by Beilke et al. (1975)

$$\frac{d[SO_4{}^{2-}]}{dt} = k_{88}\ [H^+]^{-0.16}\ [SO_3{}^{2-}]. \qquad (88)$$

It is presently unresolved as to which type of rate expression is correct. Doubt is cast on "type 3" found by Beilke et al. (1975) because of the use of a plastic vessel that could have introduced trace organic inhibitors into the system. All of the other studies (yielding "types 1 and 2") were performed with two-phase systems whose mass transfer properties were insufficiently reported.

The auto-oxidation is inhibited by trace concentrations of organic species. The classes of organic species capable of serving as inhibitors include alcohols, glycols, aldehydes, ketones, phenols, amines, and acids. Bäckström (1934) first demonstrated that the inhibition of sulfite oxidation can be expressed as:

$$\frac{d\ [SO_4{}^{2-}]}{dt} = [A/(B + m)]\ k_{89}\ [SO_3{}^{2-}] \qquad (89)$$

where

k_{89} = the uninhibited rate constant,
A,B = constants that are functions of the inhibitor, and
m = molar concentration of the inhibitor.

The influence of inhibitors on the rate has been extensively studied by Schroeter (1963), and more recently by Altwicker (1979). According to Schroeter (1963), A and B are usually on the order of 10^{-5} molar, which means that inhibitor concentrations greater than 10^{-6} molar are effective. The form of the rate equation (Equation 89) suggests that the mechanism involves a bimolecular reaction between an inhibitor molecule and a radical in the chain.

In summary, our status of knowledge of the auto-oxidation reaction is:

1. The reaction is very slow.
2. The rate is extremely sensitive to the presence of catalysts and inhibitors.
3. The rate is first order in sulfite.
4. No reaction mechanism has been satisfactorily demonstrated to account completely for the observations of the more reliable studies (e.g., the dependence of the rate of $[H^+]^{0.5}$ found by Fuller and Crist, 1941 and by Larson et al., 1978).

It is well-established that some metal cations catalyze the oxidation of HSO_3 and SO_3^{2-}. Of particular interest to the issue of atmospheric sulfur formation in particles, mist, fog, and rain is possible catalytic activity of: Mn(II), Fe(III), Cu(II), Ni(II), and V(IV). General features of the catalyzed reaction include: (a) inhibition by oxidizable organic molecules, (b) inhibition by metal ion-complexing molecules (inorganic and organic), (c) exhibition of an induction time of several seconds to several minutes, (d) detection of metal ion-S(IV) complexes, (e) no dependence of rate on dissolved O_2 concentration, (f) dependence of the rate of the inverse of the initial H^+ concentration (i.e., the rate is independent of pH change <u>after</u> the reaction has been initiated). While the catalytic reaction mechanisms are unknown, they are thought to be a modification of the initiation step of the auto-oxidation free radical mechanism (Equations 78 through 83); instead of M^+ being a trace concentration ($<10^{-9}$ M) of metal ion or a reactive wall, it is a reagent present at concentrations $>10^{-6}$ M. The rate expressions for the various catalysts have different forms, suggesting different types of initiation mechanisms (e.g., simple redox reactions or the formation of stable, reactive complexes). The agreement between independent investigators is generally poor, indicating the likelihood of mass transfer limitations of the rate or the presence of contaminants. A large percentage of the investigations were conducted with two-phase reactors for which the mass transfer characteristics were not adequately reported; therefore, those results must be considered to be unreliable for estimating the elementary rate constant and for determining the reaction order. Also, the results for investigations using supported droplets may be biased due to radical chain termination at the liquid-solid interface.

The Mn(II) catalyzed reaction kinetics have been investigated for over 75 years. The studies pertinent to the formation of sulfate in the troposphere are present in Table IX. One of the first critics of Mn(II) catalysis studies was Titoff (1903), who remarked: "in Bigelow's (1898) work the reaction occurred between two phases, and the retardation could be determined by a change in the boundary layer or by a decrease in the solution rate of oxygen." Unfortunately, that comment applies to all but three of the Mn studies in Table IX, which are: Hoather and Goodeve (1934), Neytzell-de Wilde and Taverner (1958), and Coughanowr and Krause (1965). It is odd that each of these investigators did not present rate expressions and rate constants derived from their data, and instead left to the reader the task of extracting that information. Estimates of their rate expressions are presented in Table X. There is agreement that the Mn(II) catalyzed rate is independent of dissolved O_2, SO_2, HSO_3, and SO_3^{2-} concentrations.

Clearly, Hoather and Goodeve (1934) and Coughanowr and Krause (1965) are in good agreement. However, Neytzell-de Wilde and Taverner (1958) observed a first-order dependence on [Mn(II)]. There appears to be no basis to discount any of the three investigations, yet it appears that serious errors may have been made. There is a slight preference for the expression for the results of Neytzell-de Wilde and Taverner (1958) because: (1) they measured the rate of disappearance of S(IV) by direct chemical means, and (2) the period of observation (10-100 minutes) of the experimental runs were sufficiently long that it is reasonable that the rate of oxidation was measured after the establishment of the radial chains, and not during the induction period.

TABLE IX. Investigations of SO_2-Manganese-O_2 Aqueous Systems

Investigators	Type of System	Comment
Titoff (1903)	Bulk	2
Johnstone (1931)	Bubbler	1,2
Hoather and Goodeve (1934)	Bulk	2
Bassett and Parker (1951)	Bulk	2
Johnstone and Coughanowr (1958)	Supported droplet	1,2
Neytzell-de Wilde and Taverner (1958)	Bulk	2
Johnstone and Moll (1960)	Free droplets	2
Coughanowr and Krause (1965)	Bulk and flow	2
Bracewell and Gall (1967)	Bubbler	1
Matteson et al. (1969)	Free and supported droplets	3
Cheng et al. (1971)	Supported droplets	1

1. Incompletely characterized 2-phase system; results may not be reliable.
2. Rate expression not reported.
3. Results are biased due to continued reaction (supported) droplets on filter sampler; rate expression cannot be considered to be reliable.

TABLE X. Rate Expression for the Manganese-Catalyzed Oxidation

Expression[a,b,c]	pH	Investigators
$\frac{d[SO_4^{2-}]}{dt} = 44\ [Mn(II)]^{1.7}\ [S(IV)]^0\ [H^+]^0$	3,4	Adapted from Hoather Goodeve (1934)
$\frac{d[SO_4^{2-}]}{dt} = 1.7 \times 10^{-5}\ [Mn(II)]\ [S(IV)]\ [H^+]_0^{-1}$	2.2	Adapted from Neytzell-de Wilde and Traverner (1958)
$\frac{d[SO_4^{2-}]}{dt} = 8[Mn(II)]^2\ [S(IV)]^0$	3-4	Adapted from Coughanowr and Krause (1965); dependence on pH not reported

[a] The units are: liter, mole, second.

[b] Concentrations shown with zero power (e.g., $[S(IV)]^0$) indicate that the investigators found the rate to be independent of those species. Note that any concentration to the zero power is equal to unity.

[c] The term $[H^+]_0^{-1}$ indicates that the rate is dependent only on the inverse of the initial H^+ ion concentration; changes in H^+ concentration after the reaction is in progress do not affect the rate.

The Fe(III) catalyzed reaction studies that are pertinent to the formation of sulfate in the troposphere are identified in Table XI. The only studies not using two-phase systems (subject to mass transport limitations) are those of Neytzell-de Wilde and Taverner (1958), Karraker (1963), Brimblecombe and Spedding (1974a), and Fuzzi (1978). Hegg and Hobbs (1978) have pointed out that Karraker (1963) did not investigate the catalyzed oxidation in which dissolved O_2 is the oxidant, but instead the redox system associated with the couple $Fe(III) + e^- \rightarrow Fe(II)$ in an oxygen-free system. Thus, Karraker's work is not considered applicable. Neytzell-de Wilde and Taverner (1958) reported that the sulfate formation rate was second order for [S(IV)], but Karraker (1963) has reanalyzed their data and has shown instead that the order is unity. As noted for the Mn(II) system, Neytzell-de Wilde and Taverner (1958) did not present a rate expression and constant for the Fe(III) system; an estimate derived from their paper is presented in Table XII. Brimblecombe and Spedding (1974a) have reported a rate expression and constant measured at a constant pH = 4; unfortunately, they used a plastic reaction vessel, which could have released organic inhibitors into the system, causing the rate to be diminished. (At pH = 4, their rate is 0.25 of that of Neytzell-de Wilde and Taverner, 1958, and 0.1 of that of Fuzzi, 1978). Fuzzi (1978) did not note the similarity of his observations and those of Neytzell-de Wilde and Taverner (1958), especially the dependence of the rate on the <u>initial</u> inverse H^+ concentration for pH $\leq$ 4.0. Fuzzi's (1978) rate expression has been modified by incorporating the dependence on $[H^+]_0^{-1}$ and is presented in Table XII. Note that Fuzzi's (1978) modified rate constant is 2.5 times greater than that of Neytzell-de Wilde and Taverner (1958), which is good agreement for this type of measurement; these two studies appear to be the most definitive for the Fe(III) system, and there is no basis to prefer one over the other. Fuzzi (1978) has clearly demonstrated the change in kinetics is due to the formation of colloidal $Fe(OH)_3$ for pH >4, which provides an explanation for the disagreement among earlier investigators. Because of the formation of the $Fe(OH)_3$ colloid, it is unlikely that a meaningful Fe(III) catalyzed rate expression for use in tropospheric sulfate formation can be stated for conditions in which pH >4.

TABLE XI. Investigations of SO_2-Iron-O_2 Aqueous Systems

Investigators	Type of System	Comment
Reinders and Vles (1925)	Bulk	2
Basset and Parker (1931)	Bulk	2
Higgins and Marshall (1957)	Bulk	2
Johnstone and Coughanowr (1958)	Supported droplet	1
Junge and Ryan (1958)	Bubbler	1,2
Neytzell-de Wilde and Taverner (1958)	Bulk	2
Johnstone and Moll (1960)	Free droplets	2
Danilczuk and Swinarski (1961)	Bulk	2
Karraker (1963)	Bulk	3
Bracewell and Gall (1967)	Bubbler	1
Brimblecombe and Spedding (1974a)	Bubbler	1
Brimblecombe and Spedding (1974b)	Not reported	4
Freiberg (1974)	Theoretical	
Lunak and Veprek-Siska (1975)	Flow	5
Barrie and Georgii (1976)	Supported droplet	1
Fuzzi (1978)	Bulk	

1. Incompletely characterized 2-phase system; results may not be reliable.
2. Rate expression not reported.
3. O_2-free system; results not applicable to tropospheric SO_2 oxidation.
4. Insufficient details reported to determine if the results should be considered to be reliable.
5. Photochemical initiation.

TABLE XII. Rate Expression for the Iron-Catalyzed Oxidation

Expression[a,b]	pH	Investigators
$\frac{d[SO_4^{2-}]}{dt} = 0.04\ [Fe(III)]\ [S(IV)]\ [H^+]_0^{-1}$	2	Adapted from Neytzell-de Wilde and Taverner (1958)
$\frac{d[SO_4^{2-}]}{dt} = 100\ [Fe(III)]\ [S(IV)]$	4	Brimblecombe and Spedding (1974a)
$\frac{d[SO_4^{2-}]}{dt} = 0.1\ [Fe(III)]\ [S(IV)]\ [H^+]_0^{-1}$	≤ 4	Adapted from Fuzzi (1978)

[a] The units are: liter, mole, second.

[b] The term $[H^+]_0^{-1}$ indicates that the rate is dependent only on the inverse of the initial H^+ ion concentration; changes in H^+ concentration after the reaction is in progress do not affect the rate.

The Cu catalyzed reaction kinetics have been described in the early work of Titoff (1903). The pertinent investigations are identified in Table XIII. As with the Mn and Fe studies, most of the Cu studies were performed with incompletely characterized systems. Fuller and Crist (1941) point out that the prior work is unreliable because of the likely presence of contaminants. However, the investigations of Fuller and Crist (1941) were carried out in a two-phase reactor whose mass transfer characteristics are not completely described; no one has since conducted a study that is more definitive of this system. The reagent concentrations used by Barron and O'Hern (1966) are orders of magnitude too large, and the pH range (>8) used by Mishra and Srivastava (1976) is not applicable. For that reason, no rate expression can be recommended as reliable for use in calculating sufate formation rates due to Cu catalysis in the troposphere.

Vanadium catalysis has been reported in only one study (Bracewell and Gall, 1967); a bubble reactor was used, and its mass transfer characteristics were inadequately reported. Therefore, no rate expression can be recommended as reliable. However, Bracewell and Gall (1967) did observe qualitatively that V(V) was orders of magnitude less effective that Mn and Fe. Most likely, V(V) catalysis is unimportant for sulfate formation in the troposphere. Likewise, there are no definitive studies for Cr(III), Ni(II), Zn(II), and Pb(II), but it appears from the qualitative work of Bracewell and Gall that these catalytic reactions are unimportant.

Barrie and Georgii (1976) have demonstrated qualitatively that Mn(II) and Fe(III) exhibit a synergistic rate for the catalysis of S(IV) oxidation. Their rate expression may not be reliable since they used a supported droplet.

In summary, our status of knowledge of the homogeneous metal ion catalysis systems is:

1. S(IV) oxidation rates are significantly increased by Mn(II) and Fe(III). There is serious doubt regarding the rate expression for Mn(II), but the agreement among independent studies is much better for Fe(III).

TABLE XIII. Investigations of SO_2-Copper-O_2 Aqueous Systems

Investigators	Type of System	Comment
Titoff (1903)	Bulk	2
Reinders and Vles (1925)	Bulk	2
Alyea and Backstrom (1929)	Bulk	2
Johnstone (1931)	Bubbler	1
Albu and Grof von Schweinitz (1932)	Bulk	2
Fuller and Crist (1941)	Bubbler	1
Riccoboni et al. (1949)	Bulk	2
Basset and Parker (1951)	Bulk	2
Higgins and Marshall (1957)	Bulk	2
Johnstone and Coughanowr (1958)	Supported droplet	1
Junge and Ryan (1958)	Bubbler	1
Barron and O'Hern (1966)	Flow	
Bracewell and Gall (1967)	Bubbler	1
Cheng et al. (1971)	Supported droplet	1
Veprek-Siska and Lunak (1974)	Flow	2
Barrie and Georgii (1976)	Supported droplet	1
Huss et al. (1978)	Bulk	2
Mishra and Srivastava (1976)	Flow	

1. Incompletely characterized 2-phase system; results may not be reliable.
2. Rate expression not reported.

2. These systems are presently inadequately characterized: Cu(II), V(V), V(IV), Ni(II), Zn(II), and Pb(II).

3. There are no quantitative studies of metal ion-metal ion synergism.

4. The ability of atmospheric organic compounds to inhibit the catalysis is unknown.

5. All studies have been performed in the absence of HCO_3^-; however, the reactions

   $SO_4^- + HCO_3^- \longrightarrow HCO_3 + SO_4^{2-}$, and
   $OH + HCO_3^- \longrightarrow HCO_3 + OH^-$

   may be important. It is possible that such reactions may occur, and if so, they would prevent the oxidation radical chain from establishing since HCO_3 is not a powerful oxidizer (Hoigne and Bader, 1978).

6. In general, the rate expressions for catalytic oxidation to form sulfuric acid are not well-established.

The catalysis of the oxidation of dissolved SO_2 by carbon particles suspended in the water has been studied by Chang et al. (1979) and by Eatough et al. (1979). It was found by Chang et al. (1979) that the oxidation rate of dissolved SO_2 species was:

$$-\frac{d[S(IV)]}{dt} = k_{90}[C][O_2]^{0.69}[S(IV)]^0 \exp(-E_a RT^{-1}) \qquad (90)$$

with an activation energy of $E_a = 11.7$ kcal mol^{-1} over the pH range of 1.45 to 7.5 for the carbon studied, which was Nuchar-190. (The investigators demonstrated that Nuchar-190 behaved similarly to soot from acetylene and natural gas flames.) An average value of $k_{90} = 1.17 \times 10^5$ $mol^{0.3}$ $liter^{0.7}$ $g\text{-}sec^{-1}$ was reported. The kinetics have been interpreted in terms of the rate-limiting step being the formation of an activated complex between molecular oxygen and the carbon surface (Chang et al., 1979; Eatough et al., 1979).

Chang et al. (1979) have estimated that for 10 μg of their fine carbon soot suspended in 0.05 g of liquid water and dispersed in 1 m^3 of air, the atmospheric sulfate production would be 1 μg hr^{-1}. High-molecular weight hydrocarbons are adsorbed on the surfaces of atmospheric soots and may inhibit the carbon-surface catalyzed oxidation of dissolved SO_2. At this time, it remains to be demonstrated that the laboratory soots used by Chang et al. (1979) correspond to those present in the atmosphere or that the suspension of soot at ambient levels (<10 μg m^{-3}) in aerosols, cloud droplets or rain is similar to the laboratory system.

Hydrogen peroxide, ozone, and nitrogen dioxide may be important in the oxidation of SO_2 in aqueous aerosols and fogs. Although these compounds do not demonstrate high reactivity toward SO_2 in air, their reactivity is enhanced in the liquid phase. Again, caution is advised in accepting the results of studies of two-phase systems in which the investigators have not completely accounted for the possibility of the mass transport limitation of the oxidation rate. Therefore, only the recent results for single-phase systems are discussed here.

Martin et al. (1981) have used a stopped-flow reactor to investigate the kinetics of oxidation of aqueous SO_2 species by aqueous NO, NO_2^-, and NO_3^-. Over the pH range of 0.6 to 3.2, they found for NO and NO_3^- that the disappearance of S(IV) species is:

$$\frac{d[S(IV)]}{dt} = k_{91}\ [NO\ or\ NO_3^-][S(IV)] \qquad (91)$$

$$k_{91} = 0.01\ mole\ l^{-1}\ sec^{-1}.$$

However, for the same conditions, the reaction with NO_2^- is rapid and the formation of SO_4^{2-} can be expressed as:

$$\frac{d[SO_4^{2-}]}{dt} = k_{92}\ [H^+]^{0.5}\ [HNO_2 + NO_2]\ [SO_2 \cdot H_2O + HSO_3^-] \qquad (92)$$

$$k_{92} = 142\ (liter\ mole^{-1})^{1.5}\ sec^{-1}.$$

The NO_2^- is reduced quantitatively in this reaction to N_2O. Martin et al. (1981) also observed that this reaction is not catalyzed by Fe(III), Mn(II), or VO^{2+}. It is unlikely that tropospheric nitrous acid (HNO_2) concentrations are high enough for this reaction to be important for H_2SO_4 formation.

The oxidation of dissolved SO_2 by ozone has been investigated with stopped-flow systems. Penkett (1972) and Penkett et al. (1979) have interpreted their work in terms of a decomposition of ozone to initiate a free-radical chain reaction involving OH, HSO_3, and HSO_5 radicals, after Backstrom (1934). Penkett et al. (1979) suggested that the rate expression is

$$\frac{d[SO_4^{2-}]}{dt} \simeq k_{93}[HSO_3^-]\,[O_3]\,[H^+]^{-1} \qquad (93)$$

where k_{93} = 71 sec^{-1}. Erickson et al. (1977) reported the fractional contributions to the oxidation of the three sulfur oxide species by ozone at various pH values; their rate expressions are

$$\frac{d[SO_4^{2-}]}{dt} = k_{94}[SO_2\cdot H_2O][O_3], \qquad (94)$$

$$\frac{d[SO_4^{2-}]}{dt} = k_{95}[HSO_3^-][O_3], \qquad (95)$$

$$\frac{d[SO_4^{2-}]}{dt} = k_{96}[SO_3^{2-}][O_3], \qquad (96)$$

where k_{94} = 590 liter mol^{-1} sec^{-1}, k_{95} = 3.1×10^5 liter mol^{-1} sec^{-1}, and k_{96} = 2.2×10^9 liter mol^{-1} sec^{-1}.

