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SULCAL:
A MODEL of SULFUR CHEMISTRY in a PLUME

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ORNL
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—
Ecology and Analysis
of
Trace Contaminants
Program

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SULCAL: A MODEL OF SULFUR CHEMISTRY IN A PLUME

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ABSTRACT

A computer program has been written that models the following features of the chemical behavior of sulfur emitted to the atmosphere from fossil-fuel burning power plants: (1) the rapid reactions of SO_2 with aerosol droplets to produce the dissolved sulfite species H_2SO_3, HSO_3^- and SO_3^{2-}; (2) the rapid reactions of SO_3 to produce the dissolved sulfate species HSO_4^- and SO_4^{2-}; (3) the neutralization of the acid thus produced by atmospheric ammonia and (4) the eventual formation of particulate ammonium sulfate; (5) the slow oxidation of SO_2 to sulfate species by hydroxyl radical, and (6) the slow oxidation of species of SO_2 in aerosol droplets to sulfate species by dissolved ozone and oxygen. The model employs averaged concentrations based on the Gaussian plume and can calculate deposition rates for gaseous and particulate material as a function of such variables as distance from the source, wind speed, meteorological stability class, temperature, relative humidity, and the ambient concentrations of OH radical, ozone, and ammonia.

1. INTRODUCTION

Industrially produced sulfur enters the atmosphere in reactive forms, primarily SO_2 and SO_3, that cannot be treated as inert substances while they remain in the atmosphere. This report describes a stand-alone model of atmospheric transport which includes the effects of (1) rapid chemical reactions that produce new species and (2) slow reactions by which SO_2 or its products from rapid reactions are oxidized to sulfates in various forms. As shall be seen, the most important consequence of these reactions is the production of an aerosol of liquid acidic droplets; hence, one object of the calculation is to estimate the amount and composition of the aerosol in a unit volume of the plume and its deposition rate. The model was developed for use as a sub-model in the Air Transport Model (ATM).[1]

1.1 The Rapid Reactions of Sulfur

Both gaseous SO_2 and SO_3 can undergo rapid chemical reactions with constituents of the atmosphere. Gaseous SO_2 can dissolve in aerosol droplets producing the following products in solution:*

$$SO_2(g) + H_2O(aq) \rightleftarrows H_2SO_3(aq) , \qquad (1)$$

$$H_2SO_3(aq) \rightleftarrows H^+ + HSO_3^- , \qquad (2)$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^{2-} . \qquad (3)$$

These reactions are reversible as well as rapid and as a result the concentration of the species involved are related to one another by

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*The abbreviations (g), (aq), and (c) used in chemical reactions denote species in the gaseous, aqueous, or solid states, respectively.

equilibrium constants (i.e., K_1, K_2, and K_3 in Table I) that have known values[2] as a function of temperature. These, and the other equilibrium constants in Table I, include in their expressions a quotient of so-called activity coefficients (g_i) which, as shall be seen, are functions of the composition of the solution involved. (The activity coefficients reflect the non-ideal behavior of the individual ions in the solution.) The tendency of SO_2 to form the aqueous species H_2SO_3, HSO_3^-, and SO_3^{2-} is weak and at the low concentrations of SO_2 in the atmosphere (usually <0.1 ppm) reaction occurs only if condensed water is already present.

In contrast, gaseous SO_3 reacts vigorously and completely with water, even in the gaseous form, to produce acid droplets

$$SO_3(g) + H_2O(g) \rightarrow H^+ + HSO_4^- \ .$$

The bisulfate ion HSO_4^- undergoes rapid and reversible dissociation,

$$HSO_4^- \rightleftarrows H^+ + SO_4^{2-} \ . \qquad (4)$$

As a result, no trace of SO_3 gas is found in the atmosphere. If it is introduced, it is converted completely to acid droplets containing the ions H^+, HSO_4^- and SO_4^{2-}, the concentrations of which are related to one another by K_4 (Table I).

The acid (H^+) produced by the solution of SO_2 and SO_3 in water can be neutralized by atmospheric ammonia in another set of rapid and reversible reactions, producing the aqueous ammonium ion,

$$NH_3(g) \rightleftarrows NH_3(aq) \ , \qquad (5)$$

$$NH_3(aq) + H^+ \rightleftarrows NH_4^+ \ , \qquad (6)$$

and K_5 and K_6 apply. These reactions can lead to the formation of particles of ammonium sulfate, $(NH_4)_2SO_4$, if they proceed far enough and the relative humidity is less than ~83%. When both liquid and solid are

Table I Equilibrium Constants[a]

Text Symbol[b]	Definition[b]	Log K(25°C)	Log K=A+B/T(K)		Program Name
			A	B	
K_1	$= \frac{[H_2SO_3]}{P_{SO_2} a_w}$	0.090	-4.4912	1365.9	EKS
K_2	$= \frac{[H^+][HSO_3^-]}{[H_2SO_3]} \cdot \left(g_{H^+}\, g_{HSO_3^-}\right)$	-1.765	-4.815	909.4	EK1S
K_3	$= \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} \cdot \left(\frac{g_{H^+} g_{SO_3^{2-}}}{g_{HSO_3^-}}\right)$	-7.220	-8.8549	487.36	EK2S
K_4	$= \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} \left(\frac{g_{H^+} g_{SO_4^{2-}}}{g_{HSO_4^-}}\right)$	-1.994	-5.8348	1145.2	EK3S
K_5	$= \frac{[NH_3]}{P_{NH_3}}$	1.756	-4.233	1785.5	EKN
K_6	$= \frac{[NH_4^+]}{[NH_3][H^+]} \left(\frac{g_{NH_4^+}}{g_{H^+}}\right)$	9.251	0.1026	2727.5	EK1N

Table I (continued)

Text Symbol[b]		Definition[b]	Log K(25°C)	Log K=A+B/T(K)		Program Name
				A	B	
K_7	=	$[NH_4^+]^2[SO_4^{2-}](g_{NH_4^+}^2 g_{SO_4^{2-}})$	-0.221[c]	0.929[c]	-343.1	EKSS
K_8	=	$\frac{[H_2CO_3]}{P_{CO_2} a_w}$	-1.462	-5.0160	1059.74	EKC
K_9	=	$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} (g_{H^+} g_{HCO_3^-})$	-6.368	-5.0300	-398.85	EK1C
K_{10}	=	$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \left(\frac{g_{H^+} g_{CO_3^{2-}}}{g_{HCO_3^-}}\right)$	-10.328	-7.7260	-775.85	EK2C
K_{13}	=	$\frac{[O_3]}{P_{O_3}}$	-2.146[d]	-8.488[d]	1891[d]	EKOZ
K_w	=	$\frac{[H^+][OH^-]}{a_w}$	-14.00	-4.2134	-2916.54	EKW
$P^\circ_{H_2O}$	=	$\frac{P_{H_2O}}{a_w}$	-1.505	6.2057	-2298.9	PWO

[a] Numerical values are based on NBS Technical Note 270-3, *et seq*[2] unless otherwise indicated and should represent K values with adequate accuracy from 0 to 40°C.

[b] Subscript on K refers to Eq. No. in text; concentrations of species in solution [i] are in molal units (mmol/g H_2O); gas pressures P_i are in atmospheres; activity coefficients of ions g_i are calculated as described in Appendix C.1.

[c] Adjusted to give the observed solubility of $(NH_4)_2SO_4$ in water.

[d] Based on data of Rowson quoted in Seidell,[17] Vol. II, p 1240.

present, the following equilibrium (and K_7) applies,

$$(NH_4)_2SO_4\ (c) \rightleftarrows 2NH_4^{+} + SO_4^{2-}\ . \qquad (7)$$

Another atmospheric gas that can affect the acidity (pH) of aerosol droplets is CO_2.

$$CO_2(g) + H_2O(aq) \rightleftarrows H_2CO_3(aq)\ , \qquad (8)$$

$$H_2CO_3(aq) \rightleftarrows H^{+} + HCO_3^{-}\ , \qquad (9)$$

$$HCO_3^{-} \rightleftarrows H^{+} + CO_3^{2-}\ . \qquad (10)$$

All three reactions are rapid and reversible and the concentrations of the species involved are related by K_8, K_9, K_{10}.

1.2 The Slow Oxidation of SO_2

The slower reactions to be considered are those by which SO_2 and some of the products of its rapid reactions (all of which are species of tetravalent sulfur) are oxidized to sulfate (hexavalent sulfur) species in the atmosphere. The direct oxidation of SO_2 by atmospheric oxygen

$$SO_2(g) + 1/2\ O_2(g) \rightarrow SO_3(g)\ ,$$

(followed instantly by reaction of SO_3 with H_2O) is slow and proceeds by a photochemical path. More rapid oxidation can occur by at least three other paths.

Recently Castleman et al[3] and Davis and Klauber[4] have concluded that the most rapid reaction involving a gaseous oxidant is that with the hydroxyl (OH) radical,

$$SO_2(g) + OH(g) \rightarrow \text{products}. \qquad (11)$$

The rate expression and rate constant (k_{11}) are given in Table II. The concentration of OH radical, an intermediate in other reactions, is found by Wang et al[5] to be in the range $<2\cdot10^{-13}$ to $2\cdot10^{-12}$ atm, and

Table II Rate Expressions for S(IV) Oxidation

Rate Expression	k^a (25°C)	Log k=A+B/T(K) A	Log k=A+B/T(K) B	Program Name
(1) Oxidation of $SO_2(g)$ by OH(g) ,(b)	$k_{11} = 1.83\cdot10^7$	7.26	$(0)^e$	RK4
$-\frac{dP_{SO_2}}{dt} = k_{11}P_{SO_2}P_{OH}$.				
(2) Oxidation of HSO_3^- by O_3 ,(c)				
$-\frac{d[HSO_3^-]}{dt} = k_{12}[HSO_3^-]g_{X^-}[O_3]$.	$k_{12} = 9.8\cdot10^5$	14.61	-2570^e	RK3
(3) Oxidation of SO_3^{2-} by O_2 ,(d)	$k_{14}' = 0.013$	11.438	-3973	RK1
	$k_{14}'' = 59$	15.095	-3973	RK2
$-\frac{d[SO_3^{2-}]}{dt} = [K_{14}' + K_{14}''([H^+]g_{H^+})^{1/2}]\,[SO_3^{2-}]g_{X^{2-}}$.				

[a] Subscript on k refers to the Eq. No. in text. Concentration and pressure units are as in Table I, footnote b. Time is in sec.

[b] Castleman et al,[3] Davis and Klauber.[4]

[c] Penkett[6] measured k_{12} at 9.6°C.

[d] McKay,[7] Fuller and Crist.[8]

[e] Our estimate.

hence the half-time for reaction 11 could be as short as a few hours.

Of the reactions that occur in solution, the oxidation of HSO_3^- by ozone (O_3) may be the fastest,[6]

$$HSO_3^- + O_3(aq) \rightarrow SO_4^{2-} + H^+ + O_2(aq) \ . \qquad (12)$$

This reaction is preceeded by

$$O_3(g) \rightleftarrows O_3(aq) \ . \qquad (13)$$

With an atmospheric concentration of ozone of 10^{-7} atm, we estimate from k_{12} and K_{13} (Tables I and II) a half life of 2 min. for HSO_3^- in solution.

Another reaction which is known to occur in solution involves the oxidation of SO_3^{2-} by dissolved oxygen.[7,8] While the overall reaction is

$$SO_3^{2-} + 1/2\ O_2(aq) \rightarrow SO_4^{2-} \ , \qquad (14)$$

the mechanism is apparently complex and is not known in detail. The reaction can be catalyzed by some metal ions and retarded by others. In pure solutions the kinetics are described by the equations and constants in Table II.

1.3 Other Reactions

There are, of course, other reactions that could affect the behavior of sulfur in the atmosphere, including reversible equilibria such as the solution of NO_2 in aerosol droplets and slow reactions such as the dissolution of a flyash particle in an acid droplet or the catalytic oxidation of SO_2 at particle surfaces. There are numerous other constituents of a plume which could react with SO_2 or which certainly will affect the concentrations of ozone and hydroxyl radical. Such other reactions are not included in the present model, either because they are poorly understood at present, or because they would greatly complicate the model and its validation.

2. THE MODEL

From the foregoing the essential features of the chemistry of sulfur in the atmosphere which might be included in a model are (1) the slow oxidation of SO_2 to produce acidic aerosol droplets in which (2) various rapidly attained and shifting chemical equilibria are established (Table I) including (3) progressive neutralization by ammonia, which--if the aerosol remains in the atmosphere long enough--can ultimately produce a relatively innocuous solid, $(NH_4)_2SO_4$. The computations performed by SULCAL to accomplish this may be summarized as follows (Fig. 1):*

1. M. SULCAL, the main program, first calculates the emission rate of plume components from the source.
2. S. SIG is called to obtain the effective volume of the plume for the calculation of component concentrations at a starting point a short distance (x) from the source.
3. M. SULCAL then calls S. KUTTA[9] to begin the calculation of the composition of the plume at increasing values of x.
4. S. KUTTA calls S. RATE repeatedly to determine the rate of change of the concentration of the plume components with x, to be used in a Runga-Kutta integration of the component concentrations vs. x.
5. Each time S. RATE is entered it first calls S. EXPCT which determines by extrapolation or interpolation on x the starting values of several quantities to be refined in the calculation of the composition of the plume.

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*Here and elsewhere M and S denote main and subroutine programs, respectively.