Penkett et al. (1979) used a stopped-flow reactor to determine the kinetics of oxidation of dissolved SO_2 species by hydrogen peroxide. It was found that the rate of sulfate formation is given by

$$\frac{d[SO_4{}^{2-}]}{dt} = k_{97}[H_2O_2][HSO_3{}^-][H^+] + k_{97a}[H_2O_2][HSO_3{}^-][HA], \qquad (97)$$

where $k_{97} = 2.6 \times 10^7$ liter^2 mol^{-2}.sec^{-1}, with k_{97} and ka_{97a} being the third-order rate constants for the catalysis by free protons and proton-donating buffers (HA), respectively. At $pH \leq 4$, it is found that $k_{97}/ka_{97a} \geq 3200$. Therefore, the second term is probably not important for acid aerosols and fogs. It is of great significance that the reaction rate increases as the solution becomes more acidic, which is in contrast to aqueous oxidation by metal ions and by ozone. The activation energy and the effect of ionic strength on the reaction have been measured by Penkett et al. (1979). Dasgupta (1980) has criticized the presentation of Penkett et al. (1979); use of the rate expression (equation 97) takes into account Dasgapta's (1980) points. Martin and Damschen (1981) have found that

$$\frac{d[SO_4{}^{2-}]}{dt} = k_{98}[H_2O_2][SO_2\ H_2O]/(0.1 + [H^+]), \qquad (98)$$

where $k_{98} = 7.2 \times 10^4$ sec^{-1}; their expression is applicable over the range $0<pH<5$ and is in good agreement with Penkett et al. (1979).

In summary, our status of knowledge of the formation of H_2SO_4 by dissolved oxidants is:

1. The oxidation rates are known for NO and $NO_3{}^-$ and are too low to be important.
2. The oxidation rate is known for $NO_2{}^-$, but the tropospheric concentration of HNO_2 is probably too low for this reaction to be important.
3. The oxidation rate is known for O_3, but it is usually unimportant.
4. The oxidation rate for H_2O_2 is known and appears to be potentially a highly effective reaction for formation of H_2SO_4 in the troposphere. This rate could possibly be enhanced by metal ions, but no studies have been reported.
5. Organic oxidizers may be important, but no studies have been reported.

It has been recognized for several decades that NH_3 may influence the formation rate of H_2SO_4 in aqueous particles, mist, fog, and rain. Hegg and Hobbs (1978) have reviewed the studies of the NH_3 influence. They have called attention to a misunderstanding in the literature. NH_3 is commonly reported incorrectly to be a "positive catalyst" for the oxidation of dissolved SO_3. In the strict sense of the definition of "catalyst," the term cannot be applied to the role of NH_3. The observed enhancement by NH_3 of the oxidation rates of the auto-oxidation, metal-ion oxidation, and the O_3 oxidation is due to its action to raise and maintain a high pH. The following process occurs to raise and maintain a higher pH through the conversion of NH_3 to NH_4^+:

1. Ambient gaseous $NH_{3(g)}$ dissolves in the water,
   $NH_{3(g)} \Longleftrightarrow NH_{3(aq)}$.
2. The dissolved $NH_{3(aq)}$ reacts with H^+, which raises the pH,
   $NH_{3(aq)} + H^+ \Longleftrightarrow NH_4^+$.

Therefore, the ambient pathways of auto-oxidation, Mn(II)- and Fe(III)-catalyzed oxidation, and O_3 oxidation would have their rates enhanced by absorption of NH_3. However, the ambient pathway of HNO_2 would have its rate retarded by NH_3 absorption. The rates for H_2O_2 and for soot would not be modified.

NH_3 can play other important roles. Reinders and Vles (1925) observed qualitatively that Cu(II) was complexed by NH_3 and rendered non-catalytic. At high pH's (>9) such that $NH_{3(aq)}$ is the dominant form, NH_3 may be oxidized by O_3 and by free radicals (Hoigné and Bader, 1978). The role of NH_3 is explained in terms of its influence on the pH of the water system; NH_3 is not a catalyst.

Surface Chemical Reactions

Industrial emissions of solid particles (e.g., fly ash) and fugitive dust (e.g., windblown soil and minerals) provide a solid-surface that may chemisorb SO_2 and yield sulfate ions. The work reviewed in this section will include investigations of the SO_2 oxidation on the surfaces of: metal oxides, fly ash, charcoal, and soot. Although reaction kinetics have not been identified, two general types of processes have been: a capacity-limited reaction for SO_2 removal and a catalytic SO_2 oxidation process. The initial contact of SO_2 with the solid produces a rapid loss of SO_2 from the gas phase; the reaction rate decreases with time. For the capacity-limited reaction, the rate approaches zero; for the catalytic process, the rate levels off for a time and then approaches zero. The latter phenomenon is attributed to a pH decrease caused by sulfuric acid formation.

Urone et al. (1968) and Smith et al. (1969) found a number of solids to be effective in removing SO_2. In Urone's studies, SO_2 was admitted to a flask containing a powder that was allowed to react with no mixing, and the product and remaining SO_2 were determined. Only the average reaction rates can be calculated from these experiments; more importantly, with this experimental procedure the rates may be diffusion limited. The highest rate determined was for SO_2 with ferric oxide; the value was >75% min^{-1}. Other materials found to be slightly less reactive than ferric oxide were magnetite, lead oxide, lead dioxide, calcium oxide, and aluminum oxide. The rate for the ferric oxide experiment was for 20 mg of ferric oxide in a 2-liter flask, the ferric oxide concentration would thus be 10^7 $\mu g\ m^{-3}$. Assuming a direct proportionality between rate and particle concentration, the SO_2 removal rate in the atmosphere would be calculated to be 0.04% h^{-1} for 100 $\mu g\ m^{-3}$ of particles with the same reactivity as ferric oxide. However, since the mass transfer characteristics of the reactor were not reported, these results cannot be considered reliable for estimating rates.

Smith et al. (1969) did not focus on sulfate formation kinetics; instead, they illustrated through a novel experiment the ability of solid particles to absorb SO_2 and to release SO_2 during passage through a tube with a wall that absorbs SO_2. They measured the number of SO_2 monolayers absorbed on suspended Fe_3O_4 as function of SO_2 partial pressure. (The monolayer coverage data reported in their Table I are in error by a factor of 100 too large; e.g., the number of monolayers at 1.13 ppm should be 0.38×10^{-2}.)

Chun and Quon (1973) measured the reactivity of ferric oxide to SO_2, using a flow system involving a filter containing suspended particles. They determined a removal rate constant of 9.4×10^{-3} ppm^{-1} min^{-1} [$-d(\ln\theta)dt$], where θ is the fraction of surface sites available for reaction. Extrapolating this to an atmospheric particle concentration of 100 $\mu g\ m^{-3}$ with an equivalent reactivity and an SO_2 concentration of 0.1 ppm, the data project an atmospheric removal rate of 0.1% h^{-1}.

Stevens et al. (1978) report total iron concentrations in six U.S. cities ranging between 0.5 and 1.3 $\mu g\ m^{-3}$. Other species such as manganese, copper, or vanadium had total concentrations usually below 0.1 $\mu g\ m^{-3}$. Thus actual ambient air concentrations are a factor of approximately 50 times less than that assumed by the authors in the above papers. A reactive particle concentration of 2 $\mu g\ m^{-3}$ would yield a predicted SO_2 removal rate of no more than 0.002% h^{-1}. Therefore, surface reactions are probably not important except in sources prior to or immediately after emission.

The most comprehensive study to date on SO_2 removal by pure solids was made by Judeikis (1974) and Judeikis et al. (1978), who used a tubular flow reactor in which solids were supported on an axial cylinder to measure reactivities of MgO, Fe_2O_3, Al_2O_3, MnO_2, PbO, NaCl, charcoal, and fly ash. They found that the rates of SO_2 removal diminished with exposure until the solids completely lost ability to react with SO_2. The relative humidity was important in determining the total capacity for SO_2 removal, but not the initial rate of uptake; total capacity increased as relative humidity increased. The capacity for SO_2 could be extended by exposure to NH_3. This type of behavior is consistent with the formation of H_2SO_4 on the surfaces.

Because of the ubiquitous nature of carbonaceous matter in ambient air particulate samples, various workers have studied the SO_2 removal rate by carbon. A comparison of the results is rather difficult because of the varieties of carbon available for study, such as activated charcoal, graphite, acetylene flame products, and combustion products of diesel oil and heating oil. We cite here a few investigations that deal with the gas-solid reaction of SO_2 with carbon.

Novakov et al. (1974) performed laboratory experiments that showed that graphite and soot particles oxidize SO_2 in air. The soot exposed to humidified air produced more SO_4^{2-} than that exposed only to dry air. They also observed for downtown Los Angeles a strong correlation between the concentration of ambient carbon and SO_4^{2-} formation.

Tartarelli et al. (1978) studied the interaction of SO_2 with carbonaceous particles collected from the flue ducts of oil burning power stations. They concluded that the amount of adsorption is increased by the presence of oxygen and water in the gas stream. Reaction rates were not determined in this study.

Liberti et al. (1978) studied the adsorption and oxidation of SO_2 on various particles, including soot from an oil furnace and various atmospheric particulate samples. They concluded that the main interaction between the SO_2 and particulate matter is adsorption, with most catalytic reactions occurring at high temperatures, near the combustion source. Their experiments with atmospheric particulate samples lead them to the conclusion that any heterogeneous nonphotochemical sulfate formation is strongly dependent on the reactivity of the particle surface, and hence the history (aged, freshly emitted), of the aerosol.

In summary, the status of our knowledge of surface reactions is:

1. The reactions are capacity-limited. Those that involve catalysis in liquid films can be extended by the absorption of NH_3.
2. The initial rates may be large, but quickly approach zero.
3. Except for the carbon (soot) reaction, solid surface reactions do not appear to be effective pathways for H_2SO_4 formation in the troposphere.

Estimates of SO_2 Oxidation

The important reactions for gas-phase and aqueous-phase oxidation are listed in Table XIV, and rates of SO_2 oxidation for an assumed set of conditions are present. These calculations ignore the nonhomogeneous nature of the troposphere and assume that all of the reactants are well mixed.

TABLE XIV. Estimates of SO_2 Oxidation Rates in a Well-Mixed Troposphere

	Reaction	Rate, % h^{-1}			Comments*
I.	Gas Phase				
	HO radical	0.3 - 1.3			1
	HO_2 radical	0.4 - 2.0			1,2
	CH_3O_2 radical	0.3 - 1.5			1,2
II.	Aqueous Phase pH =	1	2	3	
	Mn(II) catalysis	1E-1	1E+1	1E+3	2,3,4
	Fe(III) catalysis	5E-5	5E-1	5E+3	3,5
	C (soot) catalysis	3E+1	3E+1	3E+1	6
	O_3 (40 ppb)	2E-8	2E-6	2E-4	3,7
	O_3 (120 ppb)	6E-8	6E-6	6E-4	3,7
	H_2O_2 (1 ppb)	2E-2	3E-2	3E-2	3,8
	H_2O_2 (10 ppb)	2E-1	2E-1	3E-1	3,8

NOTE: "E" denotes "exponential to the base 10;" e.g., 3E-1 = 3×10^{-1}.

*1. Typical range for daytime at northern midlatitudes during the summer.

2. This reaction rate is not well established; see discussion section.

3. Assumed that liquid water volume of aerosol = 50×10^{-12} m^3 m^{-3}, $[SO_2]_g$ = 10 ppb (or 27 μg m^{-3}).

4. Assumed that Mn(II) mass concentration = 20 ng m^{-3}; also, the Mn(II) is assumed to be uniformly dissolved in the liquid water of the aerosol [Mn(II)] = 8.9×10^{-3} M). Rate calculation used the expression of Neytzell-de Wilde and Taverner (1958)(see Table X).

5. Assumed that Fe(III) mass concentration = 2 μg m^{-3}; also, the Fe(III) is assumed to be uniformly dissolved in the liquid water of the aerosol ([Fe(III)] = 0.9 M). Rate calculation used the expression of Neytzell-de Wilde and Taverner (1958); see Table XII.

6. Assumed that C mass concentration = 10 μg m^{-3} and behaves as the soot studied by Chang et al. (1979), whose expression was used for this calculation (Equation 90).

7. Rate calculation was based on Equation 93.

8. Rate calculation was based on Equation 97.

For this comparison, it has been assumed that the SO_2 concentration is 10 ppb for all of the reactions, and that the liquid water content of the aerosol is 50×10^{-12} m^3 m^{-3}.

The gas-phase rates and the aqueous-phase rates have been calculated based on the discussion material presented in this review without regard to several of the assumptions made without any basis, namely:

1. The ambient mass concentration of 20 ng m^{-3} for Mn is reasonable, but: (a) it is not known if the predominant form is Mn(II), and (b) it is unlikely that Mn is uniformly distributed and dissolved.

2. Likewise, the ambient concentration of 2 μg m^{-3} for Fe is reasonable, but: (a) it is not known if Fe(III) is the predominant form, and (b) it is unlikely that Fe is uniformly distributed and dissolved.

3. There is no basis to assume that the rate equation observed for laboratory-generated carbon (soot) applies to atmospheric carbon.

4. The rates for the HO_2 and CH_3O_2 reactions recommended by Calvert et al. (1978) are not well established.

It is very likely that the atmospheric SO_2 oxidation rates estimated for Mn(II) catalysis, Fe(III) catalysis, and C (soot) catalysis are gross over-estimates. Also, the HO_2 and CH_3O_2 rates may be too high.

Uncritical acceptance of all of the rates, at a pH = 3 and $[H_2O_2]$ = 10 ppb, would lead to the SO_2 conversion rate exceeding 40% h^{-1}. However, if only the well-established rates are considered, the SO_2 conversion rate becomes <1.1% h^{-1}.

Field Measurements of the Rate of SO_2 Oxidation

The majority of SO_2 oxidation studies in the atmosphere have been only carried out in recent years and of those, most have involved power plant plumes. One reason for the late start in this research area has been the lack of adequate measurement technology for particulate sulfur, but recent developments (Huntzicker et al., 1978; Cobourn et al., 1978) seem to have alleviated this problem. A summary of SO_2 oxidation rates based on field measurements in power plant, smelter and urban plume studies carried out from 1975 to the present is given in Table XV. The rates of SO_2 oxidation in industrial plant plumes consistently range from 0 to 10% h^{-1}, with urban plumes showing only a slightly greater maximum rate of 13% h^{-1}. The pre-1975 studies (Gartrell et al., 1963; Dennis et al., 1969; Weber, 1970; Stephens and McCalden, 1971), which observed conversion rates an order of magnitude larger than more recent observations, must be considered suspect due to possible artifact formations in the sulfate analysis technique and limitations in the analytical methods in general.

Newman (1980) recently reviewed the majority of the power plant and smelter plume studies presented in Table XV and arrived at the following conclusions.

1. The diurnal average oxidation rate of sulfur dioxide to sulfate is probably less than 1% h^{-1}.

2. Little or no oxidation of sulfur dioxide occurs from early evening through to early morning.

3. Maximum oxidation rates of sulfur dioxide to sulfate of 3% h^{-1} can occur under midday conditions.

4. The contribution of homogeneous and heteorogeneous mechanisms to sulfur dioxide oxidation in plumes cannot be elucidated from the present studies.

It should be noted that the reported SO_2 oxidation rates are estimates based on analyses of measured physical and chemical parameters and in many instances have incorporated within them certain simplifying assumptions which are not totally substantiated. Typically uncertainties in reported values are 50%, but may be greater if inappropriate assumptions have been used. Even with these uncertainties in mind, the overall consistency in the observed range of SO_2 oxidation rates is gratifying.

TABLE XV. Field Measurements on the Rates of SO_2 Oxidation in Plumes*

Plume Type Location	SO_2 Oxidation Rate (% h^{-1})	Method	Reference
Power Plant			
Keystone (Pennsylvania)	0-10	$^{32}S/^{34}S$ ratio, change with oxidation	Newman et al. (1975)
Labadie (Missouri)	0.41-4.9	Total change in particle volume	Cantrell and Whitby (1978)
Four Corners (New Mexico)	0.27-0.84	Sub-micron sulfate and SO_2 - change of ration with time	Ursenbach et al. (1977)
Labadie and Portage des Sioux (Missouri)			
Muscle Shoals (Alabama)	0-5	Particulate sulfur to total sulfur ratio	Forrest and Newman (1977a)
Kyger Creek (Ohio)			
Labadie (Missouri)	0-3	Particulate sulfur to total sulfur ratio	Gillani et al. (1978)
Four Corners (New Mexico)	2-8	CCN production (CCN to SO_2 ratios)	Pueschel and Van Valin (1978)
Labadie (Missouri)	0-4	Particulate sulfur to total sulfur ratio	Husar et al. (1978)
Cumberland (Tennessee)	0-7	Particulate sulfur to total sulfur ratio	Meagher et al. (1978)
Great Canadian Oil Sands (Alberta, Canada)	0-3	Particulate sulfur to total sulfur ratio	Lusis et al. (1978)
Keystone (Pennsylvania)	0-5	Particulate sulfur to total sulfur ratio	Dittenhoefer and dePena (1978)

TABLE XV. (cont.)

Plume Type Location	SO_2 Oxidation Rate (% h^{-1})	Method	Reference
Central (Washington) Four Corners (New Mexico)	0-6	Total change in particle volume	Hobbs et al. (1979)
Four Corners (New Mexico)	0.15-0.5	CCN production (CCN to SO_2 ratios)	Mamane and Pueschel (1980)
Leland-Olds (North Dakota) Sherburne County (Minnesota) Big Brown (Texas)	0-5.7	Total change in particle volume	Hegg and Hobbs (1980)
<u>Smelter</u>			
INCO Nickel (Copper Cliff, Canada)	0-7	Particulate sulfur to total sulfur ratio	Lusis and Wiebe (1976)
INCO Nickel (Copper Cliff, Canada)	1.2-5.2	Particulate sulfur to total sulfur rates	Forrest and Newman (1977b)
INCO Nickel (Copper Cliff, Canada)	<0.5	Particulate sulfur to total sulfur rates	Chan et al. (1980)
Mt. Isa Mines (MT. ISA, Australia)	0.25†	Particulate sulfur to total sulfur ratio	Roberts and Williams (1979)
<u>Urban</u>			
Los Angeles (California)	1.2-13	Particulate sulfur to total sulfur ratio	Roberts and Friedlander (1975)
St. Louis (Missouri)	7-12.5	Particulate sulfur to total sulfur ratio	Alkezweeny and Powell (1977)
St. Louis (Missouri)	3.6-4.2	Particulate sulfur to total sulfur ratio	Chang (1979)

*Adapted in part from Hegg and Hobbs (1980).
†Diurnal average rate.

SURVEY OF CHEMICAL MODULES

The objective of this section is to provide a brief review of the chemical schemes that have been used to predict the transformation of sulfur and nitrogen oxides in the atmosphere to sulfates and nitrates. The review is not intended to be all encompassing or to furnish a critical assessment of each model, but rather to give the reader an indication of what has been done since the mid-1970s when attempts at regional scale and long-range transport modeling began. Many of the available models are predicated on the photochemical smog mechanism cycle, which has a much longer history of development than the regional scale models. This will become more apparent to the reader in the subsequent discussions. Table XVI summarizes in a succinct fashion the chemical transformation models for SO_2 and NO_x.

Basically two approaches to transformation modeling have been used in the past. They are a fundamental approach and an empirical approach.

Fundamental Approach

The fundamental approach consists of explicit mechanisms that involve detailed considerations of the important reactants, their final products, and possible intermediate and/or transient species. This approach has been applied to the hydrocarbon/NO_x system leading to oxidant formation. The number of chemical reactants and equations can be very large, thus creating problems in computer time. Various workers have attempted to consolidate and simplify the HC/NO_x system in order to conserve computer storage space and running time without sacrificing basic results.

One of the earliest attempts at smog chemistry simulation was by Demerjian et al. (1974). The authors included over 200 species (compounds and radical intermediates) in the model. Many of the compounds were specific reactive hydrocarbons. Despite the explicit nature of their approach the authors cautioned that their model might be an oversimplification of the real world situation. Still, one might expect the Demerjian approach might be too complicated for a regional scale model. Various attempts at condensing or lumping hydrocarbon classes or species have been made since 1974. Graedel

TABLE XVI. Summary of SO_2 and NO_x Transformation Models

		Validation/Testing			
			Field study		
Investigator/Yr.	Model approach	Smog chamber	Urban	Power plant	Comments
Demerjian et al. (1974)	Fundamental, 200 individual species				No sulfur chemistry HC/NO_x - O_3
Graedel et al. (1976)	Fundamental, C_3H_6 as surrogate	X	X		Includes S,H,N,O chemistry
Miller (1978)	Uses NMHC meas. as representative Fundamental	X			
Hov et al. (1977)	Fundamental, lumped mech. uses	X			Uses xylene for aromatics No S chemistry
Hecht et al. (1974)	Fundamental, lumped mech.	X			HC/NO_x photochemistry Grouping by reactivity
Whitten, Hogo (1980)	Fundamental, carbon bond mech. Lumped by bonding of C atom	X			No sulfur chemistry
Rodhe et al. (1981)	A long-range transport model with photochemistry and aqueous phase rxn		Validated against European precipitation data.		Includes gas phase SO_2 + NO_2 oxid. and liq. phase SO_2 oxidation
Clark et al. (1976)	Empirical for HC/NO_x	X	X		Used ambient air sampled near freeway
Miller (1978)	Empirical for HC/NO_x and SO_2 ox.	X			

(continued)

TABLE XVI. Summary of SO_2 and NO_x Transformation Models (cont.)

		Validation/Testing			
			Field study		
Investigator/Yr.	Model approach	Smog chamber	Urban	Power plant	Comments
Penkett et al. (1979)	Empirical, based on samples				SO_2 ox. in rainwater
Gillani et al. (1978)	Empirical			X	Related met. and chem.
Hegg and Hobbs (1980)	Empirical			X	Related gas phase chem. and solar intensity
Eltgroth and Hobbs (1979)	Fundamental for HC/NO_x chem. Empirical for SO_2			X	Gas phase and one heterog. rxn (soot)
Meagher and Luria (1979)	Fundamental for HC/NO_x chem. Gas phase SO_2 ox.			X	Used carbon bond mech. to generate radicals for gas phase SO_2 rxn
Altshuller (1979)	Fundamental		Tropospheric according to latitude		2 D global model Only considered 3 gas phase SO_2 rxns
Hov and Isaksen (1981)	Fundamental mech. for H_2SO_4 and HNO_3; 85 species, 200 rxns considered	X		X	Validation of HNO_3 using smog chamber data, H_2SO_4 using power plant data

(continued)

TABLE XVI. Summary of SO_2 and NO_x Transformation Models (cont.)

		Validation/Testing			
			Field study		
Investigator/Yr.	Model approach	Smog chamber	Urban	Power plant	Comments
Bassett et al. (1981)	Fundamental, uses liq. phase ox. of SO_2 by Mn; assumes first order SO_2 gas phase ox. Generates aerosol size distribution and sulfate mass				Generalized for "average" power plant plumes
Middleton et al. (1978, 1979, 1980)	Fundamental in considering gas phase and liq. phase SO_2 ox. Uses first-order SO_2 gas phase rxn		X Used typical urban values from various cited studies		Only SO_2 + OH rxn considered in gas phase

et al. (1976) used a single compound, propylene, as a surrogate for all nonmethane hydrocarbons. The chemical set utilizes 143 reactions for 76 species. In addition to O-H-N and hydrocarbon reaction subsets, the authors include a sulfur chemistry subset of 19 reactions leading to H_2SO_4 formation through homogeneous gas phase oxidation. Twenty-four hour simulations were performed and compared with urban data from three New Jersey counties.

Miller (1978) used NMHC as a surrogate for individual hydrocarbons. A generalized mechanism in which the SO_2 reacts with $\cdot OH$, $HO_2\cdot$, and $RO_2\cdot$ predominantly to form sulfate aerosol was used and tested against Battelle-Columbus smog chamber data. Hov et al. (1977) included aromatics, using xylene as a surrogate, in their HC/NO_x mechanistic approach and used European urban data to test the model.

In the past eight years two lumped approaches for the HC/NO_x system have been reported. The HSD (Hecht, Seinfeld and Dodge, 1974) and the carbon bond mechanism (Whitten et al., 1980) both group individual compounds according to some common property. In the case of HSD organic compounds of similar reactivity are grouped together into four classes, paraffins, olefins, aldehydes and aromatics. In the CBM method similarly bonded carbon atoms are grouped into four classes. The CBM is probably closer to the explicit mechanism than the HSD, although both require significant computer time. It should be pointed out here that a mechanism that includes N species will require 2N first order, nonlinear, ordinary differential equations to be solved simultaneously for each time increment so as to evaluate the changing concentrations of the species. Various mathematical methods have been used for this, but the subject is outside the scope of this subsection.

To conclude the discussion on explicit mechanisms we cite two for different reasons. The Rodhe et al. (1981) paper is mentioned, because, to the best of our knowledge, it is the only published attempt at modeling long-range transport that involves an explicit chemical mechanism; Bottenheim and Strausz (1982) is cited because it is a realistic attempt at modeling a chemically reactive plume and incorporates the current thinking on rate constants, important radical species, etc.

Rodhe et al. used a simple photochemical box model (see below) to simulate sulfuric and nitric acid formation during long-range transport. The model generates HNO_3 through the NO_2 + OH reaction and H_2SO_4 through the SO_2/hydroxyl radical reaction. In addition the authors include a liquid phase (116) reaction for SO_2. They note the uncertainties in reaction rates and exchange rates between gases and droplets and selected a rate constant that would result in comparable gas and liquid phase SO_2 transformations for reasonable summertime hydroxyl radical concentrations. The model results are compared to nitrate and sulfate rainwater data from the European Air Chemistry Networks. The authors point out the uncertainties in their model assumptions andin the available data base and attempt model validation based on relative NO_3^- and SO_4^{2-} values. The authors conclude by noting that most present models assume constant transformation rates, which do not allow estimates for long term trends. They encourage inclusion of species such as OH, H_2O_2 and O_3 in future modeling exercises.

Rodhe-Crutzen-Vanderpol LRT Model contains these reactions:

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \tag{98}$$
$$O(^1D) + M \rightarrow O + M \tag{99}$$
$$O(^1D) + H_2O \rightarrow 2OH \tag{100}$$
$$CO + OH \rightarrow\!\!\longrightarrow HO_2 + CO_2 \tag{101}$$
$$CH_4 + OH \rightarrow\!\!\longrightarrow CH_2O + HO_2 \tag{102}$$
$$C_2H_6 + OH \rightarrow\!\!\longrightarrow HO_2 + 2CH_2O \tag{103}$$
$$CH_2O + OH \rightarrow\!\!\longrightarrow CO + HO_2 \tag{104}$$
$$CH_2O + h\nu \rightarrow\!\!\longrightarrow CO + 2HO_2 \tag{105}$$
$$CH_2O + h\nu \rightarrow\!\!\longrightarrow CO + H_2 \tag{106}$$
$$2HO_2 \rightarrow H_2O_2 + O_2 \tag{107}$$
$$HO_2 + OH \rightarrow H_2O + O_2 \tag{108}$$
$$H_2O_2 + OH \rightarrow HO_2 + H_2O \tag{109}$$
$$H_2O_2 + h\nu \rightarrow 2OH \tag{110}$$
$$NO_2 + h\nu \rightarrow NO + O \tag{111}$$
$$NO + O_3 \rightarrow NO_2 + O_2 \tag{112}$$
$$NO + HO_2 \rightarrow OH + NO_2 \tag{113}$$
$$NO_2 + OH \rightarrow HNO_3 \tag{114}$$
$$SO_2 + OH \rightarrow\!\!\longrightarrow H_2SO_4 \tag{115}$$
$$\text{"}SO_2 + H_2O_2 + \text{CLOUD} \rightarrow H_2SO_4\text{"} \tag{116}$$

While the R-C-V LRT model is useful for demonstrating the influence of non-linearity on acid formation and removal rates, it possesses serious deficiencies that limit its usefulness for assessment applications. Specifically, its major deficiencies are:

a. the use of ethylene as a surrogate for VOC in polluted atmospheres is not sufficient to represent the variety of reactive VOC present in polluted atmospheres;

b. the chemical mechanism does not provide an adequate representation of VOC-NO_x oxidation cycle as presently understood for polluted atmospheres; and

c. the representation of diffusion and deposition in the model may introduce unrealistic conditions that affect the chemistry in ways that are not representative of the real atmosphere.

Bottenheim and Strausz (1982) developed a chemically reactive plume model that describes the homogeneous gas phase chemistry of an SO_2-NO_x containing plume interacting with a background air that includes reactive hydrocarbons. The lumping approach for the hydrocarbons is a combination of the carbon bond mechanism, the SCHEME approach of Levine and Schwartz, and the mechanism for LIRAQ by Gelinas and Skewes-Cox in 1977. The resulting mechanism (38 reactions) was tested against smog chamber data before attempting to model power plant plume data. The authors assumed first order kinetics for the SO_2 oxidation rate and their predictions were within a factor of 2 of the observed values for approximately 4 hours plume travel time.

To summarize the preceding discussion, the explicit mechanisms include rather complicated and extensive reactions leading to HNO_3 formation and generally approach H_2SO_4 formation through three possible reactions: $SO_2 + OH$, $SO_2 + HO_2$ and $SO_2 + CH_3O_2$, all being gas phase processes. Only the Rodhe-Crutzen-Vanderpol model has been developed with the intent of modeling long-range transport.

Empirical or Parameterized Approach

In general this approach has been based on fitting an equation or equations to actual observed field data. They are often not chemical transformation modules, per se, but rather include parameters (both chemical and meteorological) that are thought to influence the SO_2 oxidation rate. Parameterization of the conversion rate usually involves a simple rate expression, which can then be used in regional models. A particularly attractive feature is relatively little computational time in contrast to the previously discussed explicit mechanisms. A possible weakness is that they have been based on particular source or environmental conditions. Still, successes have been reported in this technique and will be so noted in the discussion.

The rate of sulfate formation has been shown to be linearly related to SO_2 concentration by various workers. That is, the expression

$$\frac{d[SO_4^{2-}]}{dt} = K_{117}[SO_2] \qquad (117)$$

was found to fit the apparent sulfate formation rate for a variety of urban and power plant plume field studies.

Clark et al. (1976) collected ambient air samples near a freeway and performed smog chamber runs with the samples using real sunlight. SO_2 was added to the chamber and the aerosol formation rate followed. The sulfate formation rate was found to be directly proportional to the initial SO_2 and NMHC concentrations. SO_2 concentrations were varied between 10 to 70 ppb and NMHC ranged from 0.5 to 2.0 ppm. Irradiation times were approximately 2 hours. The authors noted a deviation from linearity as the reaction time progressed.

Miller (1976) using smog chamber data noted little effect of the initial NMHC/NO_x for the sulfate formation rate. Irradiation times for the runs were 4 to 6 hours.

In contrast to the above parameterizations for gas phase SO_2 oxidation, Penkett et al. (1979) have parameterized aqueous-phase SO_2 oxidation by O_3 and H_2O_2. Observed and calculated values for atmospheric concentrations led the authors to conclude that sulfate formation followed the equation:

$$\frac{d[SO_4^{2-}]}{dt} = k_{118}[OX][S(IV)] \qquad (118)$$

where K_{118} is a second order rate constant and

[OX] and [S(IV)] are concentrations of oxidant and unoxidized sulfur present in the solution. The pH range considered was 4 to 7. They conclude that droplet oxidation processes can be important in the atmospheric chemistry of sulfur dioxide and needs to be included in modeling efforts.

In contrast to attempts at parameterization via chemical concentrations, etc., various workers have used meteorological parameters as indicators for SO_2 oxidation. Gillani et al. (1981 and references listed therein) have attempted parameterization of the SO_2 oxidation rate using different meteorological factors. Initially a sunlight dependent model of the form $K_{117} \propto R_T$, total incoming solar radiation flux at ground level, was used in a diagnostic mesoscale plume model. They found that their model would not simulate day to day variations in sulfate formation. The 1981 reference includes a more complicated parameterization involving sunlight, ozone concentration, and mixing height. The authors note that agreement with multi-day transport simulations improved significantly. They point out that their model does not include parameterizations for heterogeneous or liquid phase processes, because it was validated against summertime power plant plume field study data. One would expect homogeneous gas phase oxidation to predominate in such a situation.

Another attempt at meteorological parameterization has been done by Hegg and Hobbs (1980). They also consider homogeneous gas phase oxidation as the predominant pathway and relate hydroxyl radical concentration by the expression

$$[HO] \propto \frac{(90-z)[uv][O_3][H_2O]}{[CO]} \tag{119}$$

where z is the zenith angle and [uv] is the intensity of ultraviolet sunlight. Then they compute the SO_2 oxidation rate by

$$-\frac{d[SO_2]}{dt} \propto \frac{[HO][SO_2]}{[NO_2]} \tag{120}$$

An even more complex attempt at parameterization was done by Eltgroth and Hobbs (1979). They developed a three dimensional plume model using numerous meteorological parameters and predicting transformation rates, particle size distributions and visibility degradation. Their model predicts maximum gas phase conversion rates at the edges of the plumes, where maximum mixing with background air occurs; however, the preditions for the cross-sectional averages of SO_2 conversion rates are lower (0 to 0.4% hr^{-1}) than those observed in many other plumes.

Other models that have proposed in recent years to model power plant plume data include: Meagher and Luria (1982), Hov and Isaksen (1981) and Bassett et al. (1981). In contrast to the previously discussed efforts of Gillani et al. and Eltgroth and Hobbs these models used detailed chemical mechanisms to generate radical concentrations sufficient to oxidize SO_2 at an observed rate. In some instances previously discussed explicate chemical mechanisms were used and these will be noted.

Meagher and Luria (1982) conducted computer simulations of the homogeneous gas phase chemical reactions that occur in a coal fired power plant plume. The chemical model used was the carbon bond mechanism developed by Whitten et al. (1980) and discussed earlier. The authors reduced the CBM to 65 chemical reactions. Since CBM does not include any SO_2 chemistry, three reactions were added to describe the SO_2 conversion. The added reactions were SO_2 + HO, SO_2 + HO_2 and SO_2 + CH_3O_2. The authors calculated a pseudo first-order rate constant for sulfate formation based on the following reactions:

$$HO_2 + SO_2 \rightarrow\rightarrow SO_4^{2-} \quad (121)$$

$$CH_3O_2 + SO_2 \rightarrow\rightarrow SO_4^{2-} \quad (122)$$

$$HO + SO_2 \rightarrow\rightarrow SO_4^{2-} \quad (123)$$

$$O(^3P) + SO_2 \rightarrow\rightarrow SO_4^{2-} \quad (124)$$

$$ACO_3 + SO_2 \rightarrow\rightarrow SO_4^{2-} \quad (125)$$

where ACO_3 = acetyl-peroxy radical and

$$K_{117} = k_{121}[HO_2] + k_{122}[CH_3O_2] + k_{123}[HO] + k_{124}[O] + k_{125}[ACO_3]$$

For a 12-hour simulation the average value of K_{117} was found to be 2.1% hr^{-1}, which is within reasonable agreement of observed conversion rates. In addition to analysis involving chemical speciation, the author did a sensitivity analysis on the effect of various parameters on sulfate and nitrate formation rates. The most important ones according to their model were the influence of reactive hydrocarbons in the background air and the rate of mixing of the plume with background air. This is not surprising since the model is driven solely by gas phase reactions and the hydrocarbons are needed in generating the required species (HO, HO_2, CH_3O_2) for SO_2 oxidation and HO for NO_2 oxidation leading to HNO_3.

Hov and Isaksen (1981) developed a model where the chemistry and meteorology of the boundary layer interact with a power plant plume that has spatial resolution in the horizontal. The model describes the evolution of the plume from its early stages, characterized by an ozone depletion to an intermediate stage where elevated ozone and hydroxyl radicals are formed on the edges to the aged plume, in which excess ozone and sulphate are predicted. The conversion of SO_2 to sulfuric acid and NO_2 to nitric acid is accomplished through the reactions

$$SO_2 + OH \rightarrow HSO_3 \ (\rightarrow H_2SO_4) \quad (126)$$

$$k_{126} = 1.1 \times 10^{-12} \ cm^3 \ s^{-1}$$

$$NO_2 + OH \rightarrow HNO_3 \quad (127)$$

$$k_{127} = \sim 10 k_{126}$$

and the hydroxyl radicals are generated through the following series of steps

$$NO + RO_2 \rightarrow NO_2 + RO \qquad (128)$$

where R is organic or inorganic radical, subtracted the rate of reactions such as

$$H_2O + O(^1D) \rightarrow 2OH$$
$$NO_2 + OH \rightarrow HNO_3$$
$$O_3 + HO_2 \rightarrow OH + 2OH$$

The Hov-Isaksen model predicts the average conversion of SO_2 to sulfate in the Labadie power plant plume to peak at 5% hr^{-1} about noon time and to be a minimum of $\sim$1% hr^{-1} in the early morning and late evening hours. This prediction is, of course, the result of considering only gas phase SO_2 reactions. They compare their model to observed data collected during good weather, summer episodes and got reasonably good agreement.

Bassett, Gilbard and Seinfeld (1981) is a reasonably complex attempt at incorporating aqueous-phase SO_2 oxidation in a model. Most of the previously discussed models were predicted on homogenoeus gas phase reactions and ignore aqeous phase chemistry. The B-G-S model is the first attempt at predicting both size and chemical composition evolution of plume aerosols. The model treats coagulation, homogeneous particle formation, heterogeneous condensation and particulate phase chemical equilibria and kinetics in an explicit manner. We will discuss in detail only the aspects of treating the chemical equilibria. The reader is referred to the article for more details on the aerosol evolution.