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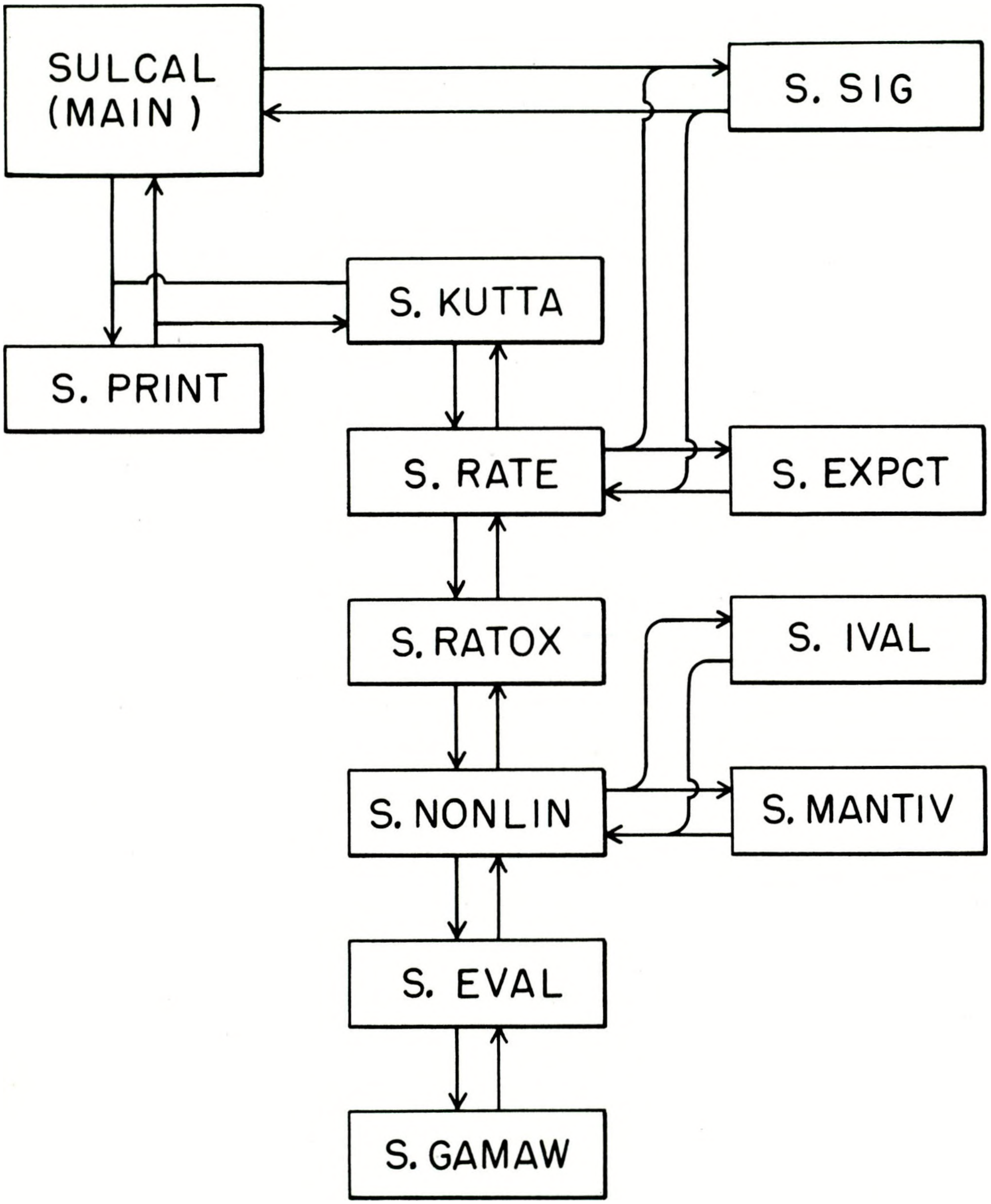

Fig. 1 Program SULCAL.

6. S. RATE next calls S. SIG to determine the effective volume of the plume at the current value of x and its rate of change with x.
7. S. RATE then calls S. RATOX to calculate the rate of S(IV) oxidation.
8. S. RATOX first calls S. NONLIN[10] which employs the secant method to refine quantities needed to calculate the composition of the gas and aerosol phases of the plume.
9. S. NONLIN calls S. EVAL repeatedly to calculate these compositions to test for convergence of the quantities being refined.
10. S. EVAL calls S. GAMAW repeatedly to refine values of needed ionic activity coefficients and the activity of water, quantities which are themselves dependent on the composition of the droplets.
11. With the amount and composition of each phase in the plume returned to S. RATOX, the rate of S(IV) oxidation is calculated in the gas phase and in the droplets.
12. With the oxidation rates returned to S. RATE, the rate of change of the component concentrations are calculated, including also the effects of dilution and deposition; these are returned to S. KUTTA.
13. S. KUTTA returns to M. SULCAL integrated values of the component concentrations at specified values of x.
14. S. KUTTA and M. SULCAL call S. PRINT to put out results as the calculation proceeds.

The important features of the calculation are described in the following sections. The program is listed in Appendix A.

2.1 The Plume Components

There are seven chemical constituents whose concentrations specify the composition of the plume in sufficient detail for the purposes of the model. They include S(IV), S(VI), CO_2, H_2O, NH_3, O_3, and OH. The first four come in part from the stack. It is assumed that S(IV) is emitted from the stack entirely as $SO_2(g)$, and S(VI) entirely as droplets with the composition $SO_3 \cdot nH_2O$. The concentrations of all seven components in the surrounding air are specified as input data.

The rates (Q_i) at which SO_2, $SO_3 \cdot nH_2O$, CO_2 and H_2O--along with unreacted atmospheric gases--are emitted from the stack are calculated from input data (Table III), including the composition of the coal and the rate at which it is burned, the excess of air used, the fraction of sulfur converted to SO_3, and the moles of water (n) condensed by a mole of SO_3. The flow rate of gas (V_p°) at the mouth of the stack is calculated from the mass flow rate and the specified exit temperature.

The total concentration (C_i) of each of the seven components is to be calculated vs. x. A Gaussian plume is assumed for the estimation of dilution and deposition.

2.2 Effective Concentrations and Plume Volume

The simplest conditions under which to study chemical reactions would involve well-mixed solutions of uniform concentration and temperature. Though the conditions in a plume are far from this ideal, it is possible to define mean concentrations and temperature, and effective rate and equilibrium constants under the assumption of rapid mixing such that the net rate of oxidation to sulfur (VI) is the same

Table III Input Data

	Units	Typical Value	Text Symbol	Program Name
Carbon in coal	wt %	82.57[a]		WPCTC
Hydrogen in coal	"	6.93		WPCTH
Sulfur in coal	"	1.0		WPCTS
Rate of coal combustion	kg/sec	100		QCOAL
Fraction of S converted to SO_3	--	0.02		FCTS6
Fractional excess of air in combustion	--	0.25		EXAIR
Moles H_2O condensed per moles SO_3	--	5	n	FCON
Temperature of plume at mouth of stack	°C	177		TCP
Ambient temperature	°C	21.11		TCA
Ambient concentration of S(IV)	$mmol/m^3$	0.004	A_1	A(1)
Ambient concentration of S(VI)	"	0	A_2	A(2)
Ambient concentration of O_3	"	0.0032	A_3	A(3)
Ambient concentration of OH	"	$2 \cdot 10^{-8}$	A_4	A(4)
Ambient concentration of CO_2	"	12.26	A_5	A(5)
Ambient concentration of NH_3	"	0.0006	A_6	A(6)
Ambient concentration of H_2O	"	930	A_7	A(7)
Effective height of stack	m	400	h	H
Meteorological stability class	--	1 to 6[b]		NSC
Roughness length of terrain	--	1 to 6[b]		NRL
Wind speed	m/sec	(a)	u_x	UX
Deposition velocity of gas	m/sec	0.01	v_d^g	VDG
Deposition velocity of particle	m/sec	0.01	v_d^p	VDP
Initial distance from source	m	300		XNEXT
Initial trial value of Δx	m	0.1		DELX

	Units	Typical Value	Text Symbol	Program Name
Fractional error of integrated quantities	--	$3 \cdot 10^{-6}$		ERRR
No. of distance intervals	--	--		NX
Size of distance interval	m	--		XINCR (NX)

---

[a] This value is higher than is typical of power plant fuels.

[b] The numbers 1 to 6 denote stability classes A to F and roughness lengths of 1, 4, 10, 40, 100, and 400 m, respectively. The range of wind speeds depends on the stability class (Table IV).

for the idealized uniform case as for a real plume or for the model Gaussian distribution of concentrations. This can be achieved for reactions involving concentrations through second order in the Gaussian distributed concentrations by the artifice of an effective volume related to the Gaussian dispersion coefficients. Higher order reaction rates can be preserved if desired through appropriate scaling of the rate constants. The justification is given in Appendix B. We use the Gaussian distribution here not because we think it fits the plume distribution better than other forms, but rather because these are existing measurements of plume volume which have been expressed in terms of the Gaussian dispersion.

In terms of the effective plume volume V_p, the concentration (C_i) of each plume component is given by

$$C_i = Q_i/V_p + A_i(1 - \overset{\circ}{V}_p/V_p) , \qquad (15)$$

where Q_i is the emission rate of component i (mmol/sec), A_i its ambient concentration (mmol/m^3), and $\overset{\circ}{V}_p$ the initial plume volume flow rate (m^3/sec). Thus the effective plume volume is a volume flow rate (m^3/sec) at a given x, or, a volume (m^3) of a length of plume u_x where u_x is the wind velocity (m/sec).

The effective plume volume V_p is related to the dispersion coefficients σ_y and σ_z (m) of the Gaussian distribution by the expression (see Appendix B)

$$V_p = 4\pi\, \sigma_y \sigma_z u_x \beta \ (\mathrm{m}^3/\mathrm{sec}) , \qquad (16)$$

where β is a correction factor which accounts for the change in the concentration distribution due to the interaction with (or "reflection" from) the ground. The factor β is given by the expression (Appendix B)

$$\beta = \left[1 + \frac{1}{\sqrt{2}} \exp\left(-h^2/\sigma_z^2\right)\right]^{-1} , \qquad (17)$$

where h is the effective stack height (m). Note that when $\sigma_z \ll h$ then $\beta = 1$ and when $\sigma_z \gg h$ then $\beta = .59$. The value of β changes smoothly as the ratio h/σ_z passes through unity.

The dispersion coefficients used in the effective reaction volume determination are instantaneous or short-time averaged coefficients (σ_s), and are smaller than the long-time averaged dispersion coefficients (σ_ℓ) described by Hosker[11] (Table IV) which are used to calculate ground level concentrations and depositions. Both coefficients are a function of the meteorological stability class, the distance x from the stack, and a roughness length characteristic of the terrain. To these dispersion coefficients we have added a small correction $\sigma°$

$$\sigma° = \sqrt{V_p^\circ/4\pi u_x} , \qquad (18)$$

which keeps the plume volume finite at the source, preventing infinite concentrations and reaction rates.

The rate of change of average component concentration with distance due to surface deposition is given by

$$\frac{dC_i}{dx} = - C_i V_d \gamma / u_x , \qquad (19)$$

where V_d is the conventionally defined deposition velocity and γ is

$$\gamma = \left(\sqrt{2/\pi}/\sigma_z\right) \exp\left(-h^2/2\sigma_z^2\right) . \qquad (20)$$

γ and V_p are calculated for each specified value of x in S. SIG; σ_z is the conventional long-time averaged dispersion coefficient.

The short-time dispersion coefficient σ_s can be related to the long-

Table IV Calculation of Dispersion Coefficients[a]

$$\sigma_y(x) = C_3 x/\sqrt{1+0.001x} + \sigma^\circ$$

$$\sigma_z(x) = \ln(c_1 x^{d_1}) \cdot \frac{a_1 x^{b_1}}{1 + a_2 x^{b_2}} + \sigma^\circ$$

$$\left(\sigma^\circ = \sqrt{V_p{}^\circ/(4\pi u_x)}\right)$$

Stability Class	u_x (m/sec)	a_1	b_1	a_2	b_2	c_3
A (1)[b]	1 - 2.5	0.112	1.06	$5.38 \cdot 10^{-4}$	0.815	0.22
B (2)	1.5 - 5	0.130	0.950	$6.52 \cdot 10^{-4}$	0.750	0.16
C (3)	2 - >6	0.112	0.920	$9.05 \cdot 10^{-4}$	0.718	0.11
D (4)	5 - >10	0.098	0.889	$1.35 \cdot 10^{-3}$	0.688	0.08
E (5)	2 - 5	0.0609	0.895	$1.96 \cdot 10^{-3}$	0.684	0.06
F (6)	2 - 3	0.0638	0.783	$1.36 \cdot 10^{-3}$	0.672	0.04

Roughness Length (cm)		c_1	d_1
1	(1)[b]	1.56	0.0480
4	(2)	2.02	0.0269
10	(3)	2.718	0
40	(4)	5.16	-0.060
100	(5)	7.37	-0.0957
400	(6)	11.7	-0.128

---

[a] From Hosker[11]; these are long-time averaged (σ_ℓ) values. A factor has been omitted from the expression for σ_z since it differs little from unity (< 10%) for the distances of interest (< 30 km).

[b] Numbers are values of NSC and NRL supplied as input data (Table III).

term coefficients σ_ℓ by

$$\sigma_s = f\ \sigma_\ell \ . \qquad (21)$$

The form of f is given in Appendix B.

In equation 15, additivity of gas volumes is assumed. By the assumption of the ideal gas law, the mean absolute temperature of the plume is then given as

$$T = \frac{T_a}{1 - (1-T_a/T_p)\ (V_p^\circ/V_p)} \ , \qquad (22)$$

where T_p and T_a are respectively the absolute temperature of the plume at the mouth of the stack and of the ambient air.

2.3 The Rate of Change of Component Concentrations

The seven derivatives dC_i/dx are evaluated at a given x in S. RATE each time it is called by S. KUTTA. There are three possible contributions to each derivative which arise from (1) dilution, (2) deposition, and (3) oxidation,

$$\frac{d\ C(i)}{dx} = R_1(i) + R_2(i) + R_3(i) \ . \qquad (23)$$

The terms due to dilution are of the form

$$R_1(i) = -\ [C(i) - A(i)]\ \frac{d\ \ell n\ V_p}{dx} \ , \qquad (24)$$

obtained by differentiation of eq 15.

For the terms arising from deposition two deposition velocities are specified $V_d{}^g$ for gases and $V_d{}^p$ for aerosol particles. For the components S(VI) and H_2O only particulate deposition is involved

$$R_2(S(VI)) = -\ C(S(VI))\cdot V_d{}^p\ \gamma/u_x \ , \qquad (25)$$

$$R_2(H_2O) = -\ (g_w/0.018)\cdot V_d{}^p\ \gamma/u_x \ . \qquad (26)$$

(Here g_w is the amount of condensed water in g/m^3.) For the components S(IV) and NH_3 the expressions are of the form

$$R_2(i) = - \left\{[P(i)/RT]\ v_d{}^g + [C(i) - P(i)/RT]\ v_d{}^p\right\} \gamma/u_x \ . \tag{27}$$

P(i) is the pressure of the gaseous species. For the other components (CO_2, O_3, and OH) the deposition rates are assumed to be zero.

The rates of oxidation of S(IV), calculated in and returned from S. RATOX are used in the following R_3 terms:

$$R_3(S(IV)) = - R_T/u_x \ , \tag{28}$$

$$R_3(S(VI)) = R_T/u_x \ , \tag{29}$$

$$R_3(O_3) = -R_{oz}/u_x \ , \tag{30}$$

where R_T is the total oxidation rate and R_{oz} is the oxidation rate from reaction of HSO_3^- with ozone in the droplets (both in mmol m^{-3} sec^{-1}). The depletion of OH by reaction with SO_2 is neglected since its concentration is controlled by other reactions not included in the model.

2.4 The Composition of the Plume

The remainder of the calculation is concerned mainly with determining for a given set of component concentrations the partial pressures of gases, the amount and composition of the aerosol droplets, and the amount--if any--of particulate ammonium sulfate in order that the oxidation rates of the various species of S(IV) (eqs 11, 12, and 14) can be calculated.

Given the concentrations of the components S(IV), S(VI), NH_3, CO_2, and H_2O, the following material balance equations may be written:

$$C(S(IV)) = P_{SO_2}/RT + \left([H_2SO_3] + [HSO_3^-] + [SO_3^{2-}]\right)g_w \ , \quad (31)$$

$$C(S(VI)) = \left([HSO_4^-] + [SO_4^{2-}]\right)g_w + C_s \ , \quad (32)$$

$$C(CO_2) = P_{CO_2}/RT + \left([H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]\right)g_w \ , \quad (33)$$

$$C(NH_3) = P_{NH_3}/RT + \left([NH_3] + [NH_4^+]\right)g_w + 2C_s \ , \quad (34)$$

$$C(H_2O) = P_{H_2O}/RT + g_w/0.018 \ . \quad (35)$$

(The pressures P_i are in atm, all solution concentrations [i] are in mmol/gH_2O--i.e., molal units--and C_s is the amount of $(NH_4)_2SO_4$ solid in mmol/m^3.) Upon appropriate substitution of equilibrium constants (Table I) in these equations, the unknown quantities which remain are $[H^+]$, g_w, C_s, and the ionic activity coefficients.

Only four activity coefficients are distinguished (see Appendix C.1),

$$g_{H^+}, g_{NH_4^+}, g_{X^-}, g_{X^{2-}} \ ,$$

the activity coefficients of all singly charged anions being assumed to be the same and similarly for doubly charged anions. The activity coefficients, and the osmotic coefficient (Ø) needed for the calculation of the activity of water, are rather complicated but not too sensitive functions of the corresponding ion concentrations $[H^+]$, $[NH_4^+]$, $[X^-]$, and $[X^{2-}]$ (Appendix C.1). They are refined each time S. EVAL is entered with trial values of $[H^+]$, g_w, and C_s by repeated cycling between S. EVAL and S. GAMAW.

The quantities $[H^+]$, g_w, and C_s (if >0) are refined by cycling between S. NONLIN and S. EVAL until the following conditions are met:

(1) Charge Balance

$$[H^+] + [NH_4^+] = [X^-] + 2[X^{2-}] \tag{36}$$

(2) Water Activity Balance

$$P_{H_2O}/P^\circ_{H_2O} = a_w \tag{37}$$

Here $P^\circ_{H_2O}$ is the saturation partial pressure of water in the atmosphere and a_w is calculated from the composition of the solution (i.e., from ϕ). This condition specifies that the vapor pressure of the droplets as defined by their composition and the temperature will equal the partial pressure of water in the atmosphere.

(3) Ammonium Sulfate Saturation (only if $C_s > 0$)

$$K_7 = [NH_4^+]^2[SO_4^{2-}]g_{NH_4^+}{}^2\, g_{X^{2-}} \tag{38}$$

The residual deviations from these conditions are defined to equal or to approximate the fractional discrepency in the concentration of ions in the droplets

$$y_1 = \left([H^+] + [NH_4^+] - [X^-] - 2[X^{2-}]\right)/\Sigma[i] \tag{39}$$

$$y_2 = \left(P_{H_2O}{}^\circ/P_{H_2O} - 1/a_w\right)/\left(0.018\cdot\Sigma[i]\right) \tag{40}$$

$$y_3 = \left(\frac{[NH_4^+]^2[SO_4^{2-}]\cdot g_{NH_4^+}{}^2\, g_{X^{2-}}}{K_7}\right)^{1/3} - 1 \tag{41}$$

This appears to give an appropriate weight to each.

Initial estimates of g_w, $[H^+]$, $[NH_4^+]$, $[X^-]$ and $[SO_4^{2-}]$ are made the first time S. RATOX is entered as described in Appendix C.2. The initial estimate of C_s is made if and when the droplets become supersaturated with ammonium sulfate ($y_3 > 0$), otherwise $C_s = 0$. Subsequent estimates of these quantities are made in S. EXPCT before entry into

S. RATOX (Fig. 1).

The quantities $[H^+]$ and g_w are refined in S. NONLIN in logarithmic form since both can adopt widely ranging values and have either a first power or higher effect on the concentration of species in solution. The quantity g_w can go to zero if the concentration ratio $[NH_4^+]/[SO_4^{2-}]$ reaches 2 and the solution is saturated with $(NH_4)_2SO_4$. If significant amounts of acid remain unreacted, however, the drops cannot dry out.* The value of g_w is monitored and if it becomes lower than 10^{-8} g/m^3 the computation of solution composition is discontinued and only the oxidation of SO_2 by OH (Eq. 11) is calculated.

The quantity C_s differs from $[H^+]$ and g_w in its effect on the calculations. When it is small it has a small effect on the composition of the droplets, but when it approaches half the amount of the NH_3 component present the difference $C(NH_3) - 2C_s$ becomes important in determining the amount of the droplets. Because of these considerations, the variable C_s is refined in S. NONLIN in the form

$$X_3 = \log[C(NH_3)/(C(NH_3) - 2C_s)] \ . \qquad (42)$$

---

*While there is evidence that under these conditions an acid salt $[(NH_4)_2SO_4]_3 \cdot H_2SO_4$ can form, for simplicity we consider only the formation of $(NH_4)_2SO_4$.

3. TEST CALCULATIONS

A series of calculations, summarized in Table V, were carried out to determine the sensitivity of the various output quantities to what are thought to be typical ranges of the input quantities. The underscored values are reference values. Some of the output quantities for the reference case are plotted versus the distance from the source in Fig. 2. The other output quantities in the table result by varying each input quantity from its reference value while holding all other inputs at the reference values. For example, entries in the first row were generated using 2.5 wt. % sulfur in coal, stability class C, wind speed 2 m/sec, OH concentration $2 \cdot 10^{-8}$ mmol/m^3, NH_3 concentration. $6 \cdot 10^{-4}$ mmol/m^3, and temperature 21.11°C.

In all calculations ERRR, the error limit parameter in S. KUTTA, was set at $3 \cdot 10^{-6}$. In test calculations this produced output values differing by $< 0.2\%$ from the limiting values obtained as ERRR was further decreased. In the calculation of the reference case: S. KUTTA called S. RATE 1345 times in performing the integration from X = 0.3 to 25 km; S. NONLIN called S. EVAL an average of 5.7 times per step of the integration; each time S. EVAL was called, it called S. GAMAW an average of 6.1 times. The computation time for the reference case on the IBM-360-91 computer was 16 sec.

Under the conditions tested, the aerosol droplets contain mostly sulfuric acid with a relatively small amount of ammonium sulfate, the latter being limited by and equivalent to the supply of ambient ammonia. The concentration of the droplets is strongly dependent on the ambient

Table V Sensitivity of Values Calculated by SULCAL to Variation of Input Values

Input Values[a,b]		Output Values at 25 km From Stack[c]					
		SO_2 (10^{-2} mmol/m^3)	Sulfate (10^{-3} mmol/m^3)	SO_2 Ox. Rate (%/hr)	Liq Water (10^{-3} g/m^3)	H_2SO_4 in Droplets (mmol/g H_2O)	$(NH_4)_2SO_4$ in Droplets (mmol/g H_2O)
Sulphur in Coal (Wt %)	2.5	14.3	19.3	3.2	7.7	2.5	0.039
	1.0	6.0	7.9	3.2	3.1	2.4	0.096
	0.5	3.2	4.0	3.2	1.6	2.4	0.189
Meteorological Stability Class	A	4.8	6.3	3.2	2.6	2.4	0.12
	C	6.0	7.9	3.2	3.1	2.4	0.096
	F	14.8	19.7	3.2	6.5	3.0	0.046
Wind Speed (m/sec)	1	9.8	25.3	3.2	9.0	2.8	0.033
	2	6.0	7.9	3.2	3.1	2.4	0.096
	4	3.5	2.5	3.2	1.0	2.2	0.29
	8	2.0	0.84	3.2	0.32	1.7	0.93
Ambient OH (10^{-8} mmol/m^3)	10	3.9	28.2	16.0	11.2	2.5	0.027
	2	6.0	7.9	3.2	3.1	2.4	0.096
	0.5	6.4	3.0	0.8	1.2	2.3	0.26
	0.1	6.6	1.6	0.16	0.60	2.1	0.50
Ambient NH_3 (10^{-4} mmol/m^3)	20	6.0	7.9	3.2	3.0	2.3	0.33
	6	6.0	7.9	3.2	3.1	2.4	0.096
Ambient Temp. (°C)	18.33	6.0	7.9	3.2	740	0.010	0.00040
	19.44	6.0	7.9	3.2	14	0.54	0.021
	21.11	6.0	7.9	3.2	3.1	2.4	0.096

Table V (continued)

Input Values[a,b]		Output Values at 25 km From Stack[c]					
		SO_2 (10^{-2} mmol/m^3)	Sulfate (10^{-3} mmol/m^3)	SO_2 Ox. Rate (%/hr)	Liq Water (10^{-3} g/m^3)	H_2SO_4 in Droplets (mmol/g H_2O)	(NH_4) SO_4 in Droplets (mmol/g H_2O)
Ambient Temp. (°C)	23.89	6.0	7.9	3.2	1.6	4.7	0.18
	26.67	6.0	7.9	3.2	1.2	6.5	0.25
	29.44	6.0	7.9	3.2	0.95	7.9	0.31

---

[a] Underscored numbers are the reference values. Each alternate value was taken while all other input values at the reference values.

[b] Other input values were: Wt % carbon in coal = 82.6; Wt % Hydrogen in coal 6.9%; Combustion rate = 100 Kg coal/sec; Effective stack height = 400 m; Deposition velocity = 0.01 m/sec; ambient water concentration = 930 mmol/m^3.

[c] Concentrations are averages across the plume (See Appendix B).

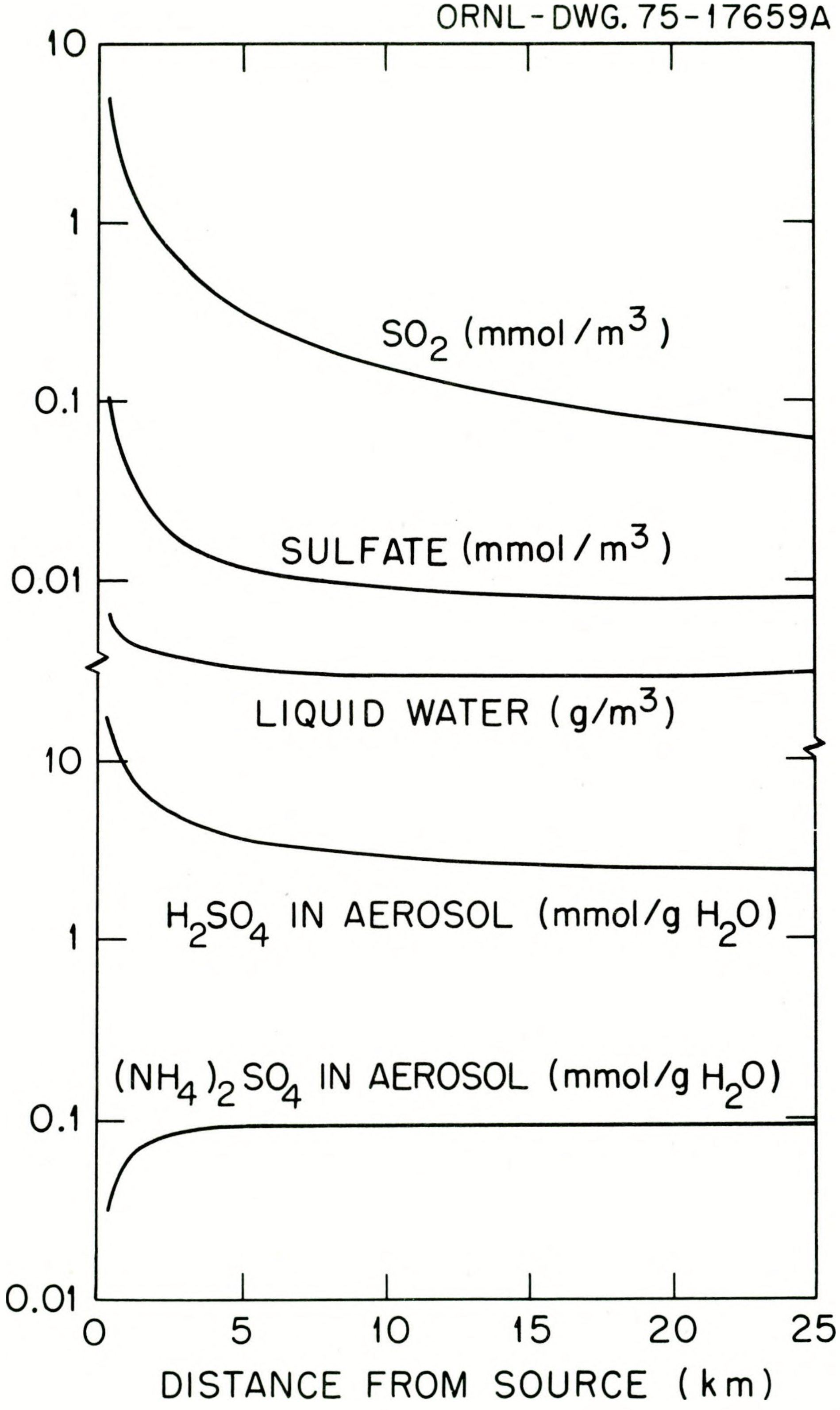

Fig. 2 Quantities calculated by SULCAL for the reference case.

temperature because of the strong inverse effect of the temperature on the relative humidity (the total concentration of water in the ambient air was not varied). The amounts of SO_2, sulfuric acid and condensed water in the plume change directly as the sulfur emission rate, which here is varied by changing the sulfur content in the coal. Increased wind speed strongly decreases the concentrations of SO_2, sulfuric acid and liquid water.