In contrast to other models the gas phase SO_2 oxidation is treated in a simple manner. The model incorporates the homogeneous gas phase oxidation of SO_2 in the form of first order in SO_2 with the rate of H_2SO_4 vapor formation being

$$\frac{dp_{H_2SO_4}}{dt} = k_{129}p_{SO_2} \qquad (129)$$

where p denotes the partial pressure of the indicated species. The plume aerosol is taken to consist of aqueous droplets of $MnSO_4$ together with other components that result from the dissolution of SO_2, NH_3, and H_2SO_4 in the droplets. The gas phase species considered are SO_2, H_2O, H_2SO_4, and NH_3.

The Mn catalyzed oxidation of dissolved SO_2 to sulfate is given the form

$$\frac{d[H_2SO_4]}{dt} = \frac{[MnSO_4](\alpha_1 y_{SO_2} - \alpha_2[H^+][HSO_4^-])}{\alpha_3 + y_{SO_2}} \qquad (130)$$

where [ ] represents concentrations in moles per liter, y is concentration in ppm, $\alpha_1 = 2.025\ min^{-1}$, $\alpha_2 = 4.254(moles\ l^{-1})^2(ppm\ min^{-1})$, and $\alpha_3 = 200$ ppm. The equilibrium reactions used in the computation include the following

$$\begin{aligned} H_2O &\Longleftrightarrow H^+ + OH^- \\ SO_{2(g)} + H_2O &\Longleftrightarrow SO_2 \cdot H_2O \\ SO_2 \cdot H_2O &\Longleftrightarrow H^+ + HSO_3^- \\ HSO_3^- &\Longleftrightarrow H^+ + SO_3^{2-} \\ NH_{3(g)} + H_2O &\Longleftrightarrow NH_3 \cdot H_2O \\ NH_3 \cdot H_2O &\Longleftrightarrow NH_4^+ + OH \\ HSO_4^- &\Longleftrightarrow SO_4^{2-} + H^+ \end{aligned}$$

Model simulation is exercised for "typical" or average power plant plume data rather than for one specific data base from an individual plume study. Three general cases were considered and aerosol growth from 1 to 10 km were calculated and presented. The model will probably have applications in visibility studies for power plant plumes, but it is not certain at this point that it could be adapted to long-range transport and incorporated into an acid rain model.

Finally, we mention briefly two other models, one for urban aerosols and one for large scale tropospheric predictions. Middleton, Kiang, and Mohnen (1978) have developed a numerical kinetic aerosol model to study conditions under which various mechanisms may be the dominant pathway to sulfate formation. The model is intended to focus on the competition between gas phase sulfate production, gas to particle conversion mechanisms and sulfate formation in wetted aerosols. Sulfate aerosol formation is formulated as

$$\frac{d[SO_4^{2-}]}{dt} = K_{O_2}[SO_3^{-2}] + \frac{K_{Fe}[Fe^{3+}][HSO_3^-]^2}{[H^+]}$$

$$+ \frac{K_{Mn}[SO_2 \cdot H_2O][Mn^{2+}]}{[SO_2 \cdot H_2O] + [Mn^{2+}] + K_s} + K_{soot}[C_x][O_2 \cdot H_2O]^{0.75}$$

$$+ K_{O_3}[O_3 \cdot H_2O][HSO_3^-] + K_{H_2O_2}[H_2O_2 \cdot H_2O][HSO_3^-]$$

$$+ K_{H_2SO_4}[H_2SO_4] \qquad (131)$$

where $[Fe^{3+}]$, $[Mn^{2+}]$, and $[C_x]$ are solution concentrations of iron, manganese, and soot, respectively. $[O_3 \cdot H_2O]$, $[H_2O_2 \cdot H_2O]$, $[O_2 \cdot H_2O]$, $[SO_2 \cdot H_2O]$, and $[H_2SO_4]$ are the concentrations of dissolved gases. The model assumes the gas vapor and gas solution concentrations are related through Henry's Law constant. K_s is a combination of experimental rate constants and is given as 5×10^{-5} moles per liter. The K's refer to the respective rate constants for the reactions considered. For example, K_{O_2} is the rate constant for the uncatalyzed oxidation of SO_2 by O_2. The $K_{H_2SO_4}$ term refers to sulfate production by condensation of gaseous sulfuric acid molecules.

The authors conclude from their modeling efforts that under daytime conditions the predominant mechanism is gas-to-particle conversion. Aqueous phase oxidation by H_2O_2 in solution is important under daytime conditions of high gas-phase H_2O_2 production. At night the rate of sulfate production is slower and appears governed by the iron and soot catalyzed reactions, assuming no H_2O_2 or O_3 is present.

Altshuller (1979) used a simple two-dimensional model involving gas phase SO_2 oxidation by three pathways: $SO_2 + OH$, $SO_2 + HO_2$, and $SO_2 + CH_3O_2$.

The rates are shown to vary substantially with latitude, season of the year and altitude. He concludes that gas phase oxidation is an important process throughout the year at lower latitudes and in the warmer months at mid-latitudes. Altshuller noted that since his model did not include liquid phase reactions, it should be considered only as a lower limit for sulfate production in the troposphere.

We conclude the section with a brief assessment of current knowledge for S- and N-oxide chemistry and the attempts at modeling them. As noted in this section various workers have tried to parameterize sulfate aerosol formation using linear expressions. Others have used first order rate expressions, which give an exponential expression for formation. In certain instances they have been reasonably successful. This may be the result of the apparently slow reaction of SO_2 -> SO_4^{2-} in the atmosphere (1 to 5% hr^{-1}). One must realize, however, that for an acid rain model the aqueous-phase reactions may be the predominant pathways. In such cases the reaction rates have been found to depend on factors such as pH, gas solubility, mass transfer to the liquid droplet, etc. None of these factors could be construed as being linear and, therefore, we would tentatively conclude an overall linear expression for SO_2 to sulfate conversion in rainwater might not be correct.

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Paper No. 2:

THE SEASONAL DEPENDENCE OF ATMOSPHERIC DEPOSITION AND CHEMICAL TRANSFORMATION RATES FOR SULFUR AND NITROGEN COMPOUNDS

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1. Introduction

The objective of this report is to compare wintertime deposition and chemical transformation rates for sulfur and nitrogen compounds with the corresponding summertime values, in order to determine if, on the basis of current theoretical and experimentally determined information, there are significant differences between the summer and wintertime parameters commonly used in mathematical long-range transport models--differences which should be taken into account by the modellers. The objective was not to recommend values of deposition/transformation rate parameters to be used in current models: indeed, in some of the relevant areas (e.g., dry deposition of particulate sulfur and nitrogen, or in-cloud processes) our lack of understanding seems to preclude any such recommendations at present. Due to time limitations, an exhaustive and critical review of the literature was not possible. However, it is hoped that the most relevant scientific investigations have been included in this report.

Chapter 2 deals with wet and dry deposition of sulfur dioxide and sulfates, both from the viewpoint of general theoretical considerations and the results of relevant field and laboratory studies. Chapter 3 takes the same approach with regard to chemical transformation rates. Since information on nitrates is so scarce, all the relevant data on these compounds are summarized in Chapter 4.

The conclusions of this investigation are given in Chapter 5, where some brief recommendations about areas badly needing further study are also given.

2. Atmospheric Deposition

2.1 Wet Deposition

The atmospheric wet deposition of particulate matter and gases has usually been parametrized either in terms of a scavenging coefficient Λ or a washout ratio W (e.g., Dana, 1979). The former results from the assumption that wet deposition is an exponential decay process (since particles or gases are repeatedly exposed to cloud or precipitation elements, with some chance of collection for each exposure) obeying the equation:

$$C_t = C_o \exp(-\Lambda t), \tag{1}$$

where

C_t = atmospheric concentration at time t,
C_o = atmospheric concentration at time zero,
Λ = scavenging coefficient (in units of time $^{-1}$).

The washout ratio is defined as the concentration of contaminant in precipitation divided by its concentration in air (usually at the surface level), i.e.,

$$W = \frac{X}{C}, \tag{2}$$

where

X = concentration of contaminant in precipitation,
C = concentration of contaminant in unscavenged air,
W = washout ratio (dimensionless).

Most of the discussion to follow will be in terms of the scavenging coefficient, but the same considerations apply to the washout ratio, since Λ and W can be related. For example, for the simple case of pollutant washout from a column of air having a uniform concentration over height h, one obtains:

$$\Lambda = \frac{WJ}{h}, \tag{3}$$

where

J = the precipitation intensity.

2.1.1 General Considerations

When comparing wet deposition rates by rain and snow, it is convenient to express the scavenging coefficient as follows (Engelmann, 1968; Slinn, 1977):

$$\Lambda = \int_0^\infty FEAdD, \tag{4}$$

where

A = the cross-sectional area of drops of diameter D,

F = the flux density of drops with diameter between D and $D+dD$ (drops/area - time - diameter interval),

E = the collection efficiency (i.e., the fraction of particles or gas molecules in the path of the drop which are washed out by it). For particulates, the collection efficiency depends not only on the size of the droplet/snowflake, but also on that of the particle under consideration.

The following approximations to Equation (4) have been suggested for rain and snow scavenging (Slinn, 1981):

For rain,

$$\Lambda \simeq \alpha \frac{JE(D_m)}{D_m}, \tag{5}$$

where

α = a constant,

D_m = mean raindrop size,

$E(D_m)$ = collection efficiency of drops with diameter D_m.

For snow,

$$\Lambda \approx \beta \frac{JE(\lambda)}{D_s} , \tag{6}$$

where

β = a constant,
λ, D_s = characteristic snowflake dimensions which depend on crystal type (see Slinn, 1981),
$E(\lambda)$ = collection efficiency of snowflakes having characteristic dimension λ.

A consideration of Equations (5) and (6) suggests a number of factors which could lead to differences between summer- and wintertime scavenging coefficients.

i. The scavenging coefficient depends on the precipitation intensity, which can have seasonal variations at any given location.

ii. It is also a function of the raindrop/snowflake size distribution and effective scavenging area. In this connection it should especially be noted that compared to rain, snow has a large surface area-to-mass ratio, and thus is potentially a much more effective scavenger of aerosol particles than is rain (Knutson and Stockham, 1977). However, there is also a strong dependence on the type of snow. Plane dendrites, for example, are predicted to be much more effective scavengers than graupel (Slinn, 1977).

iii. For <u>aerosol</u> scavenging, the value of E depends on the size and chemical composition of the particles because several processes that depend upon these factors are involved during within- and beneath-cloud scavenging (rainout and washout respectively), including Brownian motion, phoretic attachment, inertial impaction and nucleation (see, for example, Slinn, 1977; Scott, 1978). Actually, for an atmospheric aerosol consisting of a mixture of different sizes, the right-hand side of Equations (4) to (6) should be integrated over all aerosol sizes, and even relatively simple theoretical considerations indicate a resulting strong dependence of on aerosol size distribution (Hales, 1978). Hence, the scavenging coefficient for particles could have a strong seasonal variation if the particle size distribution and chemical properties vary due to seasonal changes in emission characteristics, meteorological factors such as temperature and relative humidity, or atmospheric chemical reaction mechanisms, for example.

iv. The collection efficiency of gases in Equation (4) depends on the solubility and chemical reactivity of the gas in water, and a number of other factors related to interfacial transfer between raindrop/snowflake and the ambient air--see, for example, Hales (1978) and Barrie (1978) for more detailed discussions for the case of sulfur dioxide scavenging. With reference to seasonal variations in the gas scavenging rate, snow scavenging is usually negligible compared to rain scavenging because of low gas adsorption rates on ice crystals (Engelmann, 1968; Slinn, 1981). However, the type of snow should again be considered, since wet snow can have a much higher gas scavenging efficiency than dry snow (Summers, 1977; Hales et al., 1971). Also, it should be noted that for sulfur dioxide, due to the nature of its solubility characteristics in water, the scavenging coefficient is expected to depend strongly on seasonal variations in the ambient temperature and precipitation pH (Barrie, 1981).

v. There is one more factor, which is implicit in the above discussion, but perhaps deserves elaboration--viz., the importance of seasonal variations in storm type at a given geographical location. This is especially important with regard to in-cloud (rainout) processes, because the mechanisms whereby particles and gases are removed by such processes can depend strongly on the storm type. For example, Scott (1978) has discussed the dependence of sulfate rainout upon the mechanism of precipitation formation. [It should be noted that rainout is thought to be the dominant process responsible for particulate sulfur removal on a regional scale--see, for example, Scott (1978) and Garland (1978).] Scott also has predicted scavenging rates to differ by a factor of 10 or more depending upon whether or not the precipitation originated as snow. Similarly, Summers (1977) has shown striking differences in removal rates of sulfur dioxide by summertime convective storms and snowstorms. These results will be discussed in more detail in the following section.

2.1.2 Experimental Results

For comparing wet deposition rates for sulfur dioxide under winter- and summer-like conditions, one of the more relevant data sets is that of Summers (1977). For the rainout and snowout of sulfur dioxide, he obtained the following equations:

$$\Lambda \text{ rainout} = 3 \times 10^{-5} J \text{ sec}^{-1}, \tag{7}$$

$$\Lambda \text{ (dry)snowout} = 10^{-6} J \text{ sec}^{-1}. \tag{8}$$

Taking into account representative rainfall rate data for various types of precipitation, and using Equations (7) and (8), Summers estimated the following range of values for Λ: light, moderate and heavy snow--$10^7 \Lambda = 1$, 5, and 25, respectively; moderate rain or showers, heavy rain or thunderstorms--$10^4 \Lambda = 3$ and 7.5, respectively. Clearly, for regions where the wintertime precipitation largely consists of dry snow (as for much of central Canada), the above results indicate a seasonal change in the wet scavenging rate of two or three orders of magnitude, which cannot be ignored in air quality modelling work. It is interesting to note--see Figure 1--that the snowfall drops sharply south of the states of Pennsylvania, Ohio, Indiana, and Illinois.

Other areas, such as the east and west coasts of Canada and much of the United States, receive appreciable amounts of wet snow and cold rain during the winter months. Fortunately, our understanding of the physical and chemical processes involved in sulfur dioxide wet deposition is sufficiently complete to allow estimates of the resulting seasonal deposition changes. Summers (1977) has argued that, because of the large sweep-out area associated with wet snow (which should have a collection efficiency E similar to that of rain), its scavenging coefficient should be somewhat greater than for rain at an equivalent rainfall rate. (He recommends a value approximately twice as

Figure 1: Average annual distribution of snowfall in North America (cm), from Findlay (1980).

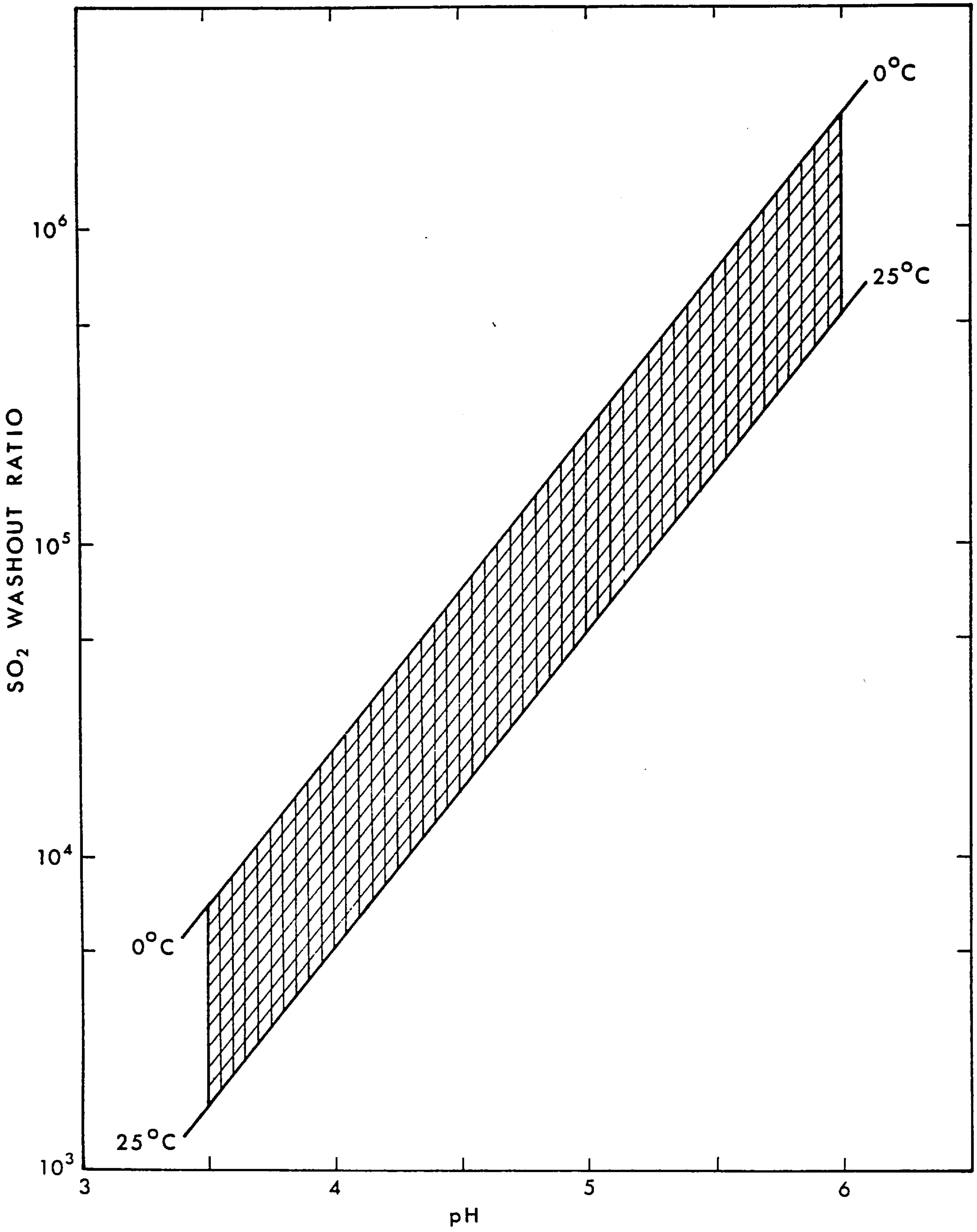

Figure 2: Dependence of the washout ratio of SO_2 on pH and temperature for equilibrium scavenging conditions, from Barrie (1981).

great.) On the other hand, for sulfur dioxide removal by rain droplets, several relevant theoretical investigations are available, which are based on the acceptable assumption that, for purposes of regional transport modelling, the sulfur dioxide in the air is in equilibrium with that in the rain (see, for example, Hales and Dana, 1979a; Barrie, 1981). Figure 2, for example, taken from Barrie (1981), shows the predicted functional dependence of W, for sulfur dioxide, on rainwater pH and temperature. In going from 25 to 0°C, for example, W increases roughly by a factor of four. It should be noted that in much of northeastern America precipitation tends to be somewhat more acidic in summer than winter (e.g., Pack and Pack, 1979), so from Figure 2 the expected difference between the winter- and summer-time values of W for rain would be even greater than predicted on the basis of temperature alone. For example, for a unit increase in pH and a change in temperature from 25 to 0°C, which might be representative of the seasonal variation at some of the stations in the northeastern U.S.A. (Pack and Pack, 1979), the predicted increase in W is one order of magnitude. Limited experimental measurements of sulfur dioxide in precipitation support the above arguments (Hales and Dana, 1979). As a matter of interest, Figure 3 gives the North American percentage frequency of hourly temperatures below 0°C in January and 10°C in July, and above 10°C in January and 21°C in July, from which the importance of the above temperature effect can be estimated.

For the case of particulate sulfur, very few data are available on which to base conclusions about winter- and summertime differences in wet deposition, and our understanding of the details of rain and snow interactions with particles is not nearly as complete as for the case of sulfur dioxide. The existing theories are of little help if one wants to go beyond order-of-magnitude washout rate estimates. The only work where a direct experimental comparison of rain and snow scavenging coefficients has been made, for particles comparable in size to sulfates, is that of Graedel and Franey (1975). They found below-cloud Λ values for snow to be twenty times or more than those for rain. However, Graedel and Franey's interpretation of their data has been questioned by Slinn (1976).

Knutson and Stockham (1977) have developed equations for the scavenging coefficient of snow from laboratory study results with single

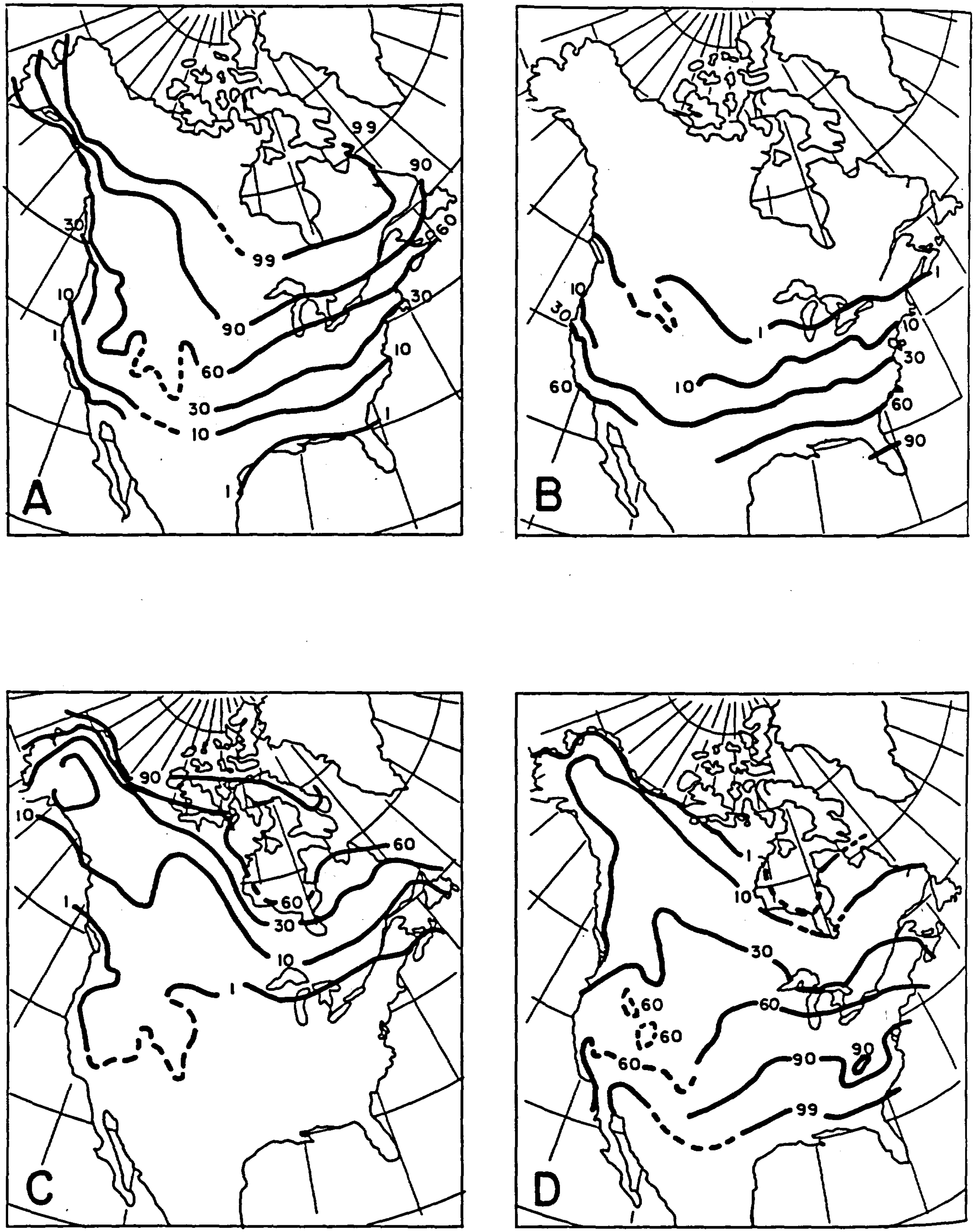

Figure 3: The percentage frequency of hourly temperature for North America: A–January, less than 0° C; B–January, greater than 10° C; C–July, less than 10°C; D–July, greater than 21°C (after Rayner, 1961).

snowflakes, which usually agreed with available field data to within a factor of three. For particles of about 0.5 microns in diameter, and a precipitation intensity of 1 mm h^{-1}, their model predicts scavenging coefficients in the range of 0.5 to 1.0 x 10^{-5} sec^{-1}, depending on the type of snow. These values may be compared to some data on rain scavenging coefficients for particles of similar size compiled by McMahon and Denison (1979). Table 1 is abstracted from their Table 9. No attempt was made at a critical evaluation of the methods used to arrive at the scavenging coefficients in this table. However, the last value shown (for 0.3 to 0.5 micron particles) was obtained by Graedel and Franey (1977) (McMahon and Denison, in their Table 9, have incorrectly labelled Graedel and Franey's data as being obtained from snowfalls), and if we accept Slinn's criticism of their methodology (see above) and reject their data point, all we can say is that, for a particle size which might be representative of sulfates, most of the available data suggest that below-cloud rain and snow scavenging coefficients should be about the same order-of-magnitude for comparable rainfall rates. The scanty relevant data on washout ratios support the above conclusion (see McMahon and Denison, 1979) although in this case, both within- and below-cloud processes are involved. Scott (1981) has recently presented data on washout ratios of sulfates in snowstorms, which fall within about the same range of values as has been observed for a number of other substances in rain. However, he found that the

Table 1. Field Measurements of Rain Scavenging Coefficients of Particles Expected to be Mainly in Submicron Size Range

Source of Data	$10^5\Lambda(s^{-1})$	Comments
Kalkstein et al. (1959)	2	SO_4 washout
Makhonko (1964)	1	Fission products washout
Bakulin et al. (1970)	3	Pb washout from thunderstorm
Burtsev et al. (1970)	$15\ J^{0.5}$	0.2 μm particle washout
Graedel and Franey (1977)	18	0.3-0.5 μm particle washout

washout ratio is strongly dependent on the microphysical processes of precipitation growth, W values being 10 to 50 times higher when abundant cloud water was available (and snowflake growth was primarily through collection of supercooled droplets) than when negligible liquid water was detected in the clouds (and growth was primarily by vapour deposition on snowflakes).

2.1.3 Summary

To summarize the above discussion on wet deposition of sulfur compounds: it would seem that for sulfur dioxide, the washout coefficient for both within- and below-cloud processes can show a strong seasonal dependence (order-of-magnitude or more), even after seasonal variations in precipitation rate are taken into account, because of temperature and pH effects on the solubility and the low uptake of the gas by ice crystals.

The available data on particulate sulfur wet scavenging is too meager to allow any definite conclusions about seasonal differences. All one can say is that below-cloud scavenging coefficients for rain and snow seem to be of the same order-of-magnitude. However, rates of in-cloud processes depend strongly on the specific mechanisms involved (Scott, 1978; 1981), and seasonal variations in storm type could result in corresponding changes in scavenging rates of an order-of-magnitude or more, but more data are needed to substantiate or disprove this speculation.

2.2 Dry Deposition

The dry deposition rate of gases and particles to the earth's surface has usually been parametrized using a deposition velocity v, defined by the equation

$$v = Mc^{-1}, \tag{9}$$

where

M = the flux of material,

C = the ambient concentration at a particular height, and v (which is a function of height) refers to the same level as the concentration measurement.

2.2.1 General Considerations

To better understand the role of different factors which affect the deposition velocity, it is convenient to work in terms of resistances to transport. The total resistance, r_t, defined as the reciprocal of v,

$$r_t = v^{-1}, \tag{10}$$

can be broken down into an aerodynamic resistance, r_a, and a surface resistance, r_s:

$$r_t = r_a + r_s. \tag{11}$$

The surface resistance can be further split into a resistance due to an usually thin stagnant air film adjacent to the absorbing surface, r_b, and an actual resistance to transport within the surface (for plants, this is largely the canopy stomatal resistance), r_c (Wesely and Hicks, 1977; Chamberlain, 1979):

$$r_s = r_b + r_c. \tag{12}$$

The magnitude of the aerodynamic resistance, r_a, is largely governed by atmospheric turbulence in the boundary layer, which in turn depends on factors such as wind speed, atmospheric stability, and characteristics of the surface (i.e., the surface roughness). There are well-known micrometeorological formulae relating r_a to meteorological and surface parameters (see, e.g., Garland, 1978; Wesely and Hicks, 1977). The value of r_a decreases as the wind speed and surface roughness increase, and also depends to a certain extent on the atmospheric stability, although the latter dependence only seems to become marked when the atmosphere is very stable--e.g., for Pasquill stability category F (Sheih et al., 1979). Because of the dominant influence of turbulent diffusion, r_a should be the same for both particles and gases, except where the particles are so large that gravitational settling plays an important role in the deposition process (e.g., Sehmel, 1980). In view of the above considerations, seasonal variations in meteorology and surface characteristics will obviously change the aerodynamic resistance to transport of both particles and gases.

The stagnant film resistance, r_b, should not be interpreted as a physical feature of all circumstances. While it may be relatively well-defined over smooth surfaces, these are rare in the "real world." Over plant canopies and even water surfaces, it is probably not a continuous phenomenon, but rather serves as a simplified, average representation of a situation where turbulent eddies approach and interact with surface elements, during which interactions molecular and Brownian diffusion plays a significant role in the mass transport. With this interpretation of the "stagnant film" in mind, it may be noted that r_b also depends to a certain extent on the same factors as r_a, since drag forces and the intensity of atmospheric turbulence will determine the "effective" thickness of the stagnant film. However, because of the importance within the film of molecular diffusion for gases, and Brownian diffusion and impaction for aerosols, r_b is also strongly dependent on the characteristics of the material under consideration--in particular, the diffusivity of gases and the particle size distribution of aerosols (see, for example, Wesely and Hicks, 1977; Sehmel, 1980). As with r_a, it can be seen that seasonal variations in meteorological and surface factors can lead to corresponding variations in r_b. In addition, if for particles there are appreciable seasonal changes in the size distribution, potentially large changes in r_b could result (e.g., Sehmel, 1980; Ibrahim et al., 1980).

As implied by its definition, for a given substance r_c depends only on the characteristics of the surface. For particles, probably for lack of reliable information to the contrary, it has sometimes been assumed that r_c is equal to zero (e.g., Ibrahim et al., 1980; Sievering, 1979a). For gases, r_c depends on the properties of the gas [mainly the solubility in water (Hill, 1971) and molecular diffusivity (Wesely and Hicks, 1977)] and the absorbing surface. For surfaces covered by vegetation, r_c depends on the nature, and state of growth and condition, of the plant in question, the latter being influenced by the water availability, solar radiation level, and air temperature, among other things. Obviously, seasonal changes in the surface coverage will lead to corresponding changes in r_c.

For a more detailed discussion of the individual resistances which determine the overall magnitude of the deposition velocity, and the factors affecting them, see Wesely and Hicks (1977), Sheih et al. (1979), Chamberlain (1979) and Sehmel (1980).

2.2.2 Experimental Results

Several authors have recently presented compilations of experimental data on the deposition velocities of gases and particulates, which are of value in assessing the effects of seasonal variations on v (see Garland, 1978; McMahon and Denison, 1979; Chamberlain, 1979; Sehmel, 1980).

For the case of sulfur dioxide, a reasonably consistent picture emerges. For a wide range of surfaces, including vegetation, water, and soils, the deposition velocity has been found to be typically in the range 0.4 to 0.8 cm s^{-1}. Garland (1978) rationalizes the above result by pointing out that, in general, there is a counter-balance between the aerodynamic and surface resistance terms [r_a and r_s in Equation (11)]. For relatively smooth surfaces, r_s has been found to be rather small, and uptake is largely determined by r_a. On the other hand, surfaces with taller vegetation, such as wheat and forest, exhibit a higher r_s, which counteracts the reduced r_a.

Of course, there are exceptions to the above generalizations: for example, much higher v values than indicated above may apply to wet or snow-covered forests (Chamberlain, 1979). However, it would seem that such exceptions have only marginal relevance when seasonal variations are being considered (unless, for example, the percentage of the time that a forest is wet changes significantly, due to seasonal changes in precipitation).

It is interesting to compare measured deposition velocities to snow with the 0.4 to 0.8 cm s^{-1} range in v noted above, which is assumed to be representative of surfaces for most of the year other than winter. Table 2 lists the available data for sulfur dioxide deposition to snow surfaces. The

Table 2. Deposition Velocities of Sulfur Dioxide to Snow

Reference	v cm s^{-1}	Comments
Whelpdale and Shaw (1974)	1.6	Lapse
	0.52	Neutral
	0.05	Stable
Garland (1976)	0.10 - 0.17	Ice - laboratory experiments; $r_s \approx \sigma$ s cm^{-1}.
Dovland and Eliasen (1976)	~ 0.1	Low wind speed, stable atmosphere; $r < 5$ s cm^{-1} (Garland, 1976).
Barrie and Walmsley (1978)	0.25 ± 0.20	Determined from simultaneous deposition and concentration measurements during a pollution episode.
	0.3 - 0.4	Determined from sulfur accumulation by snow and ambient concentrations calculated with a dispersion model.

values measured generally tend to be lower than 0.4, although a "representative" v of 0.1 cm s^{-1} for snow, as suggested by Husar et al. (1978b), would seem to be too low, except for very stable atmospheric conditions.

The above results suggest that seasonal variations in sulfur dioxide dry deposition velocities should be relatively modest--certainly less than the order-of-magnitude changes expected for wet deposition. It seems that for the wintertime, at least in Canada and the northern United States, dry deposition velocities of sulfur dioxide should be somewhat lower than in the summer, due to the larger proportion of the surface covered by snow and dead vegetation. In this connection, it is interesting to compare some estimates of v for the summer (June-August) and winter (December-February) months in Ontario, made using the methods of Sheih et al. (1979). Surfaces were characterized according to their classification, and values of surface roughnesses and resistances were taken from their Table 3. Information on the frequency of occurrence of Pasquill stability classes at 22 stations in Ontario was provided by the Atmospheric Environment Service. Calculated seasonal average deposition velocities are shown in Figures 4 and 5. A comparison of these figures supports the expectation that, for sulfur dioxide, seasonal changes in v should not be large.

The picture for sulfate particulates is much more confusing because of the current controversy regarding deposition velocities of particles in the 0.1 to 1.0 micron size range (where most of the sulfate mass is expected to occur). Theoretical predictions (see, for example, Sehmel and Hodgson, 1978; Ibrahim et al., 1980) indicate that, for this size range, $(r_a + r_b)$ should be generally larger than 10 s cm^{-1} (i.e., v should be no greater than 0.1 cm s^{-1}). Available experimental data on deposition velocities of sulfates, or other substances such as lead (which are expected to be in a similar size range) are shown in Table 3. It would seem that for relatively smooth surfaces, such as snow, water, or filter paper, the deposition velocity is about 0.1 to 0.2 cm s^{-1}, or in some cases so small that the removal of particles is countered by surface emissions (i.e., the effective deposition velocity is negative). For rougher surfaces and vegetation there is little data, but values ranging from less than 0.1 to about 1.0 cm s^{-1} have been

Table 3. Deposition Velocities for 0.1-1.0 Micron Particles

Reference	v cm s^{-1}	Comments
Cawse (1976)	0.2 to <0.7	Vanadium on filter paper at 1.5 m.
	<0.1 to <0.6	Arsenic on filter paper.
Dovland and Eliasen (1976)	0.16	Lead on snow, stable atmosphere.
Garland (1978)	<0.1	Atmospheric sulfate over grass.
Droppo (1979)	0.1, 0.27 Negative (surface source)	Sulfates over arid vegetation. Sulfates, daytime, non-arid vegetation.
Sievering (1979)	<0.5	Estimated annual average over Lake Michigan, submicron atmospheric aerosols.
Sievering et al. (1979)	0.2 ± 0.16	Atmospheric sulfate over L. Michigan, stable atmosphere.
Wesely and Hicks (1979)	~1 Negative (surface source)	Submicron particles to grass Nighttime, pine plantation, senescent maize.
	Negative	Snow, and cold, wet, bare soil.
Everett et al. (1980)	1.4	Atmospheric particulate sulfur aerosol over slightly rolling grassland.
Ibrahim et al.	0.1 to 0.2	Bimodal ammonium sulfate aerosol over snow. (These results are complicated by the fact that, although over 90% of the total mass was in the 0.7 micron mode, most of the material actually deposited came from the 10 micron mode.)

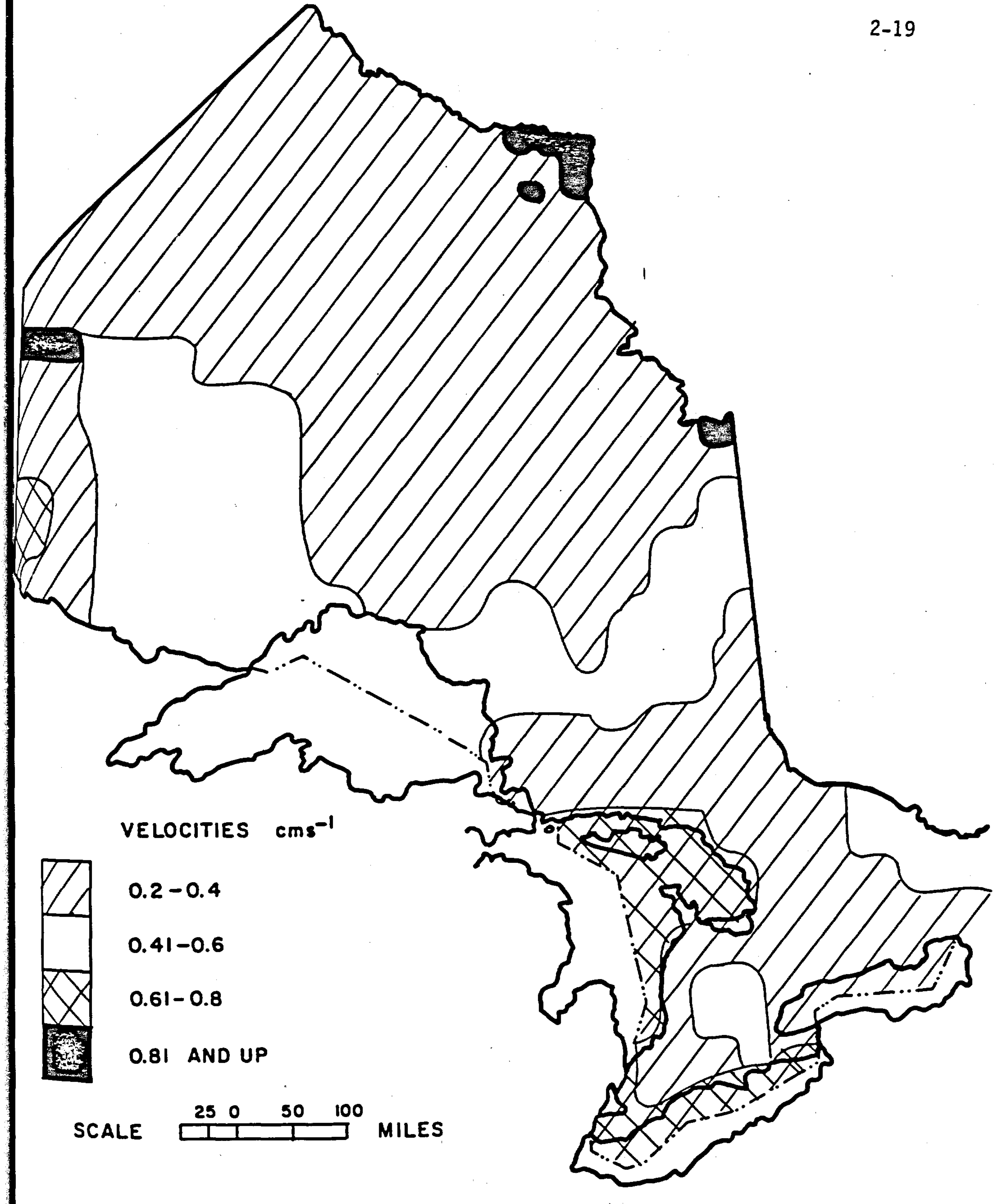

Figure 4: Deposition velocities of SO_2 for June-August.