Under all the conditions tested in Table V, only the OH radical is important in the oxidation of SO_2 and the percentage of SO_2 oxidized per hour depends almost entirely on the ambient concentration of the OH radical. This concentration is controlled at the assumed values by unspecified chemical reactions. The conditions under which the oxidation of SO_2 species in the droplets (reactions 12 and 14) becomes significant may be determined as follows: The ratio of the rate of oxidation of HSO_3^- in solution by ozone (R_{oz}) to the rate of oxidation of gaseous SO_2 by OH radical (R_{OH}) is given approximately by

$$\frac{R_{oz}}{R_{OH}} = (K_1\ K_2\ K_{13}\ k_{12}/k_{11}) \cdot RT \cdot \left(\frac{g_w\ P_{O_3}}{[H^+]\ P_{OH}} \right) . \tag{43}$$

The ratio of the rates in solution of SO_3^{2-} oxidation by oxygen R_O to HSO_3^- oxidation by ozone is given by

$$\frac{R_O}{R_{oz}} = \frac{K_3}{K_{13}} \left(\frac{k_{14}' + k_{14}''\ [H^+]}{k_{12}} \right) \Big/ [H^+]\ P_{O_3} \quad . \tag{44}$$

(Both these expressions are approximations because activity coefficients have been neglected.) With P_{O_3} and P_{OH} at their reference values ($8 \cdot 10^{-8}$ and $5 \cdot 10^{-13}$ atm, respectively) these ratios of rates at 25°C become

$$\frac{R_{oz}}{R_{OH}} \approx 3\cdot10^{-5}\,\frac{g_w}{[H^+]} \tag{45}$$

and

$$\frac{R_o}{R_{OH}} \approx \frac{1\cdot10^{-6}}{[H^+]} + \frac{5\cdot10^{-3}}{[H^+]^{1/2}} \quad . \tag{46}$$

Thus the oxidation of HSO_3^- by ozone should become significant when the ratio $g_w/[H^+]$ exceeds $\sim10^4$. The rate of SO_3^{2-} oxidation by dissolved oxygen should then become significant when the pH exceeds ~4. Since g_w and $[H^+]$ change in opposite directions and almost logarithmically with the relative humidity, the rate of oxidation of SO_2 species in aerosol droplets increase rapidly in importance as the relative humidity increases (Fig. 3). This rate is also favored by conditions that produce a more complete neutralization of the acid droplets. In general, neutralization is favored by a lower sulfur emission rate and a lower OH radical concentration, both tending to reduce the rate of production of the acid SO_3. It is favored as well by a high ambient concentration of ammonia and a high wind speed, both tending to deliver more ammonia to the acid droplets.

We emphasize that, in addition to the approximations in the present model arising from the use of averaged concentrations in the plume, the oxidation mechanisms are oversimplified and incomplete. The concentration of OH radical, which may often determine the rate of the most rapid oxidation reaction, is controlled by other chemical reactions not included in the model. The species of SO_2 in solution oxidized by ozone may include others in addition to (or perhaps instead of) HSO_3^-.

ORNL-DWG. 75-17658A

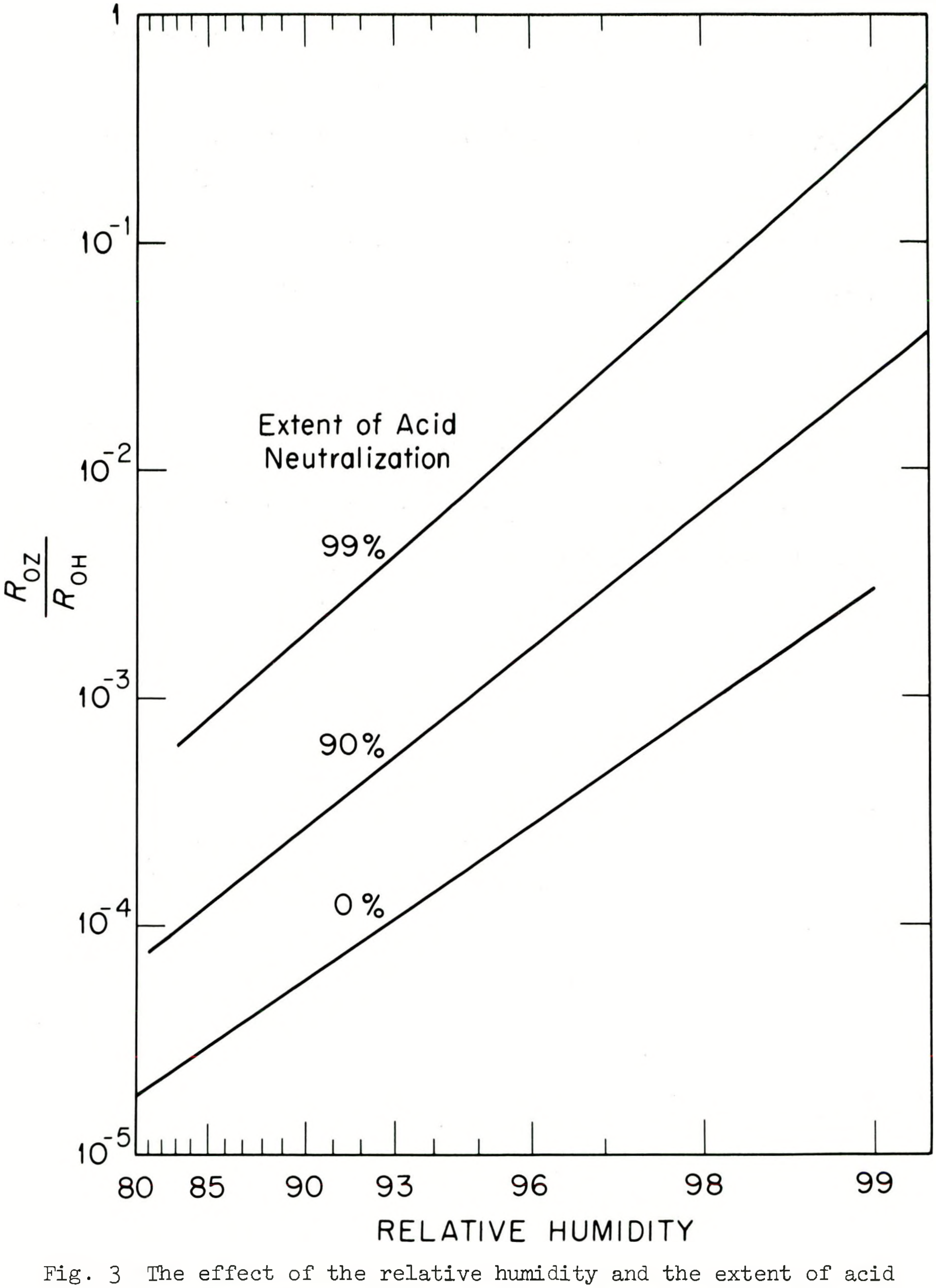

Fig. 3 The effect of the relative humidity and the extent of acid neutralization on the ratio of the rates of SO_2 oxidation by ozone (R_{oz}) and by hydroxyl radical (R_{OH}) at 25°C.

The oxidation of SO_3^{2-} by oxygen can be catalyzed or poisoned by certain metal ions in solution. Finally, possible catalytic oxidation of SO_2 at the surface of solid particles and droplets has not been included. It does not seem worthwhile to include all such effects at present, nor may it be so even when sufficient knowledge has been gained. As more information does become available, however, it will be relatively easy to modify the rate expressions in the S. RATOX and to add others as may be desired.

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APPENDIX A

Program SULCAL

1. Partial List of Symbols

In Text	Definition	In Program
a_w	Activity of water	AWI
B°_{JK}, B^{1}_{JK}	Parameters for calculating interaction coefficients between cation J and anion K $B^{\circ}_{JK} = B(1,J,K)$ $B^{1}_{JK} = B(2,J,K)$	B(I,J,K)
β	Correction factors (Eq. 17) for reflection of plume from ground, for short-time (BETAS) and time-averaged (BETAL) plumes	BETAS, BETAL
C_i or $C(i)$	Total concentration of component; ($mmol/m^3$)	QC(I)
C_s	Concentration of $(NH_4)_2SO_4$ particles in plume ($mmol/m^3$)	CSS
ERRR	Error limit employed in S. KUTTA	ERRR
f	Factor relating short-time and long-time sigmas (Eq. 22, App. B)	FLS
g_i	Activity coefficient of an ion; $G(1,1) = g_{H^+}$, $G(1,2) = g_{NH_4^+}$, $G(2,1) = g_{x^-}$, $G(2,2) = g_{x^{2-}}$	G(I,J)
g_w	Concentration of condensed water in plume ($g\ H_2O/m^3$)	CGW
γ	Factor (Eq. 20) which corrects effective plume concentration to ground level concentrations	GAMMA
P_j	Pressure of a gaseous constituent (atm)	P(J)
P°_w	Vapor pressure of pure water (atm)	PWO
ϕ	Osmotic coefficient of aerosol droplets (Eq. 4, App. C)	P
Q_i	Emission rate of component; (mmol/sec)	Q(I)
R	The gas constant ($m^3\ mmol^{-1}\ {}^{\circ}K^{-1}$)	R

In Text	Definition	In Program
$\frac{1}{RT}$	Factor for conversion of pressure (atm) to concentration (mmol/m^3)	CONST
$\sigma^*_{\ell,y}$, $\sigma^*_{\ell,z}$	Time-averaged dispersion coefficients for a point source	SGPY, SGPZ
σ°	Correction which makes σ_y and σ_z finite at $x = 0$ (Eq. 18)	SGO
$\sigma_{\ell,y}$, $\sigma_{\ell,z}$	Time-averaged dispersion coefficient (m)	SGLY, SGLZ
$\sigma_{s,y}$, $\sigma_{s,z}$	Short-time dispersion coefficient (m)	SGSY, SGSZ
T	Absolute temperature of plume (°K)	T
u_x	Wind velocity (m/sec)	UX
V_d^g, V_d^p	Disposition velocity for gases and particles (m/sec)	VDG, VDP
V_p	Effective volume (m^3/sec) (the effective volume of a length of plume equal to u_x, the wind velocity in m/sec). VRG is calculated using short-time dispersion coefficients and VLG is calculated with time-averaged dispersion coefficients	VRG, VLG
V_p°	Gas flow rate at mouth of stack (m^3/sec)	VRGO
x	Distance (m) from source in wind direction	X