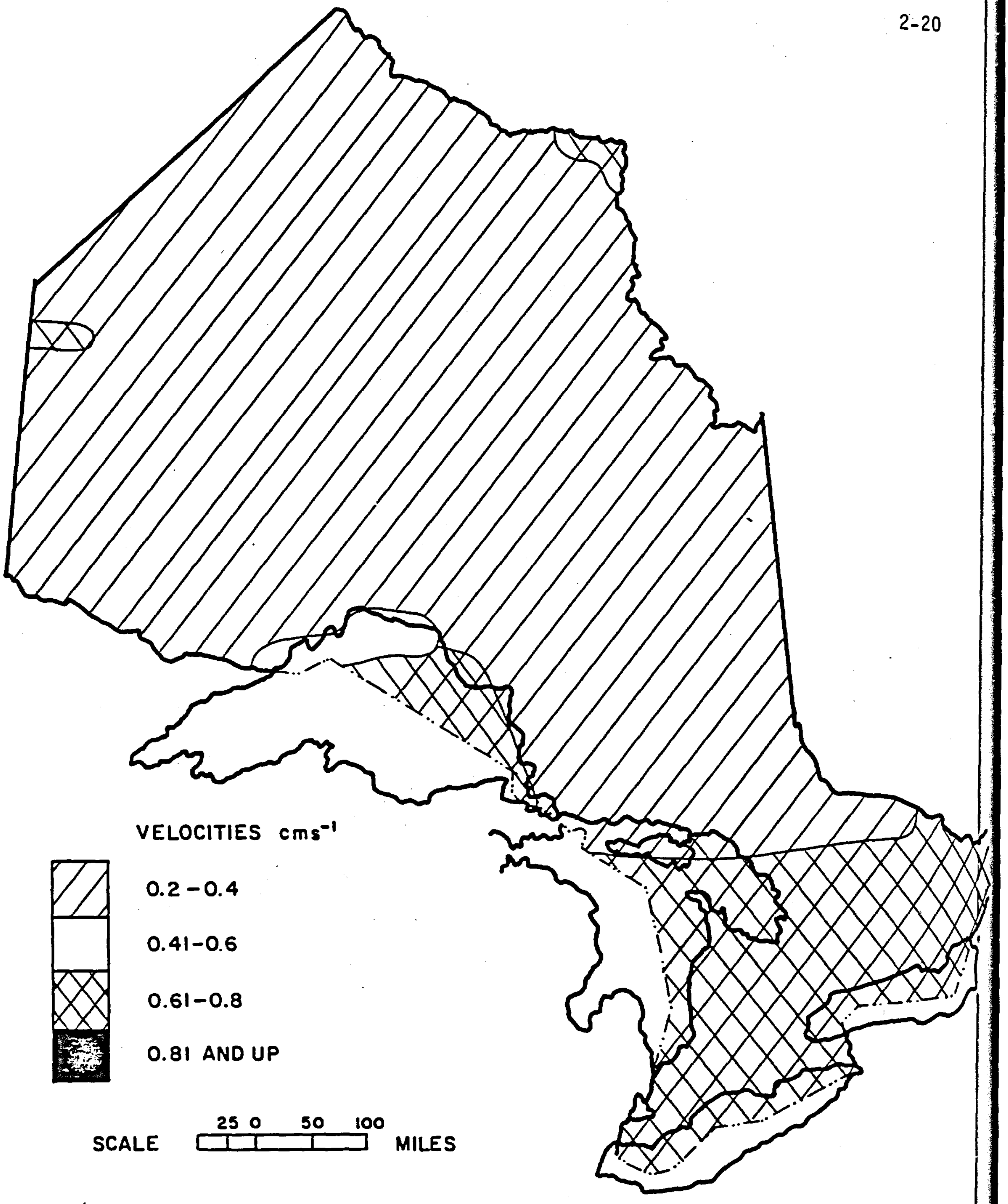

Figure 5: Deposition velocities of SO_2 for December–February.

reported, including a number of negative values. For such surfaces, Sheih et al. (1979) have proposed sulfate deposition velocities comparable to those for sulfur dioxide. However, at present, because of the large uncertainty in v for particulate sulfate, little can be said about seasonal variations in this parameter.

2.2.3 Summary

To summarize: there are several theoretical reasons why dry deposition velocities for both gaseous and particulate sulfur could have a significant seasonal variation. However, for sulfur dioxide, this variation is probably rather small, as far as long-range-transport modeling is concerned. Summertime values have been typically observed to be in the range of 0.4 to 0.8 cm s^{-1}. Wintertime observations (Table 2) indicate a "representative" range of 0.1 to 0.4 cm s^{-1}. The few available data suggest that this latter range is also representative of the deposition of particulate sulfates to smooth surfaces. However, for rougher surfaces and vegetation, the picture is so confusing at present that little can be said concerning seasonal variations in the particulate dry deposition velocity.

3. Atmospheric Chemical Transformations

3.1 General Considerations

Both laboratory studies and computer simulations of atmospheric chemical reactions have shown that gas-phase homogeneous, as well as heterogeneous, reactions are potentially important for oxidation of sulfur dioxide to sulfates in polluted air--see, for example, Calvert et al. (1978) and Beilke and Gravenhurst (1978).

Homogeneous reactions can lead to conversion rates as high as 4% h^{-1} in the summertime, largely due to attack of sulfur dioxide by hydroxyl, hydroperoxy and alkylperoxy radicals (Paper 1, this report). The seasonal dependence of homogeneous reactions has been discussed by a number of authors, and is reasonably well-understood. Thus, Altshuller (1979), on the basis of computer modelling studies, found that while seasonal effects are small at lower latitudes, at middle and higher latitudes the ratio of summer-winter noontime and average diurnal photochemical rates can be large: for example, at 35°N, summer noontime and average diurnal rates are 4 to 5 times greater than the corresponding winter values. At 55°N, the summertime values are 16 to 20 times greater. In fact, Altshuller finds that during the winter months, homogeneous oxidation reactions cannot account for any significant conversion of SO_2 to sulfate at latitudes greater than 45°N. Bottenheim et al. (1977), in their study of seasonal effects on photochemical air pollution at 60°N, have come to similar conclusions. These results are largely due to changes in available ultraviolet solar intensity (Nieboer et al., 1976; Bottenheim et al., 1977; Altshuller, 1979), although temperature effects may also play a role (Carter et al., 1979). Table 4, taken from Altshuller (1979), illustrates the expected effects of season and latitude on noontime sulfur dioxide homogeneous oxidation rates in clean air. In polluted air, the corresponding rates be a factor-of-two or so higher (Calvert et al., 1978; Altshuller, 1979).

Heterogeneous sulfur dioxide oxidation processes are less well-understood than their homogeneous counterparts. Oxidation can take place in droplets, liquid films surrounding particles at high relative humidity, or on dry particle surfaces (Paper 1, this report). At present, the most important heterogeneous reactions which take place in the aqueous phase are thought to be (Beilke and Gravenhurst, 1978): (1) SO_2 oxidation by O_2 in the presence of catalysts (e.g., dissolved transition metals); and (2) SO_2 oxidation by strongly oxidizing agents (e.g., ozone and hydrogen peroxide). The reaction with hydrogen peroxide in particular has recently excited the interest of the scientific community, due to its potential atmospheric importance (see, for example, Penkett et al., 1979; Dasgupta, 1980; Martin and Damschen, 1981). To date, there has been no clear demonstration that SO_2--dry particle reactions are of atmospheric significance, except possibly in smokestack plumes close to the chimney (where concentrations are relatively high). For example, Britton and Clark (1980) have recently reviewed past work on heterogeneous SO_2 reactions on dry particles and have presented the results of some of their own studies with soot and SO_2/NO_2 mixtures. In their conclusions, they state: "From the point of view of the overall SO_2 oxidation process in the atmosphere, the heterogeneous reactions on soot or other particles play a

Table 4. Effects of Month and Latitude on Photochemical Homogeneous Oxidation of Sulfur Dioxide in Clean Air (Noontime rates in % h^{-1} from Altshuller 1979)

	Latitude (°N)						
Month	5	15	25	35	45	55	65
January	1.81	1.10	0.61	0.26	0.08	0.01	0.01
February	1.81	1.21	0.74	0.32	0.13	0.04	0.01
March	2.06	1.55	1.01	0.48	0.21	0.09	0.03
April	2.01	0.79	1.36	0.73	0.35	0.17	0.07
May	1.82	1.68	1.48	1.01	0.58	0.30	0.16
June	1.81	1.72	1.56	1.22	0.74	0.42	0.25
July	0.78	1.80	1.58	1.30	0.88	0.52	0.31
August	1.86	1.78	1.61	1.31	0.82	0.45	0.26
September	1.91	1.68	1.50	1.15	0.76	0.34	0.17
October	1.79	1.54	1.29	0.84	0.39	0.17	0.06
November	1.56	1.33	0.98	0.48	0.19	0.06	0.02
December	1.58	1.16	0.74	0.33	0.11	0.02	0.01

negligible part compared to either photochemical or droplet phase mechanisms...." Therefore, such processes will not be considered further here.

It was noted above that, for homogeneous processes, large seasonal changes may be theoretically expected in the oxidation rate, depending on the latitude. The picture is not as clear for heterogeneous reactions. It has been theorized (e.g., Foster, 1969; Freiberg, 1974) that the oxidation rate involving trace metal catalysts should be increased at high ambient ammonia concentrations and relative humidities, both of these factors leading to lower solution acidity and hence higher sulfite ion concentrations (sulfite ions are thought to be the species actually oxidized to sulfate by dissolved O_2). Lower temperatures may also promote oxidation by hydrogen peroxide or trace metal catalysts (Penkett et al., 1979; Freiberg, 1974). Thus, seasonal variations in all these factors (e.g., lower wintertime temperatures and ambient ammonia concentrations) could potentially have an effect on the conversion rate. These effects are difficult to predict. For example, Middleton et al. (1980) have carried out a modelling study into the relative importance of various urban sulfate aerosol production mechanisms, including photochemical reactions followed by sulfuric acid vapour condensation and catalytic, as well as non-catalytic, heterogeneous oxidation. They conclude that the dominant mechanism for sulfate production can depend on the season and time of day. During the daytime in summer, photochemical reactions/sulfuric acid vapour condensation are the most important, followed by liquid-phase oxidation by hydrogen peroxide. At night, however, catalytic and non-catalytic oxidation mechanisms on the wetted aerosol surface become important. In the winter, most of the daytime SO_2 oxidation is predicted to take place by reactions with hydrogen peroxide in droplets at overall rates comparable to those in the summer. However, the above conclusions are based on a large number of assumptions about reaction mechanisms and model input conditions, and should not be regarded as final. For a better assessment of winter/summertime differences in atmospheric chemical transformation rates, the results of actual field studies were consulted (see below).

3.2 Experimental Results

A large number of field investigations have been carried out into the oxidation of sulfur dioxide in urban, industrial and power plant plumes. Since, on the basis of our present understanding of atmospheric chemistry, there is a fundamental difference between urban plumes and those from strong point sources (at least, before the latter have been well-mixed into the "background" air), the two will be considered separately. Also, in view of the suggested importance of latitude when considering winter and summertime differences in photochemical processes (see above), the geographic location of each experiment will be noted whenever possible in the following discussion.

Newman (1980) has recently summarized the available results on atmospheric oxidation of SO_2 from power plant and smelter plume studies. Table 5 is largely based on the most relevant references taken from his paper. In preparing this table, we have concurred with Newman in that some of the early, and often-cited, studies of plume oxidation, such as that by Gartrell et al. (1963) and Stephens and McCaldin (1971), are probably flawed, and the results are unreliable. Rather we have emphasized those particular more recent studies which have a direct bearing on seasonal effects on the plume oxidation rate.

An inspection of Table 5, and the references cited therein, leads to the following general conclusions about the sulfur dioxide oxidation rate in power plant and smelter plumes.

1. The "dry" oxidation rate is usually small--no more than a few percent per hour.

2. Although there is still a debate about the relative importance of homogeneous gas-phase reactions, and heterogeneous processes involving catalytic plume aerosols, most of the evidence suggests the former are important, and can lead to SO_2 transformation rates of up to about 4% h^{-1}. Heterogeneous reactions may dominate near the point of emission where the particle concentration is high, or under high humidity conditions.

Table 5. Conversion of SO_2 in Power Plant and Smelter Plumes

Source	SO_2 Oxidation Rate ($\% \ h^{-1}$)	Comments
Forrest and Newman (1977)	<1.5	-four coal-fired power plants (30° to 40°N) -no correlation could be found between conversion and temperature (10 to 25°C), humidity or time of day
Husar et al. (1978a)	1 to 4 (noontime) <0.5 (night)	-St. Louis (38°N) -power plant -photochemistry may be the dominant mechanism
Lusis et al. (1978)	1 to 3 (June, noon and p.m.) <0.5 (winter, or summer early a.m.)	-Fort McMurray (57°N) -power plant -evidence of photochemical activity during relatively high conversion rates -temperature varied from -13 to 23°C
Dittenhoefer and de Pena (1979)	0 (<65% RH) ~1 (65 to 90% RH) 2 to 6 (90% RH)	-Pennsylvania (41°N) -power plant -evidence that both gas phase and aqueous phase oxidation are important
Forrest et al. (1979a)	<2	-Tarpon Springs, Florida (28°N) -oil-fired power plant -no correlation was found between individual meteorological parameters and extent of oxidation, although higher conversions were observed in August than in February
Forrest et al. (1980)	0.1 to 0.8 (night, early a.m.) 1 to 4 (late a.m. and afternoon)	-Cumberland coal-fired power plant (35°N) -reactions were correlated with solar radiation

Table 5. Conversion of SO_2 in Power Plant and Smelter Plumes (cont.)

Source	SO_2 Oxidation Rate ($\% \ h^{-1}$)	Comments
Garber et al. (1980)	<1	-Northport oil-fired power plant (41°N) -a wide range of meterological conditions were examined. The data suggest a weak positive correlation of coversion rate with temperature, water partial pressure and isolation
Hegg and Hobbs (1980)	0 to 5.7	-five coal-fired power plants, W. and Midwest U.S.A. -various times of year -evidence of photochemical reactions; conversion depended on u.v. light intensity
Gillani et al. (1980)	rate = $0.03 \ R.H.O_3$ R = solar radiation H = mixing height O_3 = background ozone	-plumes from Labadie, Cumberland and Johnsonville power plants -for dry conditions only
Chan et al. (1980)	<0.5	-Sudbury smelter plume (47°N) -no correlation of rate with temperature, relative humidity
Eatough et al. (1980)	<0.5 to 6	-Western U.S. smelter and power plant plumes -positive temperature dependence of oxidation rate; data are consistent with a homogeneous mechanism

3. Under conditions where homogeneous photochemical reactions are not expected to be significant (e.g., during the night or early morning, or during the winter at far northern locations), conversion rates have been observed to be small--generally, well below 1% h^{-1}.

4. Temperature or relative humidity may or may not have an effect on the conversion rate (compare Lusis et al., Forrest et al., Chan et al., Garber et al., with Eatough et al., Dittenhoefer and De Pena in Table 5). However, the degree of plume dilution due to atmospheric mixing is certainly important (Wilson and Gillani, 1980).

It must be emphasized that the above summary represents a considerable simplification of what happens during atmospheric SO_2 oxidation in chimney plumes, and a more rigorous treatment would require separate consideration of each point source, including the composition of the emissions as well as that of the background air into which the plume is mixing.

Consider now the corresponding data obtained from studies of urban plumes. Although urban plume data are more relevant to long-range transport modelling than chimney plume data, which generally have represented conditions within the first hour or two of emission, they are also more difficult to interpret. To extract the oxidation rate from the data, assumptions have to be made about other atmospheric processes such as air parcel dilution and dry deposition (see, for example, Alkezweeny and Powell, 1977). This should be kept in mind when evaluating the urban plume results.

Alkezweeny (1980) has summarized the available data on SO_2 oxidation in urban plumes, and the results in Table 6 are largely taken from his paper. An inspection of this table suggests that:

1. "Dry" oxidation rates in urban plumes are somewhat higher than those in chimney plumes (at least, before the latter have been mixed into the background air), possibly by a factor of two or more.

Table 6. Conversion Rates of SO_2 in Urban Plumes

Source	SO_2 Oxidation Rate ($\% \ h^{-1}$)	Comments
Benarie et al. (1972)	6 to 25	-Rouen (49°N) -wintertime results -aerosol catalysis important; acid formation increases as temperature decreases
Robert and Friedlander (1975)	1.2 to 13	-Los Angeles (34°N) -July, October
Mezaros et al. (1977)	30	-Budapest (48°N) -mainly June to September
Alkezweeny and Powell (1977)	10 to 14	-St. Louis (38°N) -August
Alkezweeny (1978)	8 to 12	-St. Louis (38°N) -summertime
Breeding et al. (1976)	5 to 32	-St. Louis (38°N) -October, April
Alkezweeny (1980)	1 to 5	-Chicago, Gary (42°N) -summertime -conversion dominated by photochemical reactions
Forrest et al. (1979b), Chang (1979)	4	-St. Louis (38°N) -Flight Da Vinci II, June
Alkezweeny (1980)	0, 6.8	-Milwaukee (44°N) -measurements on two days in August
Elshout et al. (1978)	0.6 to 4.4	-Arnheim, Amsterdam (52°N) -January to March
Prahm et al. (1976)	1.1	-Faroe Island and British Isles (50 to 60°N) -February
Smith and Jeffrey (1975)	0 to 3	-British Isles (52 to 56°N) -mainly September to November -relative humidity is important
Lavery et al. (1979)	0.7	-Ohio Valley (40°N) -August

2. Although homogeneous photochemical processes are important (Alkezweeny, 1980), heterogeneous mechanisms may play a greater role in urban than in power plant and smelter plumes (close to the source). Thus, whereas power plant and smelter plume data suggested very low oxidation rates under conditions where homogeneous processes are not expected to be significant, the urban plume data in Table 6 indicate that quite high oxidation rates have been observed in the wintertime at latitudes greater than 45°N (see, for example, the results of Benarie et al., Elshout et al., Prahm et al., and Smith and Jeffrey). Alkezweeny (1980) also has noted in his own data that high oxidation rates seem to be associated with high aerosol loadings.

3. There is some indication that temperature may have an effect on the conversion rate, although, as with chimney plume studies, the information is conflicting (compare Benaire et al. with Meszaros et al.). There is also confusion on the correlation of conversion rate and relative humidity (compare Benaire et al. with Smith and Jeffrey).

Before drawing any conclusions on the seasonal dependence of the SO_2 transformation rate from the above data, one must mention the possibly important role of clouds (both precipitating and fair weather) in converting SO_2 to sulfates. Recently, there has been a considerable amount of speculation that in-cloud processes contribute significantly to SO_2 oxidation. Laboratory studies have suggested that the observed sulfate concentration in rainwater can be accounted for by the oxidation of SO_2 in cloud droplets, especially by hydrogen peroxide and ozone (Penkett et al., 1979; Martin and Damschen, 1981), conversion rates as high as several percent per minute being inferred by this mechanism under atmospheric conditions. Limited field measurements (Hegg and Hobbs, 1978, 1981; Newman, 1979; Hales and Dana, 1979b; Alkezweeny, 1981) and mathematical modelling results (Scott, 1980; McNaughton and Scott, 1980; Fisher, 1980) also support higher in-cloud conversion rates than the values generally observed in plumes. Work is currently in progress by several groups of researchers to examine the role of clouds in atmospheric chemistry and transport.

3.3 Summary

The above experimental results make it difficult to draw any firm conclusions on the seasonal variation of SO_2 oxidation rate. Perhaps this much can be said: during the summer months, photochemical processes are important, and both point source and urban plume data indicate daytime "dry" rates of several percent per hour (a summertime diurnal average of 1 to 2% h^{-1} might be suitable for long-range transport modelling, although some of the urban plume data suggest rates several times greater than this). In the winter, it is not clear what one should expect. The chimney plume data, most of which may be of questionable relevance to long-range transport modelling because of high pollutant concentrations, indicate oxidation rates generally considerably less than 0.5% h^{-1} at latitudes where photochemical reactions should not be contributing appreciably. On the other hand, the limited urban plume data suggest a greater role of heterogeneous processes, and therefore appreciable oxidation rates, but at the same time they have been derived with more assumptions about the history of the air parcel, and are therefore more open to criticism (see, for example, Forrest et al., 1979b). It must be concluded that at present the available plume data is too conflicting to draw any firm conclusions about the seasonal dependence of the SO_2 oxidation rate. The potential role of clouds in converting SO_2 to sulfates further complicates matters. If current work shows that clouds are indeed as important as suspected, then expected seasonal variations in SO_2 transformation could increase considerably, especially in areas where clouds consist largely of dry ice crystals in the winter (and hence have very low chemical transformation potential, as compared to summertime conditions).

4. Nitrogen Oxides Deposition and Chemistry

The atmospheric chemistry and deposition of sulfur oxides has in the past received considerably more attention than that of nitrogen oxides. However, the recognition that the latter are important precursors of acid deposition, and that emissions of nitrogen oxides will grow considerably more than those of sulfur oxides in the coming two decades (U.S.-Canada Research Consultation Group on LRTAP, 1979), has recently led to a substantial increase in the level of research devoted to the atmospheric nitrogen compounds. Nevertheless, at present, relatively little has been published on deposition and chemical transformation rates of nitrogen oxides. Most information we are aware of is summarized in the present chapter.

Since many of the general physical and chemical considerations regarding deposition and transformation (outlined in Sections 2.1.1, 2.2.1, and 3.1) also apply to nitrogen oxides, some speculation is possible in the absence of field data regarding their transformation and deposition rates and the seasonal dependence of these rates, but this has been kept to a minimum in the discussion below. The situation is somewhat more complicated than for the sulfur oxides, because the behavior of more species must be considered. Thus, although anthropogenic emissions are primarily in the form of nitric oxide (NO), this compound is converted relatively rapidly to nitrogen dioxide (NO_2), nitric acid (HNO_3) and particulate nitrates, and peroxyacetyl nitrate (PAN) (see Spicer, 1979; Spicer et al., 1980). The chemical reactions and atmospheric deposition of each of these species will be considered separately below.

<u>Nitric oxide</u> has a very low solubility in water (Sherwood and Pigford, 1952). Since the rate of wet deposition, especially under the "equilibrium scavenging" conditions of relevance to long-range transport (Hales, 1978), is directly dependent on the solubility of the gas under consideration, the wet scavenging coefficient of NO is also expected to be low. As far as dry deposition is concerned, a number of investigators, working with different types of surfaces (see Table 7), have found the deposition velocity of NO to be very small--about one-tenth that for SO_2 over the same surface. Moreover, NO is oxidized to products fairly rapidly (in the order of a few hours) in the summertime, so the short lifetime and low wet and dry scavenging rates of this gas suggest that its contribution to deposition is small. Under wintertime conditions, at latitudes where photochemical reactions are of relatively little importance (see Section 3.1), the atmospheric lifetime of NO could be increased considerably, and the amount deposited by wet and dry removal processes could become important. However, no information is available on scavenging coefficients and deposition velocities of NO under these conditions, especially to snow surfaces.

Nitrogen dioxide is formed in the atmosphere mainly from the oxidation of NO by ozone and various free radicals (see, for example, Bottenheim et al., 1977; Calvert et al., 1978; Altshuller, 1979). It dissolves in water according to a fairly complex chemical mechanism (Sherwood and Pigford, 1952), the overall reaction being

$$2NO_2 + H_2O \Longleftrightarrow HNO_3 + HNO_2 .$$

As can be seen from the above reaction, the solubility of NO_2 will, like that for SO_2, depend on the acidity of the rain or cloud droplet, and laboratory experiments (Beilke, 1970) have shown the scavenging coefficient of NO_2 to be roughly one-quarter that for SO_2. Experiments on dry deposition rates of NO_2 to a number of surfaces have shown the deposition velocity of NO_2 to be roughly one-half that for SO_2 under comparable conditions (see Table 7). No wet and dry deposition data for NO_2 under wintertime conditions are available, especially to snow, but it seems reasonable that qualitatively the same differences in winter and summertime deposition behavior will obtain as for SO_2.

As far as atmospheric chemistry is concerned, NO_2 is formed so quickly from NO under summertime conditions that, in mathematical modeling of long-range transport (where time steps of the order of several hours are involved in the calculations), as a first approximation emissions can probably be assumed to consist of NO_2 (i.e., the role of NO as an independent precursor species of nitrates and PAN can be neglected). This may not be true under nighttime conditions, or in the winter at northerly latitudes, but the scope of this report does not allow for more detailed speculation on this point.

Nitric acid is now thought to be one of the major products of NO emissions (e.g., see Spicer, 1979; Spicer et al., 1980). Under typical atmospheric conditions, it exists mainly in the vapour form. However, it is a highly soluble vapour (e.g., Okita and Ohta, 1979), and potentially has a higher scavenging coefficient than that of SO_2 (no experimental data are available to verify this). There are also reports of unpublished experimental results, which suggest that, unlike SO_2, HNO_3 is scavenged very efficiently by snow. Thus, even though no experimental data are available on wet removal rates of HNO_3, one can speculate that the seasonal dependence of Λ for this substance is probably smaller than that for SO_2 (and its overall magnitude is larger). Similarly, because of the apparently high reactivity of HNO_3 with all types of surfaces, it would seem reasonable to assume that the total resistance to mass transport is approximately equal to the aerodynamic resistance (i.e., $r_s \ll r_a$ in Equation 11), and to use values calculated from micrometeorological theories (see, for example, Table 1 in Garland, 1978). This leads us to expect fairly small seasonal variations of the deposition velocity for HNO_3, probably smaller than those for SO_2.

Nitric acid can be formed by homogeneous reaction pathways, mainly by reaction with hydroxyl radicals, or in the droplet phase (Orel and Seinfeld, 1977; Middleton and Kiang, 1979). Homogeneous processes are relatively well-understood compared to the heterogeneous ones, and are probably more important during the daytime in summer, and display a similar seasonal dependence to those for SO_2 oxidation (see Section 3.1 and also Bottenheim and Strausz, 1980). Nitrogen oxides transformation rates of over 20% h^{-1} have been observed in urban plumes, most likely due to homogeneous reactions (Spicer, 1979), and power plant plume studies have also yielded nitrate formation rates several-fold those of sulfates (e.g., Forrest et al., 1980), which are consistent with a homogeneous reaction mechanism. Heterogeneous processes may be an important source of nitrates at night and in the winter (Middleton and Kiang, 1979), but too little reliable information is available on the chemistry involved to speculate on seasonal trends in the HNO_3 formation rate.

Particulate nitrates are probably formed by heterogeneous processes, and consist of a number of salts, with ammonium nitrate being one of the most important (Orel and Seinfeld, 1977; Middleton and Kiang, 1979). During the summertime, particulate nitrate concentrations are apparently relatively small compared to those of vapour phase nitric acid (e.g., see Spicer, 1979; Spicer et al., 1980; Tang, 1980). During the winter, especially at northern latitudes, the reverse could be true, but due to difficulties involved in sampling HNO_3 and particulate nitrates separately, insufficient data are available to answer this question. Little can be said about the wet and dry deposition of nitrates and its seasonal dependence. In the absence of experimental data, one might postulate a behavior similar to that of sulfates. As far as chemical formation rates are concerned, some theoretical estimates suggest that wintertime rates for particulate nitrate may be considerably greater than those in the summer (Middleton and Kiang, 1979), but again, this result requires experimental verification.

The other major nitrate product to be considered is peroxyacetyl nitrate. This substance is stated by Hill (1971) as being "relatively insoluble," and Garland and Penkett (1976) found negligible PAN uptake rates by water in a wind tunnel. This suggests a relatively low value of the scavenging coefficient. The dependence of PAN solubility on the temperature, and the nature of its interactions with snow, are unknown; therefore, we will not speculate on the seasonal dependence of its wet scavenging rate. Some data are available on the dry deposition rate of PAN over a number of surfaces (Table 7), and, with the exception of water, the PAN deposition velocity seems to be about one-third that for SO_2. Again, due to lack of supporting data, speculation on the seasonal dependence of the PAN dry deposition rate is not possible.

As far as chemical formation rates are concerned, PAN is the product of photochemical reactions involving peroxyacetyl radicals and NO_2:

$$CH_3CO(O_2) + NO_2 \Longleftrightarrow PAN \, .$$

The proportion of PAN and HNO_3 appearing in the irradiated, polluted air mixture depends on the level of hydrocarbons present in the mixture (Spicer et al., 1980), but limited field measurements suggest that the two products can exist in comparable amounts (e.g., Spicer, 1979). Thus, PAN formation rates are expected to be several percent per hour under conditions where photochemical reactions are important. As far as the seasonal dependence of the PAN formation rate is concerned, one would expect it to be qualitatively similar to that resulting from the photochemical components of the sulfuric and nitric acid formation rates (see also Bottenheim et al., 1977), but it must be noted that the PAN formation reaction (see above) is reversible. The stability of PAN is a strong function of the temperature, and its atmospheric half-life at 275°K is about two orders of magnitude greater than that at 305°K

(Hendry and Kenley, 1979). This will offset some of the seasonal dependence in net PAN formation rate due to photochemical reactions alone, but quantitative conclusions are not possible at present.

Table 7 summarizes the published data on wet and dry deposition rates that we are aware of. Also shown are some of the chemical transformation rates that have been measured in field experiments.

5. Conclusions

A literature survey has been carried out into the seasonal variations of the wet and dry deposition rate, as well as the chemical transformation rate, of sulfur and nitrogen oxides, with particular reference to deposition and transformation parameters of relevance to long-range transport mathematical models. Both relevant theoretical and experimental results have been considered, although a critical evaluation of the references has not been attempted.

As indicated in Chapters 2, 3, and 4, from a theoretical viewpoint, the deposition and transformation rates of sulfur and nitrogen compounds could potentially have a substantial seasonal variation. However, it is difficult to draw conclusions about the magnitude of this variation with any degree of confidence from the current theories, with the possible exception of the wet and dry deposition of sulfur dioxide and the photochemical component of its chemical transformation rate. Therefore, the available field data were also considered, although these were often too scanty to be of much assistance.

An attempt is made in Table 8 to summarize the available information on the seasonal variation of transformation/deposition rates for the sulfur compounds. It is not intended to recommend the values shown in this table for use by the long-range transport modeller--much more experimental and theoretical work is needed before this will be possible--but, rather, to indicate whether seasonal changes in the parameter of interest are expected to be greater or less than an order of magnitude (at present, little more than this can be done). The following conclusions can be made on the basis of Table 8 and the discussions in Chapters 2 to 4:

Table 7. Deposition and Chemical Transformation Rates for Nitrogen Compounds

Compound	Parameter	Rate	Reference	Comments
NO_2		$NO_2 \approx \frac{1}{4} SO_2$	Beilke (1970)	
	v	0.3 to 0.8 cms^{-1}	Judeikis and Wren (1978)	Soil, cement surfaces. For the same surfaces, deposition velocities for SO_2 were in the range of 0.3 to 2.5 cms^{-} with most values around 1 cms^{-1}.
		1.9 cms^{-1}	Sehmel (1980)	Alfalfa canopy, calculated from experiments of Hill (1971). For the same canopy, deposition velocity for SO_2 was 2.7 $cms^{-1.2}$.
		0.05 to 0.6 cms^{-1}	Wesely et al. (1981)	Nighttime and maximum daytime eddy correlation measurements, respectively, at 5 m above a soybean field.
NO	v	0.1 to 0.2 cms^{-1}	Judeikis and Wren (1978)	Soil, cement surfaces. See comments for NO_2 above.
		0.1 cms^{-1}	Sehmel (1980)	Alfalfa canopy. See comments for NO_2 above.
PAN	v	0.8 cms^{-1}	Sehmel (1980)	Alfalfa canopy. See comments for NO_2 above.
		0 0.25 cms^{-1}	Garland and Penkett (1976)	Water. Grass and soil surfaces.

Table 7. Deposition and Chemical Transformation Rates for Nitrogen Compounds (cont.)

Compound	Parameter	Rate	Reference	Comments
HNO_3	Conversion rate from NO_x	3 to 10 times SO_2 conversion rate	Richards et al. (1980)	Daytime measurements, Navajo generating station, plume (Arizona); June-July and December
HNO_3 and partiulates nitrates	Conversion from NO_x	0.1 to 3% h^{-1} (nighttime) 3 to 12% h^{-1} (daytime)	Forrest et al. (1980)	Cumberland coal-fired generating station, August. NO_x conversion rate was 2 to 4 times SO_2 rate.
NO_x	Removal rate	14 to 24% h^{-1}	Spicer (1979)	Boston urban plume, August.
NO_x	Removal rate	4% h^{-1}	Chang et al. (1979)	Annual average, Los Angeles.

Summary of Deposition and Chemical Transformation Rates for Sulfur Compounds

Parameter	Representative Range (Observed) Summer Conditions	 Winter Conditions	Suggested (Winter/Summer) Ratio	Comments
$\Lambda (s^{-1})$ Sulfates	$\sim 10^{-5}$	$\sim 10^{-5}$	~ 1	washout: based on very few data
			10^{-1}(?)	rainout: order-of-magnitude seasonal variation could be possible, depending on storm types (e.g., Scott, 1981)
$\Lambda (s^{-1}) SO_2$	$(3-8) \times 10^{-4}$	$(1-25) \times 10^{-7}$	$\sim 10^{-3}$	rainout: based on data of Summers (1977); applies to areas where wintertime precipitation is largely in the form of dry snow
			~ 10(?)	theoretically predicted possibility for areas which largely receive cold rain or wet snow during the winter
$v(cms^{-1})$ Sulfates	(?)	<0.2	(?)	very large uncertainty about deposition velocity for sulfates
$v(cms^{-1})$ SO_2	0.4 to 0.8	0.1 to 0.4	$\sim 1/2$	seasonal changes expected to be modest (i.e., not order-of-magnitude)
$SO_2 \longrightarrow SO_4$ transformation rate h^{-1}	1 to 4 (chimney plumes) 1 to 30 (urban plumes)	<1 (chimney plumes) 1 to 25 (urban plumes)	(?)	gas-phase homogeneous processes should be small at latitudes greater than 45°N in the winter. However, there is too much uncertainty about the magnitude of heterogeneous processes, including in-cloud SO_2 conversion, to allow conclusions about seasonal variations

1. The scanty available data suggest that the washout rates of sulfates (and probably nitrates) should be comparable in summer and winter. The rainout rates could be strongly dependent on storm type, and hence the time of year, because of the different mechanisms whereby particles can be incorporated into precipitation (some data suggest variations of an order-of-magnitude or more).

2. Experimental results and theoretical considerations suggest a seasonal variation of the wet scavenging coefficient for sulfur dioxide, which can be up to several orders of magnitude, depending on the latitude, being most pronounced in the northern parts of America that receive appreciable amounts of snow in the winter. Probably the same conclusions also apply to nitrogen dioxide. Nitric acid vapour, being highly reactive with all kinds of surfaces, is expected to show a smaller seasonal dependence of the scavenging coefficient.

3. The situation is too confusing at present to draw any conclusions about the seasonal dependence of the dry deposition rate for sulfates (or nitrates). In the winter, deposition velocities would seem to be 0.2 cms^{-1} or less, but values reported for summertime conditions range over an order of magnitude, including negative numbers.

4. The dry deposition velocity of sulfur dioxide is expected, from available experimental and theoretical results, to show only a modest seasonal variation--generally, less than a factor of two or so in any given area. The same is probably true of nitrogen dioxide and nitric acid vapour.

5. The gas-phase homogeneous component of sulfuric and nitric acid formation rates is relatively well-understood and has a strong seasonal variability, especially at the northern latitudes. However, our knowledge of the heterogeneous component, including in-cloud processes, is too poor at present to allow any conclusions regarding the seasonal dependence of the overall chemical transformation rate of sulfur and nitrogen oxides.

6. For many of the parameters under consideration, during the winter months, rates are strongly dependent on latitude--e.g., photochemical conversion rates of sulfur and nitrogen oxides above 45°N become negligible, as do also wet deposition rates of gases such as sulfur dioxide (because precipitation is largely in the form of dry snow). This indicates that not only the seasonal, but also the spatial variability of deposition and transformation rates should be taken into account in long-range transport models. Although it may be too early to speculate, the following approach does not seem unreasonable: during the summer months, one might assume, as a first approximation, the same values for deposition/transformation parameters regardless of location, for each species of interest. During the winter months, while rates at the southerly latitudes might stay roughly the same as those in the summer, the models would include a dependence of deposition/transformation on latitude, which could be quite pronounced for some of the parameters (such as wet deposition of sulfur dioxide).

7. For the sulfur compounds, more experimental data are badly needed, both under summer and wintertime conditions, particularly on wet and dry deposition rates of particulates and chemical transformation rates in regional scale air masses (as opposed to chimney plumes). Very little is also known about in-cloud transformation and deposition processes. For the nitrogen compounds, data are required in almost every area of interest, and immediate support for laboratory and field investigations into deposition and transformation rates of the major species (NO, NO_2, HNO_3, nitrates, and PAN) is strongly recommended.