2. Program Listing

```
C PROGRAM FOR CALCULATION OF  CHEMICAL FORMS OF SULFUR IN AND THEIR      BLCK
C DEPOSITION  FROM A PLUME                                               BLCK
      BLOCK DATA                                                         BLCK
      IMPLICIT REAL*8(A-H,O-Z)                                           BLCK
C R = GAS CONSTANT (M**3/ATM/K,MMOL)                                     BLCK
C PI = 3.1416, FLN = LN(10), FMW = GMS H2O/MMOL                          BLCK
C B(I,J,K) = INTERACTION COEF'S. OF CATION I WITH ANION J, TWO           BLCK
C    PARAMETERS FOR EACH IJ PAIR                                         BLCK
C Z = ION CHARGE (FIRST SUBSCRIPT IS 1 FOR CATIONS AND 2 FOR ANIONS)     BLCK
      COMMON/BLK/R,PI,FLN,FMW,B(4,4,2),Z(2,4)                            BLCK
      DATA B(1,1,1),B(1,1,2),B(1,2,1),B(1,2,2),B(2,1,1),                 BLCK
     &B(2,1,2),B(2,2,1),B(2,2,2)                                         BLCK
     &/0.2722D+0,3.0803D+0,0.0502D+0,-4.0054D+0,0.0D+0,0.319D+0,         BLCK
     &-0.04873D+0,-1.18580D+0/                                           BLCK
      DATA PI,FLN,R,FMW/3.1415927D+0,2.302585D+0,82.0597D-9,18.0153D-3/  BLCK
     &,Z(1,1),Z(1,2),Z(2,1),Z(2,2)/1.0D+0,1.0D+0,-1.0D+0,-2.0D+0/        BLCK
      END                                                                BLCK
C
C MAIN PROGRAM                                                           MAIN
      IMPLICIT REAL*8(A-H,O-Z)                                           MAIN
      EXTERNAL RATE                                                      MAIN
      COMMON/BLK/R,PI,FLN,FMW,B(4,4,2),Z(2,4)                            MAIN
C NOX = TOTAL NUMBER OF TIMES S. RATE IS ENTERED FOR A GIVEN CASE        MAIN
      COMMON/CASE/NOX                                                    MAIN
      COMMON/RTE/NSC,NRL,VRGO,TP,H,UX,A(7),TA,DELX,VDG,VDP               MAIN
      COMMON/SIGMA/SGO,SGPY,SGPZ,SGLY,SGLZ,SGSY,SGSZ,BETAL,BETAS         MAIN
      COMMON/ARG/CGW,PH,CSS,C(2,4),T,RTT,RTOH,RTOZ,RTO,NCAL,NITN         MAIN
      COMMON/EQK/EKN,EK1N,EKC,EK1C,EK2C,EKS,EK1S,EK2S,EK3S,EKSS,EKW      MAIN
      COMMON/CON/CMH,CMN,CM1N,CMC,CM1C,CM2C,CMS,CM1S,CM2S,CM3S,CM4S,     MAIN
     &PN,PC,PS                                                           MAIN
      COMMON/ACT/DHA,G(2,4),P,PWO,CONST                                  MAIN
      COMMON/GIVN/WPCTC,WPCTH,WPCTS,QCOAL,FCTS6,EXAIR,FCON,TCP,TCA,      MAIN
     &XLAST,XNEXT,ERRR                                                   MAIN
      COMMON/VAR/QC(7)                                                   MAIN
      DIMENSION Q(7),FDMY(7),XINCR(50)                                   MAIN
C WPCTI=WT. % OF ELEMENT I IN COAL                                       MAIN
C QCOAL=COMBUSTION RATE IN KG/SEC                                        MAIN
C FCTS6=FRACT OF S CONVERTED TO S(VI),EXAIR=FRACTION OF EXCESS AIR USED  MAIN
C FCON=NO.OF MOLES OF WATER CONDENSED/MOLE SO3, TCP=TEMP OF EXIT GAS (C) MAIN
C H=APPARENT STACK HEIGHT IN METERS                                      MAIN
    1 READ(20,100) WPCTC,WPCTH,QCOAL,FCTS6,EXAIR,FCON,TCP,H              MAIN
C STABILITY CLASS,ROUGHNESS LENGTH,WIND SPEED (M/SEC)                    MAIN
C AND AMBIENT CONCENTRATIONS (MMOL/M**3) AND TEMPERATURE (C)             MAIN
    2 READ(20,100) NSC,NRL,UX,VDG,VDP,(A(I),I=1,7),TCA,WPCTS             MAIN
C CALCULATE MOLES OF GASES PER KG OF COAL BURNED                         MAIN
      RMLC=WPCTC/1.200115                                                MAIN
      RMLW=0.5*WPCTH/0.100797                                            MAIN
      RMLS4=(WPCTS/3.2064)*(1.0-FCTS6)                                   MAIN
      RMLS6=(WPCTS/3.2064)*FCTS6                                         MAIN
C CALCULATE MOLES OF OXYGEN CONSUMED PER KG OF COAL BURNED               MAIN
      CMLO2=RMLC+0.5*RMLW+RMLS4+1.5*RMLS6                                MAIN
C CALCULATE TOTAL MOLES OF EFFLUENT GAS PER KG OF COAL BURNED            MAIN
      RMLGAS=RMLC+RMLW+RMLS4+((79.05/20.95)*(1.0+EXAIR)+EXAIR)*CMLO2     MAIN
     &-FCON*RMLS6                                                        MAIN
      TP=TCP+273.15                                                      MAIN
      TA=TCA+273.15                                                      MAIN
C CALCULATE RATE OF EMISSION OF GAS  (M**3/SEC)                          MAIN
      VRGO=RMLGAS*QCOAL*(82.0597D-6)*TP                                  MAIN
```

```
C CALCULATE EMISSION RATES OF COMPONENTS IN MMOLS/SEC                    MAIN
      BNFCT=1000.0*QCOAL                                                  MAIN
      Q(1)=RMLS4*BNFCT                                                    MAIN
      Q(2)=RMLS6*BNFCT                                                    MAIN
      Q(3)=0.0                                                            MAIN
      Q(4)=0.0                                                            MAIN
      Q(5)=RMLC*BNFCT                                                     MAIN
      Q(6)=0.0                                                            MAIN
      Q(7)=RMLW*BNFCT                                                     MAIN
      NOX=1                                                               MAIN
C READ FIRST VALUE OF X (M), DELTA X AND ERROR LIMIT                      MAIN
      READ(20,100) XNEXT,DELX,ERRR                                        MAIN
C READ NO. OF STEPS IN X AND THE SIZE OF EACH                             MAIN
      READ(20,100) NX,(XINCR(I),I=1,NX)                                   MAIN
      NCAL=0                                                              MAIN
      NITN=0                                                              MAIN
C CALCULATE CONCENTRATIONS AT STARTING VALUE OF X (MMOLS/M**3)            MAIN
      CALL SIG(XNEXT,VRG,FEX)                                             MAIN
      DO 10 I=1,7                                                         MAIN
      QC(I)=Q(I)/VRG+A(I)*(1.0-VRGO/VRG)                                  MAIN
   10 CONTINUE                                                            MAIN
      CALL PRINT(1)                                                       MAIN
C START CALCULATION OF QC(I) VS. X                                        MAIN
      DO 20 I=1,NX                                                        MAIN
      XLAST=XNEXT                                                         MAIN
      XNEXT=XNEXT+XINCR(I)                                                MAIN
      CALL KUTTA(XLAST,XNEXT,QC,7,DELX,ERRR,40,RATE)                      MAIN
   20 CONTINUE                                                            MAIN
C CALL RATE FOR FINAL CALCULATION OF PLUME COMPOSITION                    MAIN
      CALL RATE(XNEXT,QC,FDMY,1)                                          MAIN
      XLAST=XNEXT                                                         MAIN
      CALL PRINT(2)                                                       MAIN
      GO TO 2                                                             MAIN
  100 FORMAT(7G10.0)                                                      MAIN
      END                                                                 MAIN
C
C SUBROUTINE TO CALCULATE EFFECTIVE VOLUME OF PLUME (VRG)                 SIG
C     AND THE DEPOSITION FACTOR (FEXD)                                    SIG
C CALCULATION OF SIGMA(Y) AND SIGMA(Z) ACCORDING TO HOSKER                SIG
      SUBROUTINE SIG(X,VRG,FEXD)                                          SIG
      IMPLICIT REAL*8(A-H,O-Z)                                            SIG
      DIMENSION GC3(6),GA1(6),GB1(6),GA2(6),GB2(6),GC1(6),GD1(6),FCTL(6)  SIG
      COMMON/CASE/NOX                                                     SIG
      COMMON/RTE/NSC,NRL,VRGO,TP,H,UX,A(7),TA,DELX,VDG,VDP                SIG
      COMMON/SIGMA/SG0,SGPY,SGPZ,SGLY,SGLZ,SGSY,SGSZ,BETAL,BETAS          SIG
      DATA GC3/0.22D+0,0.16D+0,0.11D+0,0.08D+0,0.06D+0,                   SIG
     &0.04D+0/                                                            SIG
      DATA GA1/0.112D+0,0.130D+0,0.112D+0,0.098D+0,                       SIG
     &0.0609D+0,0.0638D+0/                                                SIG
      DATA GB1/1.06D+0,0.950D+0,0.920D+0,0.889D+0,0.895D+0,               SIG
     &0.783D+0/                                                           SIG
      DATA GA2/0.000538D+0,0.000652D+0,0.000905D+0,                       SIG
     &0.00135D+0,0.00196D+0,0.00136D+0/                                   SIG
      DATA GB2/0.815D+0,0.750D+0,0.718D+0,0.688D+0,0.684D+0,              SIG
     &0.672D+0/                                                           SIG
      DATA GC1/1.56D+0,2.02D+0,2.71828D+0,5.16D+0,7.37D+0,                SIG
     &11.7D+0/                                                            SIG
      DATA GD1/0.0480D+0,0.0269D+0,0.0D+0,-0.06D+0,-0.0957D+0             SIG
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     &,-0.128D+0/                                                       SIG
      DATA FCTL/5.0D+2,2.5D+2,1.0D+2,0.5D+2,0.2D+2,0.1D+2/              SIG
C UPON FIRST ENTRY ASSIGN VALUES TO PARAMETERS THAT DEPEND ON STABILITY  SIG
C     CLASS, ROUGHNESS LENGTH, AND WIND SPEED                           SIG
      IF(NOX.GT.1) GO TO 1                                              SIG
      PI=3.1415927                                                      SIG
      C3=GC3(NSC)                                                       SIG
      A1=GA1(NSC)                                                       SIG
      B1=GB1(NSC)                                                       SIG
      A2=GA2(NSC)                                                       SIG
      B2=GB2(NSC)                                                       SIG
      C1=GC1(NRL)                                                       SIG
      D1=GD1(NRL)                                                       SIG
      RL=FCTL(NSC)                                                      SIG
      FLS=DSQRT(X/(X+50.0*RL))                                          SIG
      SG0=DSQRT(VRG0/(4.0*PI*UX))                                       SIG
C CALCULATE POINT-SOURCE TIME-AVERAGED SIGMA(Y)                         SIG
    1 DTY=1.0+0.001*X                                                   SIG
      SGPY=C3*X/DSQRT(DTY)                                              SIG
      F=DLOG(C1*X**D1)                                                  SIG
      G=A1*X**B1/(1.0+A2*X**B2)                                         SIG
C CALCULATE POINT-SOURCE TIME-AVERAGED SIGMA(Z)                         SIG
      SGPZ=F*G                                                          SIG
C CALCULATE TIME-AVERAGED SIGMA(Y) AND SIGMA(Z) FOR REAL SOURCE         SIG
      SGLY=SGPY+SG0                                                     SIG
      SGLZ=SGPZ+SG0                                                     SIG
C CALCULATE SHORT-TIME SIGMA(Y) AND SIGMA(Z) FOR REAL SOURCE            SIG
      SGSY=FLS*SGPY+SG0                                                 SIG
      SGSZ=FLS*SGPZ+SG0                                                 SIG
C EVALUATE CORRECTION FACTOR BETA                                       SIG
      EXFS=-(H/SGSZ)**2                                                 SIG
      IF(EXFS.LT.-25.0) EXFS=-25.0                                      SIG
      EXFL=-(H/SGLZ)**2                                                 SIG
      IF(EXFL.LT.-25.0) EXFL=-25.0                                      SIG
      BETAL=1.0/(1.0+0.70711*DEXP(EXFL))                                SIG
      BETAS=1.0/(1.0+0.70711*DEXP(EXFS))                                SIG
C CALCULATE EFFECTIVE REACTION VOLUME VRG (M**3)                        SIG
C     AND EFFECTIVE DEPOSITION VOLUME VLG (M**3)                        SIG
      VRG=4.0*PI*SGSY*SGSZ*UX*BETAS                                     SIG
      VLG=4.0*PI*SGLY*SGLZ*UX*BETAL                                     SIG
C CALCULATE FACTOR RELATED TO DRY DEPOSITION                            SIG
      GAMA=DSQRT(2.0/PI)/SGLZ*DEXP(EXFL/2.0)                            SIG
      FEXD=(VRG/VLG)*GAMA                                               SIG
      RETURN                                                            SIG
      END                                                               SIG
C
C SUBROUTINE CALLED BY KUTTA TO CALCULATE RATE OF CHANGE OF COMPONENT  RATE
C     CONCENTRATIONS YI(I) WITH DISTANCE X (DYDX)                      RATE
C IN = INTEGER WHICH (WHEN 1) SIGNALS CALCULATION OF DYDX AT X         RATE
      SUBROUTINE RATE(X,YI,DYDX,IN)                                    RATE
      IMPLICIT REAL*8(A-H,O-Z)                                         RATE
      DIMENSION YI(7),DYDX(7)                                          RATE
      COMMON/BLK/R,PI,PLN,FMW,B(4,4,2),Z(2,4)                          RATE
      COMMON/CASE/NOX                                                  RATE
      COMMON/RTE/NSC,NRL,VRG0,TP,H,UX,A(7),TA,DELX,VDG,VDP             RATE
      COMMON/ARG/CGW,PH,CSS,C(2,4),T,RTT,RTOH,RTOZ,RTO,NCAL,NITN       RATE
      COMMON/CON/CMH,CMN,CM1N,CMC,CM1C,CM2C,CMS,CM1S,CM2S,CM3S,CM4S,   RATE
     &PN,PC,PS                                                         RATE
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      COMMON/ACT/DHA,G(2,4),P,PW0,CONST                                 RATE
      COMMON/VAR/Y(7)                                                   RATE
      DO 10 I=1,7                                                       RATE
      Y(I)=YI(I)                                                        RATE
   10 CONTINUE                                                          RATE
C HAVE DROPLETS DRIED UP?                                               RATE
      IF(CGW.LE.0.0) GO TO 2                                            RATE
C ESTIMATE STARTING VALUES OF CGW,PH,CSS, AND ACTIVITY COEFFICIENTS     RATE
      CALL EXPCT(NOX,IN,X,CGW,PH,CSS,C(1,2),C(2,1),C(2,2))              RATE
C EVALUATE DLN(V)/D(X) NUMERICALLY                                      RATE
    2 X1=X+DELX/2.0                                                     RATE
      X2=X-DELX/2.0                                                     RATE
      CALL SIG(X,VRG,FEXD)                                              RATE
      CALL SIG(X1,VRG1,FEX)                                             RATE
      CALL SIG(X2,VRG2,FEX)                                             RATE
      DLVDX=2.0*(VRG1-VRG2)/(DELX*(VRG1+VRG2))                          RATE
C CALCULATE TEMPERATURE IN PLUME (K)                                    RATE
      T=TA/(1.0-(1.0-TA/TP)*VRG0/VRG)                                   RATE
      CONST=1.0/(R*T)                                                   RATE
C CALCULATE RATE OF OXIDATION OF S(IV)                                  RATE
      CALL RATOX                                                        RATE
      NOX=NOX+1                                                         RATE
C CALCULATE DYDX(I)                                                     RATE
      DYDX(1)=-(RTT+(PS*CONST*(VDG-VDP)+Y(1)*VDP)*FEXD)/UX              RATE
      DYDX(2)=(RTT-Y(2)*VDP*FEXD)/UX                                    RATE
      DYDX(3)=-RTOZ/UX                                                  RATE
      DYDX(4)=0.0                                                       RATE
      DYDX(5)=0.0                                                       RATE