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Paper No. 3:

DRY DEPOSITION OF ACID SUBSTANCES

Executive Summary
from
EPA Critical Assessment Document on Acid Deposition

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DRY DEPOSITION OF ACID SUBSTANCES

Recent workshops and committee deliberations have agreed that it is not possible to monitor the dry deposition of acidic atmospheric materials directly. Several factors combine to cause this problem. Flat plate collectors, buckets, and other similar devices fail to collect small particles in a manner that can be related in a direct fashion to natural circumstances. Moreover, these artificial collecting devices give no indication of the rate of gaseous deposition, especially of species such as SO_2 and vapor phase HNO_3 that are likely to contribute significantly to the net acidic flux. However, it is possible to measure the flux of some airborne quantities by micrometeorological means (e.g., Droppo, 1980; Shepherd, 1974; Fowler, 1978; Wesely et al. 1977), without interfering with the natural processes involved. These studies, and laboratory and wind tunnel investigations (Chamberlain, 1967; Hill, 1971; etc.), provide convincing evidence that the controlling properties in the deposition of many gaseous pollutants are associated with surface structure, rather than with atmospheric properties. Exceptions to this generalization are the nocturnal case and the winter-time case in which atmospheric stability may often be sufficient to impose a severe restriction on the rate of delivery of all airborne quantities to the surface below.

Recent field studies investigating the fluxes of small particles have also confirmed wind tunnel results which point to a surface limitation. Studies of the rate of deposition of particles to the internal walls of pipes (e.g., Friedlander and Johnstone, 1957) and investigations of fluxes to surfaces more characteristic of nature, exposed in wind tunnels, tend to confirm theoretical expectations that surface uptake is controlled by the ability of particles to penetrate a quasi-laminar layer adjacent to the surface in question. The mechanisms that limit the rate of transfer of particles involve their finite mass. Particles fail to respond to the high frequency turbulent fluctuations that cause transfer to take place in the immediate vicinity of a surface. However, the inertia of particles also causes an inertial deposition phenomenon that serves to enhance the rate of deposition of particles in the 10 to 20 μm size range (q.v. Slinn, 1976).

The general features of the question of particle deposition to smooth surfaces are fairly well understood. All studies conducted so far support the theoretical expectation that particles smaller than about 0.1 μm in diameter will be deposited at a rate that is largely determined by the Brownian motion of the particles concerned. In this instance, the limiting factor is the transfer by Brownian motion across the quasi-laminar layer referred to earlier. On the other hand, particles larger than around about 5 μm in diameter are effectively transferred via gravitational settling, at rates determined by the familiar Stokes-Cunningham formulation. Particles in the intermediate size ranges are transferred very slowly. In terms of the deposition velocity, v_d, defined as the ratio of the flux to the concentration at some convenient height, the minimum value of the "well" of the deposition velocity versus particle size curve is approximately 0.0001 cm/s.

However, natural surfaces are rarely aerodynamically smooth. Wind tunnel studies have shown that the well in the deposition velocity curve is filled in as the surface becomes rougher (see Sehmel, 1980). Although studies have been conducted, in wind tunnels, of deposition fluxes to surfaces such as gravel, grass, and pieces of foliage from trees and shrubs, the situation involving natural vegetation such as corn, or even pasture, remains uncertain. It is well known that many plant species have foliage with exceedingly complicated microscale surface roughness features. In particular, leaf hairs have been shown to increase the rate of particle deposition in wind tunnel studies (Chamberlain, 1967), and it has been postulated that their influence in natural circumstances might be considerable. Other factors, such as electrical charges associated with foliage and stickiness of the surface, have also been investigated. In every case, there is evidence that at least in some circumstances, a natural canopy might be considerably different from the simplified surface that is suitable for investigation in laboratory and wind tunnel investigations.

It is frequently emphasized that caution should be taken in extending laboratory studies using artificially produced aerosol particles to the situation of the deposition of acidic quantities. Special concern is associated with the hygroscopic nature of many acidic species. At humidities that are frequently attained near vegetated surfaces, these hygroscopic particles will become liquid. Their growth as they enter into a region of high humidity, and their liquid nature when they impact upon the surface, are both potentially important factors that might work to increase otherwise small deposition velocities. Moreover, there is evidence that suggests that acidic particles, especially sulfates, might be carried by larger particles, sometimes graphitic in nature (q.v., the laboratory studies of Cofer et al., 1981). The rates of deposition of such complicated particle structures are essentially unknown. However, it is known that the shape of particles can have a considerable influence upon their gravitational settling speed (Chamberlain, 1975).

It is not clear to what extent special considerations appropriate for acidic species, such as those mentioned above, contribute to the finding of unexpectedly high deposition velocities for atmospheric sulfate particles, as reported in some recent North American studies (Hicks and Wesely, 1980; Everett et al., 1979; Sievering, 1981). It is especially intriguing that European experience has failed to produce these high values, which have sometimes been reported to be as high as several cm/s. European work has been fairly uniform in producing deposition velocities closer to 0.1 cm/s, while North American experience has been in favor of larger values. It has been postulated that the difference is due to the predominance of aged aerosol in the North American situation, with much more sulfate material present on larger particles. In this scenerio, the net flux of sulfate material is seen to be dominated by the rapid transport of a few larger particles, which particles are not likely to be found in the nearer-source European situation. However, it should be emphasized that the small amount of evidence that is presently available provides no convincing basis for any arguments of this kind.

It is informative to consider the flux of any airborne quantity to the surface underneath in terms of an electrical analog, the so-called resistance model developed initially in studies of agrometeorology (e.g., see Fowler, 1978). In this model, we identify the flux of the atmospheric property in question with the flow of electrons in an electrical circuit, in which individual resistances can be associated with readily identifiable atmospheric and surface properties. While the electrical analogy has obvious shortcomings, it permits an easy visualization of many contributing processes and enables a comparison of their relative importance. Micrometeorological support the theoretical expectation that particles smaller than about 0.1 μm in diameter will be deposited at a rate that is largely determined by the Brownian motion of the particles concerned. In this instance, the limiting factor is the transfer by Brownian motion across the quasi-laminar layer referred to earlier. On the other hand, particles larger than around about 5 μm in diameter are effectively transferred via gravitational settling, at rates determined by the familiar Stokes-Cunningham formulation. Particles in the intermediate size ranges are transferred very slowly. In terms of the deposition velocity, v_d, defined as the ratio of the flux to the concentration at some convenient height, the minimum value of the "well" of the deposition velocity versus particle size curve is approximately 0.0001 cm/s.

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The same conceptual model can be applied to the case of particle transfer with considerable utility. While the roles of factors such as stomatal opening become less clear when particles are being considered, the concept of a residual surface resistance to particle uptake appears to be rather useful. Studies of the transfer of sulfate particles to a pine forest have shown that this residual surface resistance is of the order of 1 to 2 s/cm, with a standard error margin of approximately 25% (Hicks and Wesely, 1980). A similar value has been identified for the transfer of small particles (about 0.1 μm) to pasture (Wesely et al., 1977). Sheih et al. (1978) have assumed a constant value for this surface resistance in estimating spatial and temporal variations of deposition velocities of sulfate particles across North America. Their analysis of sulfur dioxide deposition utilized the equivalent concept of stomatal resistance. In retrospect, their assumption of a constant value for sulfate surface resistance appears somewhat bold. In particular, it now appears likely that substantially larger values for residual surface resistance will be appropriate for non-vegetated surfaces, especially to snow, in which case values are more likely to be approximately 15 s/cm. At this time, an exceedingly limited quantity of field information is available; however, it appears that in North American conditions the surface resistance to uptake of sulfate particles is likely to take values in the range of 1.5 to 15 s/cm.

While sulfate particles have received most of the recent emphasis, the general question of acid deposition requires that equal attention be paid to nitrate and ammonium particles. There is no information regarding the deposition velocity of these particles, but likewise there is no strong indication that they are different from the case of sulfate.

Regarding trace gas uptake, sulfur dioxide has received the majority of recent attention. The ordered set of results produced by Hill (1971) provides a means for comparing the deposition velocities of a range of trace gases. Some of the quantities considered by Hill have also been investigated in recent field studies (e.g., Wesely et al., 1981). Some recent wind tunnel studies are also relevant in this regard. These results are combined in Table 1, where it is seen that highly reactive materials such as hydrogen fluoride (and presumably iodine vapor, nitric acid vapor, etc.) are readily taken up by a vegetative surface. A second set of pollutants, including SO_2, NO_2, and O_3 (also taken up through stomates), also seems to be easily transferred (presumably via stomates); and a third category of relatively unreactive trace gases are poorly taken up by vegetation.

Transfer to water surfaces presents special problems, especially when the surface concerned is snow. As mentioned above, surface resistances to particle uptake by snow are likely to be of the order 15 s/cm. Soluble gases will be readily absorbed by all water surfaces, and so equivalence with transfer of water vapor might be expected. An important exception occurs in

TABLE 1

Resistances to deposition of selected trace gases, measured for solid surfaces in a cylindrical flow reactor (Judeikis and Stewart, 1976) and for alfalfa in a growth chamber (Hill, 1971). Solid-surface data are derived from Table 2 of Judeikis and Wren (1978). The alfalfa values are obtained from Table 1 of Hill (1971). Resistances (in s cm^{-1}) refer to transfer between air contained in the vessel and the substrate; they, therefore, represent only part of the overall transfer process, but in many instances other resistances will be small in comparison to the values given here.

	Substrate surface		
Pollutant	Adobe clay	Sandy loam	Alfalfa
CO	-	-	∞
H_2S	62	67	-
$(CH_3)_2S$	3.6	16	-
NO	7.7	5.3	10
CO_2	-	-	3.3
O_3	-	-	0.7
NO_2	1.3	1.7	0.5
Cl_2	-	-	0.5
SO_2	1.1	1.7	0.4
HF	-	-	0.3

the case of SO_2, in which case absorbed SO_2 can increase the acidity of the surface moisture layer to the extent that further SO_2 transfer is cut off. Work by Liss and coworkers addressing the case of trace gas transfer to liquid water surfaces shows a clear influence of the Henry's Law constant as a determining factor (Liss and Slater, 1974). For readily soluble gases the evaporation analogy appears adequate in most cases, an assumption that leads to rather simple descriptions of deposition velocity as functions of windspeed (as done by Hicks and Liss, 1976).

Wind tunnel studies of particle transfer to water surfaces all show exceedingly small deposition velocities of particles in the 0.1 to 1 μm range. Several workers have suggested mechanisms by which larger deposition velocities might exist in natural circumstances. Slinn and Slinn (1980) suggest that the growth of hygroscopic particles in highly humid, near-surface air can cause accelerated deposition of such particles. On the other hand, Hicks and Williams (1980) suggest that breaking waves might provide a route for transfer that bypasses the otherwise limiting quasi-laminar layer in contact with the surface. Once again field observations are lacking.

One of the few sets of field data that is available (Wesely and Williams, 1980) shows clear differences in general behavior patterns for very small particles of the order 0.05 to 0.1 μm diameter, and optically active particles of size about 0.6 μm. The cause for much of the difference in behavior is assumed to be the production of particles by breaking waves themselves. The net consequences on deposition of atmospheric acidic materials to underlying water surfaces is not clear.

While large deposition velocities of soluble trace gases to open water surfaces appear quite likely, water bodies are frequently sufficiently small that the large expectations cannot be achieved. Air blowing from warm land across a small cool lake, for example, will not rapidly equilibrate with the smooth, cooler surface. Flow will then be largely laminar, with the consequence that very small deposition velocities will apply for all atmospheric quantities. In many circumstances, especially in daytime summer occasions, deposition velocities are likely to be so small as to be disregarded for all practical purposes. On the other hand, during winter, when the land surface is likely to be cooler than the water itself, rapid equilibrium with the water surface is likely to be achieved and rather high deposition velocities, in agreement with the open water surface expectations, are likely to be attained.

An associated special case concerns the effect of dewfall. Processes of diffusiophoresis and Stephan flow combine to cause a net transfer of trace gases and particles in circumstances in which condensation is occurring. The velocities of deposition involved are small; however, they do permit an accumulation of material at the surface in conditions in which the atmospheric considerations are likely to predict minimal rates of exchange (i.e., limited by stability to an extreme extent). When surface fog layers exist, the highly humid conditions near the surface will permit airborne hygroscopic particles to nucleate and grow rapidly. The process provides a mechanism for cleansing the lower layers of the atmosphere of most acidic airborne particles. The small fog droplets that are formed around the hygroscopic acidic nuclei are removed by the classical process of fog interception, to foliage and other surface roughness elements.

All of the many deposition processes considered above have aspects that are strongly surface dependent. While broad generalities can be made about the velocities of deposition of acidic species in areas of North America, there will be wide temporal and spatial ranges of deposition velocity within any such region. The detailed nature of the vegetation covering the surface is often a critical consideration. If acidic inputs to special sensitive areas need to be estimated, then this can only be accomplished if the depositional characteristics specific to the vegetation cover of the area in question are taken into account in an adequate manner.

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Paper No. 4

PRECIPITATION SCAVENGING PROCESSES

Executive Summary
from

EPA Critical Assessment Document
on Acid Deposition

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PRECIPITATION SCAVENGING PROCESSES

The complex process of precipitation scavenging can be subdivided into a number of distinct steps, which occur interactively within a composite storm system. These are itemized as follows:

- intermixing of pollutant and condensed water within the same airspace,
- attachment of pollutant to the condensed water elements,
- chemical reaction of pollutant within the aqueous phase, and
- delivery of pollutant-laden water elements to the surface via the precipitation process.

Each of these steps can be associated with a corresponding processing time that is dependent upon the pollutant, synoptic circumstances, and storm type. In the most simple sense the scavenging process occurs as a forward progression through these steps; reverse processes are common, however, and a pollution element may experience several cycles through segments of this process before its ultimate wet deposition to the earth's surface.

Circumstances often exist wherein one or more of the above steps occur considerably more slowly than the rest. Under such conditions these steps dominate the processing time of the scavenging phenomenon; these are known as rate-limiting steps. Individual processing times, as noted previously, are strongly dependent upon pollutant type and meterological conditions; these are discussed sequentially in the following paragraphs.

Pollutant-condensed-water intermixing, the process that introduces pollutant to the immediate vicinity of cloud and precipitation systems, can involve considerable time lags between a pollutant's emission and its subsequent processing by the strom. Usually it is not cloudy or raining in the vicinity of a pollutant's release point, and often several days may occur before a storm is encountered. During this period the pollutant may become involved in a variety of processes (e.g., dry deposition, chemical reaction) that may alter its concentration and physical state, and consequently alter its scavenging characteristics once a storm is encountered. Thus, while the storm-pollutant intermixing process is not usually considered totally within the realm of wet removal, it is a highly important determinant of scavenging time and distance scales and the resulting chemical composition of precipitation.

Estimates of time scales for the storm-pollutant intermixing processes can be obtained from airflow, storm-frequency and budget analyses using a variety of methods. Several statistical-climatological characterizations of these processes are available in the current literature.

The actual physical attachment of pollutant to condensed water elements (ice, cloud droplets, rain) is highly dependent upon both the physical and chemical states of the pollutant. For aerosol particles any or all of the following collection mechanisms may be active:

- nucleation of cloud droplets on the pollutant particles,
- electrical attachment,
- diffusiophoretic and thermophoretic attachment,
- Brownian motion, and
- inertial attachment.

All mechanisms in the above list are dependent upon particle size, and usually several mechanisms operate simultaneously to provide a composite capture process in given situations.

Diffusional and convective transport are the primary attachment mechanisms for gaseous pollutants. Gas scavenging differs from aerosol scavenging in the important respect that gases may desorb from as well as absorb in cloud particles and hydrometeors. Thus relative rates of absorption and desorption often determine to a large extent the net efficiency of attachment, and for this reason gas solubility emerges as an important factor in the scavenging process.

The current section deals only briefly with the aqueous-phase reaction step, owing to the fact that it is treated elsewhere within this document

It should be stressed, however, that although reaction is not <u>necessary</u> for scavenging to occur, it often emerges as an important rate-limiting step. This importance stems primarily from chemical conversion's capability, in some circumstances, of devolatizing absorbed gaseous pollutants and thus inhibiting their tendency for desorption noted earlier. The conversion of dissolved SO_2 to sulfate is an important example.

The final stage of the composite scavenging process is the actual wet delivery of pollutant to the ground. This step is linked closely to rain formation and precipitation processes and thus depends strongly upon the variety of cloud-physics phenomena commonly associated with water extraction. These include autoconversion of cloud elements to form precipitation, accretion and condensation processes, and a host of ice-formation phenomena. The kinetics of such processes often have a significant influence on the rate of the overall scavenging process.

Areal deposition by storm systems is strongly dependent on climatological features of the storms themselves. Although a detailed treatise on North American storm climatology is well beyond the scope of this work, some limited insight in this regard may be gained by a partial classification of storm types and a climatological analysis of storm tracks. Important storm types in this regard include cyclonic or "frontal" storm systems and convective storms. Orographic and lake-effect storms are also important in particular localities, although these are relatively insignificant on an average continental basis. Climatological aspects of both convective and frontal storm types are presented in the existing literature, and climatological maps of cyclonic storm tracks are also available.

Much of what is known presently with regard to precipitation scavenging has been learned as a consequence of field studies. Beginning during the early 1950s in England and Europe, these studies have expanded from simple investigations of simulated plumes to include power-plant plumes, airborne tracer-injection experiments, urban plumes, and regional phenomena. The most comprehensive scavenging experiment pertaining to acidic substances performed to date has been the Oxidation and Scavenging Characteristics of April Rains, which extended throughout the northeastern sector of the U.S. and into southern Canada.

Pertinent field experiments are summarized in tabular form in this section.* Although it is impossible to adequately summarize the results of this ensemble of studies here, several key aspects may be noted with regard to the efficiency of wet removal of commonly emitted pollutants. Starting with the local scale, it generally has been observed that SO_x emitted from power-plant stacks is removed with low efficiency by storms occurring near the source. This is true also for NO_x, and in fact there are very few local plume measurements that have detected any rainborne NO_x whatsoever above background. This situation seems to change as atmospheric residence times increase to mesoscale proportions. Studies of urban-plume scavenging, for example, have observed several tens of percent of the SO_x pollutant burden to be removed in the 0 to 100 km range, with lesser but still significant removals of NO_x. On a regional scale an inversion seems to occur, wherein the wet-removal of NO_x is actually greater (in proportion to its regional emission rate) than that from SO_x. Although the competing effects of dry deposition probably play an important role in influencing this behavior, the general increase of wet deposition with scale provides a strong indication that the atmospheric aging process has a significant influence on precipitation scavenging efficiency.

Mathematical models of precipitation scavenging tend to reflect the stepwise sequence discussed above. Based upon conservation equations for pollutant material, these models are similar in many respects to typical air pollutant models, but differ in the sense that they must account for gas-liquid exchange and wet delivery. A profusion of different wet removal models is currently available, and is presented in tabular form in this section.* Despite this abundance of models, however, there is still a strong need for reliable techniques for characterizing wet removal with adequate precision. The relatively poor predictive capability of present models stems from a lack of knowledge regarding attachment and chemical conversion processes, as well as from the difficulty in providing an adequate mathematical characterization of the complex dynamical behavior of storm systems. Much remains to be accomplished in this research area before a really satisfactory modeling capability is obtained.

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*Reference is to complete original document.