      DYDX(6)=-(PN*CONST*(VDG-VDP)+Y(6)*VDP)*FEXD/UX                    RATE
      DYDX(7)=-CGW/FMW*VDP*FEXD/UX                                      RATE
      DO 1 I=1,7                                                        RATE
      DYDX(I)=DYDX(I)-(Y(I)-A(I))*DLVDX                                 RATE
    1 CONTINUE                                                          RATE
      RETURN                                                            RATE
      END                                                               RATE
C
C SUBROUTINE TO CALCULATE RATE OF S(IV) OXIDATION                       RTOX
      SUBROUTINE RATOX                                                  RTOX
      IMPLICIT REAL*8(A-H,O-Z)                                          RTOX
      EXTERNAL IVAL                                                     RTOX
      EXTERNAL EVAL                                                     RTOX
      DIMENSION X(10)                                                   RTOX
      COMMON/BLK/R,PI,FLN,FMW,B(4,4,2),Z(2,4)                           RTOX
      COMMON/CASE/NOX                                                   RTOX
      COMMON/ARG/CGW,PH,CSS,C(2,4),T,RTT,RTOH,RTOZ,PTO,NCAL,NITN        RTOX
      COMMON/EQK/EKN,EK1N,EKC,EK1C,EK2C,EKS,EK1S,EK2S,EK3S,EKSS,EKW     RTOX
      COMMON/CON/CMH,CMN,CM1N,CMC,CM1C,CM2C,CMS,CM1S,CM2S,CM3S,CM4S,    RTOX
     &PN,PC,PS                                                          RTOX
      COMMON/ACT/DHA,G(2,4),P,PW0,CONST                                 RTOX
      COMMON/VAR/C4,C6,COZ,COH,CC,CN,CW                                 RTOX
C CONSTANTS FOR THE CALCULATION OF RATE AND EQUILIBRIUM CONSTANTS       RTOX
C     AS A FUNCTION OF THE TEMPERATURE                                  RTOX
      DATA EKN0,EKNT,EKC0,EKCT,EKS0,EKST,EK1N0,EK1NT,                   RTOX
     &EK1S0,EK1ST,EK2S0,EK2ST,EK1C0,EK1CT,EK2C0,EK2CT,EK3S0,            RTOX
     &EK3ST,EKSS0,EKSST,EKW0,EKWT,EKOZ0,EKOZT,RK10,RK1T,RK20,RK2T,      RTOX
     &RK30,RK3T,RK40,RK4T,EPW0,EPWT                                     RTOX
     &/-4.233D+0,1.7855D+0,-5.016D+0,1.05974D+0,-4.4912D+0,1.3659D+0,   RTOX
     &0.1026D+0,2.7275D+0,-4.815D+0,0.9094D+0,-8.8549D+0,0.48736D+0,    RTOX
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     &-5.030D+0,-0.39885D+0,-7.7260D+0,-0.77585D+0,-5.8348D+0,1.1452D+0,      RTOX
     &0.929D+0,-0.3431D+0,-4.2134D+0,-2.91654D+0,-8.488D+0,1.891D+0,          RTOX
     &11.4378D+0,-3.9725D+0,15.0947D+0,-3.9725D+0,14.61D+0,-2.57D+0,          RTOX
     &2.65D+0,0.0D+0,6.2057D+0,-2.2989D+0/                                    RTOX
C ALL CONCENTRATIONS ARE IN MMOLES/METER**3 OR MMOLS/G                        RTOX
C CALCULATE TEMPERATURE DEPENDENT PARAMETERS                                  RTOX
      FT=1000.0/T                                                             RTOX
      DHA=(4.91D-1+8.0D-4*(T-273.15))*FLN                                     RTOX
      EKN=DEXP((EKN0+EKNT*FT)*FLN)                                            RTOX
      EKC=DEXP((EKC0+EKCT*FT)*FLN)                                            RTOX
      EKS=DEXP((EKS0+EKST*FT)*FLN)                                            RTOX
      EK1N=DEXP((EK1N0+EK1NT*FT)*FLN)                                         RTOX
      EK1S=DEXP((EK1S0+EK1ST*FT)*FLN)                                         RTOX
      EK2S=DEXP((EK2S0+EK2ST*FT)*FLN)                                         RTOX
      EK1C=DEXP((EK1C0+EK1CT*FT)*FLN)                                         RTOX
      EK2C=DEXP((EK2C0+EK2CT*FT)*FLN)                                         RTOX
      EK3S=DEXP((EK3S0+EK3ST*FT)*FLN)                                         RTOX
      EKSS=DEXP((EKSS0+EKSST*FT)*FLN)                                         RTOX
      EKW=DEXP((EKW0+EKWT*FT)*FLN)                                            RTOX
      EKOZ=DEXP((EKOZ0+EKOZT*FT)*FLN)                                         RTOX
      RK1=DEXP((RK10+RK1T*FT)*FLN)                                            RTOX
      RK2=DEXP((RK20+RK2T*FT)*FLN)                                            RTOX
      RK3=DEXP((RK30+RK3T*FT)*FLN)                                            RTOX
      RK4=DEXP((RK40+RK4T*FT)*FLN)                                            RTOX
      PW0=DEXP((EPW0+EPWT*FT)*FLN)                                            RTOX
C TEST TO SEE IF CGW AND PH ARE GIVEN                                         RTOX
      IF(NOX.GT.1) GO TO 1                                                    RTOX
      CSS=0.0                                                                 RTOX
C ESTIMATE STARTING VALUES OF CGW, ION CON'NS AND GAMAS                       RTOX
      FNI=3.0                                                                 RTOX
      TB=(PW0*CONST-CW+FNI*C6)/2.0                                            RTOX
      TC=-FNI*C6*CW                                                           RTOX
      CGW=FMW*(-TB+DSQRT(TB**2-TC))                                           RTOX
      X(1)=DLOG10(CGW)                                                        RTOX
      G(1,1)=1.0                                                              RTOX
      G(2,1)=1.0                                                              RTOX
      G(2,2)=1.0                                                              RTOX
      CALL NONLIN(X,1,ICONV,IVAL)                                             RTOX
      CGW=DEXP(X(1)*FLN)                                                      RTOX
      PH=-DLOG10(C(1,1))                                                      RTOX
C BEGIN REFINEMENT                                                            RTOX
C HAVE DROPLETS DRIED OUT?                                                    RTOX
    1 IF(CGW.LE.0.0) GO TO 10                                                 RTOX
      X(1)=DLOG10(CGW)                                                        RTOX
      X(2)=PH                                                                 RTOX
C ARE DROPLETS UNSATURATED?                                                   RTOX
      IF(CSS.LE.0.0) GO TO 2                                                  RTOX
C IS ENOUGH ACID PRESENT TO PREVENT DRYING OUT OF DROPLETS?                   RTOX
      IF(CN/C6.LT.2.0) GO TO 4                                                RTOX
   10 CGW=0.0                                                                 RTOX
      CSS=C6                                                                  RTOX
      RTO=0.0                                                                 RTOX
      RTOZ=0.0                                                                RTOX
      PS=C4/CONST                                                             RTOX
      PN=(CN-2.0*CSS)/CONST                                                   RTOX
      PC=CC/CONST                                                             RTOX
      GO TO 11                                                                RTOX
    2 CSS=0.0                                                                 RTOX
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      CALL NONLIN(X,2,ICONV,EVAL)                                       RTOX
C IS SOLUTION SUPERSATURATED WITH (NH4)2SO4?                            RTOX
      GFS=G(1,2)**2*G(2,2)                                              RTOX
      DSS=CM1N**2*CM4S*GFS-EKSS                                         RTOX
      IF(DSS.LT.0.0) GO TO 6                                            RTOX
C IS ENOUGH ACID PRESENT TO PREVENT DRYING OUT OF DROPLETS?             RTOX
      IF((CN/C6).LT.2.0.AND.CGW.GT.1.0D-8) GO TO 3                      RTOX
      GO TO 10                                                          RTOX
C ESTIMATE AMOUNT OF SOLID (NH4)2SO4                                    RTOX
    3 CSS=DSS*CGW/((CM1N+4.0*CM4S)*CM1N*GFS)                            RTOX
      IF((CN-2.0*CSS).GT.0.0) GO TO 4                                   RTOX
      CSS=0.4*CN                                                        RTOX
    4 X(3)=DLOG10(CN/(CN-2.0*CSS))                                      RTOX
      CALL NONLIN(X,3,ICONV,EVAL)                                       RTOX
C HAS SOLUTION BECOME UNSATURATED WITH (NH4)2SO4?                       RTOX
      IF(X(3).LE.0.0) GO TO 2                                           RTOX
C HAVE DROPLETS DRIED UP?                                               RTOX
      IF(CGW.LE.1.0D-8) GO TO 10                                        RTOX
      CSS=CN/2.0*(1.0-DEXP(-X(3)*FLN))                                  RTOX
    6 CGW=DEXP(X(1)*FLN)                                                RTOX
      PH=X(2)                                                           RTOX
      CMH=DEXP(-PH*FLN)                                                 RTOX
C BEGIN CALCULATION OF RATE OF OXIDATION OF S(IV)                       RTOX
C RATE OF OXIDATION OF SO32- BY OXYGEN IN SOLUTION (MMOL/M**3/SEC)      RTOX
      RQ1=RK1*G(2,2)                                                    RTOX
      RQ2=RK2*G(1,1)**0.5*G(2,2)                                        RTOX
      RTO=(RQ1+RQ2*CMH**0.5)*CM2S*CGW                                   RTOX
C RATE OF OXIDATION OF HSO3- BY OZONE IN SOLUTION (MMOL/M**3/SEC)       RTOX
      RQ3=RK3*G(2,1)                                                    RTOX
      CMOZ=EKOZ*COZ/(CONST+EKOZ*CGW)                                    RTOX
      RTOZ=RQ3*CMOZ*CM1S*CGW                                            RTOX
C RATE OF OXIDATION OF SO2 BY OH RADICAL IN GAS PHASE (MMOL/M**3/SEC)   RTOX
   11 RTOH=RK4*COH*PS*CONST                                             RTOX
C TOTAL OXIDATION RATE OF S(IV) (MMOL/METER**3/SEC)                     RTOX
      RTT=RTOH+RTOZ+RTO                                                 RTOX
      RETURN                                                            RTOX
      END                                                               RTOX
C
C SUBROUTINE TO REFINE CGW, PH, CSS BY SECANT METHOD                    NLIN
      SUBROUTINE NONLIN(XIN,N,ICONV,EVAL)                               NLIN
C  PROGRAM AUTHORS  R. E. FUNDERLIC AND J. RINZEL,                      NLIN
C  COMPUTING TECHNOLOGY CENTER, UNION CARBIDE CORP., NUCLEAR DIV.,      NLIN
C  OAK RIDGE, TENN.                                                     NLIN
C                                                                       NLIN
C  CTC ORD PROGRAM NO. 9066                                             NLIN
      IMPLICIT REAL*8 (A-H,O-Z)                                         NLIN
      LOGICAL WRT                                                       NLIN
      COMMON/HONON/WRT                                                  NLIN
      DIMENSION XIN(N),X(20,21),XBAR(20,2),A(21,21),AINV(21,21),P(21),  NLIN
     1B(21),XNORM(21),BNORM(20)                                         NLIN
      WRT=.FALSE.                                                       NLIN
      ICONV=0                                                           NLIN
      NP1=N+1                                                           NLIN
      DO 110 J=1,NP1                                                    NLIN
      DO 120 I=1,N                                                      NLIN
      IF(J.NE.1) GO TO 130                                              NLIN
      X(I,J)=XIN(I)                                                     NLIN
      GO TO 120                                                         NLIN
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  130 X(I,J)=XIN(I)                                                     NLIN
      IF(J-1.EQ.I)X(I,J)=0.005+X(I,J)                                   NLIN
  120 CONTINUE                                                          NLIN
  110 CONTINUE                                                          NLIN
      DO 1 J=1,NP1                                                      NLIN
      B(J)=1.                                                           NLIN
      A(NP1,J)=1.                                                       NLIN
    1 CALL EVAL(X(1,J),A(1,J))                                          NLIN
      DO 2 I=1,NP1                                                      NLIN
      DO 2 J=1,NP1                                                      NLIN
      AINV(I,J)=0.0D0                                                   NLIN
      IF(I.EQ.J)AINV(I,J)=1.0D0                                         NLIN
    2 CONTINUE                                                          NLIN
      DO 4 J=1,NP1                                                      NLIN
      SUM =0.                                                           NLIN
      DO 3 I=1,N                                                        NLIN
    3 SUM=SUM+DABS(A(I,J))                                              NLIN
    4 XNORM(J)=SUM                                                      NLIN
      CALL MATINV(A,AINV,NP1)                                           NLIN
      DO 5 I=1,N                                                        NLIN
    5 XBAR(I,1)=X(I,NP1)                                                NLIN
      ITER=40                                                           NLIN
      DO 15 K=1,ITER                                                    NLIN
      XBNUM=0.                                                          NLIN
      XBDEN=0.                                                          NLIN
      DO 7 I=1,N                                                        NLIN
      XB=0.                                                             NLIN
      DO 6 J=1,NP1                                                      NLIN
    6 XB=XB + AINV(J,NP1)*X(I,J)                                        NLIN
      XBAR(I,2)=XB                                                      NLIN
      XBNUM=XBNUM + (XBAR(I,2)-XBAR(I,1))**2                            NLIN
    7 XBDEN =XBDEN + XBAR(I,2)**2                                       NLIN
      ICONV=ICONV+1                                                     NLIN
      IF((XBNUM/XBDEN).LT.1.D-14) GO TO 16                              NLIN
      DO 8 I=1,N                                                        NLIN
    8 XBAR(I,1)=XBAR(I,2)                                               NLIN
      BIGNOR =0.                                                        NLIN
      DO 9 J=1,NP1                                                      NLIN
      BNORM(J)=XNORM(J)*DABS(B(J))                                      NLIN
      IF(BNORM(J).LE.BIGNOR) GO TO 9                                    NLIN
      BIGNOR=BNORM(J)                                                   NLIN
      JCOL = J                                                          NLIN
    9 CONTINUE                                                          NLIN
      CALL EVAL(XBAR,P)                                                 NLIN
      P(NP1)=1.                                                         NLIN
      XNORM(JCOL)=0.                                                    NLIN
      DO 10 I=1,N                                                       NLIN
       X(I,JCOL)=XBAR(I,1)                                              NLIN
   10 XNORM(JCOL)=XNORM(JCOL)+DABS(P(I))                                NLIN
      DO 11 I=1,NP1                                                     NLIN
      B(I)=0.                                                           NLIN
      DO 11 J=1,NP1                                                     NLIN
   11 B(I)=B(I)+AINV(I,J)*P(J)                                          NLIN
      DO 13 I=1,NP1                                                     NLIN
      IF(I.EQ.JCOL) GO TO 13                                            NLIN
      DO 12 J=1,NP1                                                     NLIN
   12 AINV(I,J)=AINV(I,J)-AINV(JCOL,J)*(B(I)/B(JCOL))                   NLIN
   13 CONTINUE                                                          NLIN
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      DO 14 I=1,NP1                                                     NLIN
   14 AINV(JCOL,I)=AINV(JCOL,I)/B(JCOL)                                 NLIN
   15 CONTINUE                                                          NLIN
      WRITE(20,101)                                                     NLIN
  101 FORMAT('1********THE FOLLOWING CASE DID NOT CONVERGE********')    NLIN
   16 WRT=.TRUE.                                                        NLIN
      CALL EVAL(XBAR,P)                                                 NLIN
      DO 17 I=1,N                                                       NLIN
   17 XIN(I)=XBAR(I, 2)                                                 NLIN
      RETURN                                                            NLIN
      END                                                               NLIN
C
      SUBROUTINE MATINV(A,B,III)                                        MINV
      IMPLICIT REAL*8 (A-H,O-Z)                                         MINV
      DIMENSION A(21,21), B(21,21)                                      MINV
      KK=III                                                            MINV
      NV=III                                                            MINV
      KKM=KK-1                                                          MINV
      DO9I=1,KKM                                                        MINV
      S=0.0                                                             MINV
      DO1J=I,KK                                                         MINV
      R=DABS(A(J,I))                                                    MINV
      IF(R.LT.S) GO TO 1                                                MINV
      S=R                                                               MINV
      L=J                                                               MINV
    1 CONTINUE                                                          MINV
      IF (L.EQ.I) GO TO 5                                               MINV
      IF(L-I)2,5,2                                                      MINV
    2 DO3J=I,KK                                                         MINV
      S=A(I,J)                                                          MINV
      A(I,J)=A(L,J)                                                     MINV
    3 A(L,J)=S                                                          MINV
      DO4J=1,NV                                                         MINV
      S=B(I,J)                                                          MINV
      B(I,J)=B(L,J)                                                     MINV
    4 B(L,J)=S                                                          MINV
    5 IF(A(I,I).EQ.0.) GO TO 9                                          MINV
      IPO=I+1                                                           MINV
      DO8J=IPO,KK                                                       MINV
      IF(A(J,I).EQ.0.) GO TO 8                                          MINV
      S=A(J,I)/A(I,I)                                                   MINV
      A(J,I)=0.0                                                        MINV
      DO6K=IPO,KK                                                       MINV
    6 A(J,K)=A(J,K)-A(I,K)*S                                            MINV
      DO7K=1,NV                                                         MINV
    7 B(J,K)=B(J,K)-B(I,K)*S                                            MINV
    8 CONTINUE                                                          MINV
    9 CONTINUE                                                          MINV
      KMO=KK-1                                                          MINV
      DO11K=1,NV                                                        MINV
      B(KK,K)=B(KK,K)/A(KK,KK)                                          MINV
      DO11I=1,KMO                                                       MINV
      N=KK-I                                                            MINV
      DO10J=N,KMO                                                       MINV
   10 B(N,K)=B(N,K)-A(N,J+1)*B(J+1,K)                                   MINV
   11 B(N,K)=B(N,K)/A(N,N)                                              MINV
      RETURN                                                            MINV
      END                                                               MINV
```

```
C
C SUBROUTINE CALLED BY S NONLIN TO CALCULATE ION CONCENTRATIONS C(I),   IVAL
C    ACTIVITY COEFFICIENTS G(I), AND THE RESIDUAL IN THE WATER          IVAL
C    ACTIVITY BALANCE Y(1) FOR THE CURRENT VALUE OF CGW AS GIVEN BY X(1) IVAL
      SUBROUTINE IVAL(X,Y)                                              IVAL
      IMPLICIT REAL*8(A-H,O-Z)                                          IVAL
      DIMENSION X(10),Y(21)                                             IVAL
      COMMON/BLK/R,PI,FLN,FMW,B(4,4,2),Z(2,4)                           IVAL
      COMMON/ARG/CGW,PH,CSS,C(2,4),T,RTT,RTOH,RTOZ,RTO,NCAL,NITN        IVAL
      COMMON/EQK/EKN,EK1N,EKC,EK1C,EK2C,EKS,EK1S,EK2S,EK3S,EKSS,EKW     IVAL
      COMMON/ACT/DHA,G(2,4),P,PWO,CONST                                 IVAL
      COMMON/VAR/C4,C6,COZ,COH,CC,CN,CW                                 IVAL
      CGW=DEXP(X(1)*FLN)                                                IVAL
      GHS=G(1,1)*G(2,2)/G(2,1)                                          IVAL
      QHS=EK3S/GHS                                                      IVAL
C BEGIN REFINEMENT OF ACTIVITY COEFFICIENTS AND ION CONCENTARIONS       IVAL
C    FOR CURRENT VALUE OF X(1)                                          IVAL
      DO 10 I=1,100                                                     IVAL
      BT=(QHS+(CN-C6)/CGW)/2.0                                          IVAL
      CT=QHS*(CN-2.0*C6)/CGW                                            IVAL
      C(1,1)=-BT+DSQRT(BT**2-CT)                                        IVAL
      C(1,2)=CN/CGW                                                     IVAL
      TERM=C6/(CGW*(C(1,1)+QHS))                                        IVAL
      C(2,1)=C(1,1)*TERM                                                IVAL
      C(2,2)=QHS*TERM                                                   IVAL
      QL=QHS                                                            IVAL
      CALL GAMAW(DHA,2,2,B,C,Z,G,P,AWI)                                 IVAL
      GHS=G(1,1)*G(2,2)/G(2,1)                                          IVAL
      QHS=EK3S/GHS                                                      IVAL
      IF(((QL-QHS)/QHS)**2.LT.1.0D-12) GO TO 20                         IVAL
   10 CONTINUE                                                          IVAL
   20 RAW=(CW-CGW/FMW)/(PWO*CONST)                                      IVAL
C CALCULATE RESIDUAL IN WATER ACTIVITY BALANCE                          IVAL
      Y(1)=(AWI-RAW)*FMW*(C(1,1)+C(1,2)+C(2,1)+C(2,2))                  IVAL
      RETURN                                                            IVAL
      END                                                               IVAL
C
C SUBROUTINE,CALLED BY NONLIN, CALCULATES ION CONCENTRATIONS,           EVAL
C    ACTIVITY COEFFICIENTS AND RESIDUALS FOR CURRENT VALUES OF          EVAL
C    CGW,PH AND CSS AS GIVEN BY X(1),X(2), AND X(3)                     EVAL
      SUBROUTINE EVAL(X,Y)                                              EVAL
      IMPLICIT REAL*8 (A-H,O-Z)                                         EVAL
      DIMENSION X(10),Y(21)                                             EVAL
      COMMON/BLK/R,PI,FLN,FMW,B(4,4,2),Z(2,4)                           EVAL
      COMMON/CASE/NOX                                                   EVAL
      COMMON/ARG/CGW,PH,CSS,C(2,4),T,RTT,RTOH,RTOZ,RTO,NCAL,NITN        EVAL
      COMMON/EQK/EKN,EK1N,EKC,EK1C,EK2C,EKS,EK1S,EK2S,EK3S,EKSS,EKW     EVAL
      COMMON/CON/CMH,CMN,CM1N,CMC,CM1C,CM2C,CMS,CM1S,CM2S,CM3S,CM4S,    EVAL
     &PN,PC,PS                                                          EVAL
      COMMON/ACT/DHA,G(2,4),P,PWO,CONST                                 EVAL
      COMMON/VAR/C4,C6,COZ,COH,CC,CN,CW                                 EVAL
      IF(CSS.EQ.0.0) GO TO 10                                           EVAL
      CSS=CN/2.0*(1.0-DEXP(-X(3)*FLN))                                  EVAL
   10 CMH=DEXP(-X(2)*FLN)                                               EVAL
      CGW=DEXP(X(1)*FLN)                                                EVAL
      C(1,1)=CMH                                                        EVAL
C BEGIN REFINEMENT OF ACTIVITY COEFFICIENTS                             EVAL
      DO 1 J=1,100                                                      EVAL
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```
      CALL GAMAW(DHA,2,2,B,C,Z,G,P,AWI)                                 EVAL
      GQ1=G(2,1)*G(1,1)                                                 EVAL
      GQ2=G(2,1)/(G(2,2)*G(1,1))                                        EVAL
      EQ1N=EK1N*G(1,1)/G(1,2)                                           EVAL
      EQC=EKC*AWI                                                       EVAL
      EQ1C=EK1C/GQ1                                                     EVAL
      EQ2C=EK2C*GQ2                                                     EVAL
      EQS=EKS*AWI                                                       EVAL
      EQ1S=EK1S/GQ1                                                     EVAL
      EQ2S=EK2S*GQ2                                                     EVAL
      EQ3S=EK3S*GQ2                                                     EVAL
      EQSS=EKSS/(G(1,2)**2*G(2,2))                                      EVAL
      EQW=EKW*AWI/GQ1                                                   EVAL
      CMHSQ=CMH*CMH                                                     EVAL
      PN=(CN-2.0*CSS)/(CONST+EKN*(1.0+EQ1N*CMH)*CGW)                    EVAL
      CMN=EKN*PN                                                        EVAL
      CM1N=EQ1N*CMN*CMH                                                 EVAL
      PC=CC/(CONST+EQC*(1.0+EQ1C/CMH+EQ1C*EQ2C/CMHSQ)*CGW)               EVAL
      CMC=EQC*PC                                                        EVAL
      CM1C=EQ1C*CMC/CMH                                                 EVAL
      CM2C=EQ2C*CM1C/CMH                                                EVAL
      PS=C4/(CONST+EQS*(1.0+EQ1S/CMH+EQ2S*EQ1S/CMHSQ)*CGW)               EVAL
      CMS=EQS*PS                                                        EVAL
      CM1S=EQ1S*CMS/CMH                                                 EVAL
      CM2S=EQ2S*CM1S/CMH                                                EVAL
      CMOH=EQW/CMH                                                      EVAL
      CM3S=(C6-CSS)/((1.0+EQ3S/CMH)*CGW)                                EVAL
      CM4S=EQ3S*CM3S/CMH                                                EVAL
      CMA1=CM1C+CM1S+CM3S+CMOH                                          EVAL
      CMA2=CM2C+CM2S+CM4S                                               EVAL
      DLSQI=((C(1,2)-CM1N)/CM1N)**2+((C(2,1)-CMA1)/CMA1)**2             EVAL
     &+((C(2,2)-CMA2)/CMA2)**2                                          EVAL
      C(1,2)=CM1N                                                       EVAL
      C(2,1)=CMA1                                                       EVAL
      C(2,2)=CMA2                                                       EVAL
      IF(DLSQI.LT.1.0D-12) GO TO 2                                      EVAL
    1 CONTINUE                                                          EVAL
C CALCULATE RESIDUALS IN CHARGE BALANCE Y(1), WATER ACTIVITY BALANCE    EVAL
C     Y(2), AND (NH4)2SO4 SOLUBILITY BALANCE Y(3) (IF APPLICABLE)       EVAL
    2 SUMI=C(1,1)+C(1,2)+C(2,1)+C(2,2)                                  EVAL
      Y(1)=(C(1,1)+C(1,2)-C(2,1)-2.0*C(2,2))/SUMI                       EVAL
      SUMN=CMN+CMS+CMC                                                  EVAL
      AWI=DEXP(-FMW*SUMI*P)                                             EVAL
      CRAW=1.0/AWI+FMW*SUMN                                             EVAL
      ARAW=PWO*CONST/(CW-CGW/FMW)                                       EVAL
      Y(2)=(ARAW-CRAW)/(FMW*SUMI)                                       EVAL
      IF(CSS.EQ.0.0) GO TO 20                                           EVAL
      AQSS=CM1N**2*CM4S                                                 EVAL
      Y(3)=(AQSS/EQSS)**(1.0/3.0)-1.0                                   EVAL
   20 NCAL=NCAL+1                                                       EVAL
      NITN=NITN+J                                                       EVAL
      RETURN                                                            EVAL
      END                                                               EVAL
C
C SUBROUTINE TO CALCULATE ACTIVITY COEFFICIENTS AND ACTIVITY OF WATER   GMAW
C DHA = DEBEYE-HUCKEL CONSTANT,NC = NO. OF CATIONS                      GMAW
C     NA = NO. OF ANIONS,B = INTERACTION COEFFICIENTS,                  GMAW
C     C = ION CONCENTRATIONS (MMOL/G H2O),Z = ION CHARGE                GMAW
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C     P = OSMOTIC COEFFICIENT, AWI = WATER ACTIVITY CALCULATED FROM     GMAW
C     ION CONCENTRATIONS                                                GMAW
      SUBROUTINE GAMAW(DHA,NC,NA,B,C,Z,G,P,AWI)                         GMAW
      IMPLICIT REAL*8(A-H,O-Z)                                          GMAW
      DIMENSION B(4,4,2),BG(4,4),BP(4,4),C(2,4),Z(2,4),G(2,4),ZQ(2,4)   GMAW
      SP=0                                                              GMAW
      SI=0                                                              GMAW
      DO 10 K=1,2                                                       GMAW
      IF(K.EQ.1) GO TO 1                                                GMAW
      N=NA                                                              GMAW
      GO TO 2                                                           GMAW
    1 N=NC                                                              GMAW
    2 DO 10 I=1,N                                                       GMAW
      ZQ(K,I)=Z(K,I)*Z(K,I)                                             GMAW
      SP=SP+C(K,I)                                                      GMAW
      SI=SI+ZQ(K,I)*C(K,I)                                              GMAW
   10 CONTINUE                                                          GMAW
      CI=0.5*SI                                                         GMAW
      IF(CI.GT.0.0) GO TO 5                                             GMAW
      CALL PRINT(3)                                                     GMAW
      CALL EXIT                                                         GMAW
    5 SCI=DSQRT(CI)                                                     GMAW
      TI=1.0+SCI                                                        GMAW
      FG=-DHA*SCI/TI                                                    GMAW
      FP=-2.0*DHA*(TI-1.0/TI-2.0*DLOG(TI))                              GMAW
      FPI=DEXP(-2.0*SCI)                                                GMAW
      FGI=(1.0-FPI*(1.0+2.0*SCI-2.0*CI))/(4.0*CI)                       GMAW
      SBM=0                                                             GMAW
      DO 20 I=1,NC                                                      GMAW
      DO 20 J=1,NA                                                      GMAW
      BG(I,J)=B(I,J,1)+FGI*B(I,J,2)                                     GMAW
      BP(I,J)=B(I,J,1)+FPI*B(I,J,2)                                     GMAW
      SBM=SBM+BP(I,J)*C(1,I)*C(2,J)                                     GMAW
   20 CONTINUE                                                          GMAW
      DO 30 I=1,NC                                                      GMAW
      SG=0                                                              GMAW
      DO 40 J=1,NA                                                      GMAW
      SG=SG+BG(I,J)*C(2,J)                                              GMAW
   40 CONTINUE                                                          GMAW
      G(1,I)=DEXP(ZQ(1,I)*FG+SG)                                        GMAW
   30 CONTINUE                                                          GMAW
      DO 50 J=1,NA                                                      GMAW
      SG=0                                                              GMAW
      DO 60 I=1,NC                                                      GMAW
      SG=SG+BG(I,J)*C(1,I)                                              GMAW
   60 CONTINUE                                                          GMAW
      G(2,J)=DEXP(ZQ(2,J)*FG+SG)                                        GMAW
   50 CONTINUE                                                          GMAW
      P=1.0+(FP+SBM)/SP                                                 GMAW
      AWI=DEXP(-0.0180153*SP*P)                                         GMAW
      RETURN                                                            GMAW
      END                                                               GMAW
C
C SUBROUTINE TO CALCULATE STARTING VALUES OF ARGUEMENTS                 XPCT
C NOX = NO OF CALCULATION CALLED BY KUTTA                               XPCT
C IN = SIGNAL (IF 1) THAT THIS IS FIRST CALCULATION OF EACH INCREMENT   XPCT
C X = DISTANCE FROM SOURCE, Y = ARRAY OF ARGUEMENTS                     XPCT
      SUBROUTINE EXPCT(NOX,IN,X,Y)                                      XPCT
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      IMPLICIT REAL*8(A-H,O-Z)                                          XPCT
      DIMENSION Y(6),YL(6),YLL(6),DYDX(6)                               XPCT
      IF(NOX.EQ.1) GO TO 211                                            XPCT
      IF(NOX.EQ.2) GO TO 121                                            XPCT
      IF(IN.EQ.0.AND.IX.EQ.1.AND.ID.EQ.1) GO TO 111                     XPCT
      IF(IN.EQ.1.AND.ID.EQ.1) GO TO 311                                 XPCT
      IF(IN.EQ.0.AND.IX.EQ.3) GO TO 132                                 XPCT
      IF(IN.EQ.0.AND.IX.EQ.1.AND.ID.EQ.2) GO TO 112                     XPCT
      IF(IN.EQ.1.AND.ID.EQ.2) GO TO 312                                 XPCT
C IX=1 DO NOT SAVE X, IX=2 SAVE X, IX=3 SAVE X AND LAST X               XPCT
C IY=1 DO NOT SAVE Y, IY=2 SAVE Y, IY=3 SAVE Y AND LAST Y AND           XPCT
C     CALCULATE VALUES OF DYDX                                          XPCT
C ID=1 DO NOT CHANGE Y, ID=2 INTERPOLATE OR EXTRAPOLATE Y               XPCT
C FIRST ENTRY, SAVE X                                                   XPCT
  211 IX=2                                                              XPCT
      IY=1                                                              XPCT
      ID=1                                                              XPCT
      GO TO 2                                                           XPCT
C SECOND ENTRY, SAVE Y VALUES FROM PREVIOUS CALCULATION                 XPCT
  121 IX=1                                                              XPCT
      IY=2                                                              XPCT
      ID=1                                                              XPCT
      GO TO 5                                                           XPCT
C NOX=3,4,OR 5, RETURN CURRENT VALUES OF Y                              XPCT
  111 IX=1                                                              XPCT
      IY=1                                                              XPCT
      ID=1                                                              XPCT
      RETURN                                                            XPCT
C FIRST CALL FROM KUTTA IN SECOND INCREMENT, SAVE X AND XL              XPCT
  311 IX=3                                                              XPCT
      IY=1                                                              XPCT
      ID=1                                                              XPCT
      GO TO 3                                                           XPCT
C SECOND CALL FROM KUTTA IN AN INCREMENT AFTER FIRST, SAVE Y AND YL,    XPCT
C     CALCULATE DYDX AND RETURN NEW VALUES OF Y                         XPCT
  132 IX=1                                                              XPCT
      IY=3                                                              XPCT
      ID=2                                                              XPCT
      GO TO 6                                                           XPCT
C 3RD, 4TH, OR 5TH CALL FROM KUTTA IN AN INCREMENT AFTER FIRST,         XPCT
C     RETURN NEW Y VALUES                                               XPCT
  112 IX=1                                                              XPCT
      IY=1                                                              XPCT
      ID=2                                                              XPCT
      GO TO 8                                                           XPCT
C FIRST CALL FROM KUTTA IN AN INCREMENT AFTER SECOND,                   XPCT
C     SAVE X AND XL, AND RETURN NEW Y VALUES                            XPCT
  312 IX=3                                                              XPCT
      IY=1                                                              XPCT
      ID=2                                                              XPCT
    3 XLL=XL                                                            XPCT
    2 XL=X                                                              XPCT
      IF(ID.EQ.2) GO TO 9                                               XPCT
      RETURN                                                            XPCT
    5 DO 10 I=1,6                                                       XPCT
   10 YL(I)=Y(I)                                                        XPCT
      RETURN                                                            XPCT
    6 DO 20 I=1,6                                                       XPCT
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      YLL(I)=YL(I)                                                          XPCT
      YL(I)=Y(I)                                                            XPCT
   20 DYDX(I)=(YL(I)-YLL(I))/(XL-XLL)                                       XPCT
    8 DO 30 I=1,6                                                           XPCT
   30 Y(I)=YL(I)+DYDX(I)*(X-XL)                                             XPCT
      RETURN                                                                XPCT
    9 DO 40 I=1,6                                                           XPCT
   40 Y(I)=YL(I)+DYDX(I)*(XL-XLL)                                           XPCT
      RETURN                                                                XPCT
      END                                                                   XPCT
C
C SUBROUTINE TO DETERMINE COMPONENT CONC'N BY RUNGA-KUTTA INTEGRATION       KUTA
      SUBROUTINE KUTTA(XL,XU,Y,NE,DEL,ACCURC,IMAX,EQUA)                     KUTA
C  PROGRAM AUTHOR   F. D. HAMMERLING,                                       KUTA
C  COMPUTING TECHNOLOGY CENTER, UNION CARBIDE CORP., NUCLEAR DIV.,          KUTA
C  OAK RIDGE, TENN.                                                         KUTA
CC MODIFIED AS INDICATED  FOR  THIS PROGRAM                                 KUTA
      EXTERNAL EQUA                                                         KUTA
      DIMENSION Y(10),YI(10),YN(10),K1(10),K2(10),K3(10), K4(10),K5(10),    KUTA
     > F(10),E(10),F1(10)                                                   KUTA
      DOUBLE PRECISION Y,F,E,F1,XN,XL,DEL,XU,H,TEST,ACCURC, YN,YI,K1,       KUTA
     > K2,K3,K4,K5                                                          KUTA
      LOGICAL QUIT,FIRST                                                    KUTA
      ITTER=0                                                               KUTA
      N=NE                                                                  KUTA
      XN=XL                                                                 KUTA
      H=DEL                                                                 KUTA
      FIRST=.TRUE.                                                          KUTA
      QUIT=.FALSE.                                                          KUTA
      DO 10 I=1,N                                                           KUTA
   10    YN(I)=Y(I)                                                         KUTA
   20 IF (XN+H.LT.XU) GO TO 30                                              KUTA
      DEL=H                                                                 KUTA
      H=XU-XN                                                               KUTA
      IF (FIRST) DEL=H                                                      KUTA
      QUIT=.TRUE.                                                           KUTA
CC THE INTEGER (IN = 1 OR 0) HAS BEEN ADDED TO ARGUEMENT LIST               KUTA
CC    OF S. EQUA TO SIGNAL FIRST CALCULATION OF EACH INCREMENT              KUTA
   30 CALL EQUA(XN,YN,F1,1)                                                 KUTA
CC PRINT OUT RESULTS OF THIS FIRST CALCULATION AT THE BEGINNING OF          KUTA
CC    EACH INTERVAL IN X SPECIFIED IN THE MAIN PROGRAM                      KUTA
      IF(FIRST) CALL PRINT(2)                                               KUTA
   40 DO 50 I=1,N                                                           KUTA
         K1(I)=H*F1(I)/3.                                                   KUTA
   50    YI(I)=YN(I)+K1(I)                                                  KUTA
      CALL EQUA(XN+H/3.,YI,F,0)                                             KUTA
      DO 60 I=1,N                                                           KUTA
         K2(I)=H*F(I)/3.                                                    KUTA
   60    YI(I)=YN(I)+K1(I)/2.+K2(I)/2.                                      KUTA
      CALL EQUA(XN+H/3.,YI,F,0)                                             KUTA
      DO 70 I=1,N                                                           KUTA
         K3(I)=H*F(I)/3.                                                    KUTA
   70    YI(I)=YN(I)+3.*K1(I)/8.+9.*K3(I)/8.                                KUTA
      CALL EQUA(XN+H/2.,YI,F,0)                                             KUTA
      DO 80 I=1,N                                                           KUTA
         K4(I)=H*F(I)/3.                                                    KUTA
   80    YI(I)=YN(I)+3.*K1(I)/2.-9.*K3(I)/2.+6.*K4(I)                       KUTA
      CALL EQUA(XN+H,YI,F,0)                                                KUTA
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      TEST=0.0                                                          KUTA
      DO 90 I=1,N                                                       KUTA
         K5(I)=H*F(I)/3.                                                KUTA
         E(I)=(K1(I)-9.*K3(I)/2.+4.*K4(I)-K5(I)/2.)/5.                  KUTA
         TEST=DMAX1(TEST,DABS(E(I)))                                    KUTA
   90    CONTINUE                                                       KUTA
      IF (TEST.LT.ACCURC) GO TO 100                                     KUTA
      ITTER=ITTER+1                                                     KUTA
      IF (ITTER.GE.IMAX) GO TO 140                                      KUTA
      H=H/2.                                                            KUTA
      QUIT=.FALSE.                                                      KUTA
      FIRST=.FALSE.                                                     KUTA
      GO TO 40                                                          KUTA
  100 DO 110 I=1,N                                                      KUTA
  110    YN(I)=YN(I)+(K1(I)+4.*K4(I)+K5(I))/2.                          KUTA
      XN=XN+H                                                           KUTA
      FIRST=.FALSE.                                                     KUTA
      IF (TEST.GE.ACCURC/32.) GO TO 120                                 KUTA
      H=2.*H                                                            KUTA
      ITTER=ITTER-1                                                     KUTA
  120 IF (.NOT.QUIT) GO TO 20                                           KUTA
      DO 130 I=1,N                                                      KUTA
  130    Y(I)=YN(I)                                                     KUTA
      GO TO 150                                                         KUTA
  140 WRITE(21,1000)                                                    KUTA
  150 RETURN                                                            KUTA
 1000 FORMAT(1X,'IMAX EXCEEDED')                                        KUTA
      END                                                               KUTA
C
C SUBROUTINE FOR PRINTING OUTPUT ON LINE PRINTER                        PRNT
      SUBROUTINE PRINT(N)                                               PRNT
      IMPLICIT REAL*8(A-H,O-Z)                                          PRNT
      COMMON/BLK/R,PI,FLN,FMW,B(4,4,2),Z(2,4)                           PRNT
      COMMON/CASE/NOX                                                   PRNT
      COMMON/RTE/NSC,NRL,VRGO,TP,H,UX,A(7),TA,DELX,VDG,VDP              PRNT
      COMMON/SIGMA/SGO,SGPY,SGPZ,SGLY,SGLZ,SGSY,SGSZ,BETAL,BETAS        PRNT
      COMMON/ARG/CGW,PH,CSS,C(2,4),T,RTT,RTOH,RTOZ,RTO,NCAL,NITN        PRNT
      COMMON/EQK/EKN,EK1N,EKC,EK1C,EK2C,EKS,EK1S,EK2S,EK3S,EKSS,EKW     PRNT
      COMMON/CON/CMH,CMN,CM1N,CMC,CM1C,CM2C,CMS,CM1S,CM2S,CM3S,CM4S,    PRNT
     &PN,PC,PS                                                          PRNT
      COMMON/ACT/DHA,G(2,4),P,PWO,CONST                                 PRNT
      COMMON/GIVN/WPCTC,WPCTH,WPCTS,QCCAL,FCTS6,EXAIR,FCON,TCP,TCA,     PRNT
     &XLAST,XNEXT,ERRR                                                  PRNT
      COMMON/VAR/C4,C6,COZ,CCH,CC,CN,CW                                 PRNT
      GO TO (1,2),N                                                     PRNT
    1 WRITE(21,100) WPCTC,WPCTH,WPCTS,QCCAL,FCTS6,EXAIR,FCON,H,         PRNT
     &TCE,NSC,NRL,UX,VDG,VDP,TCA                                        PRNT
      WRITE(21,125) (A(I),I=1,7)                                        PRNT
      WRITE(21,150) ERRR,SGO                                            PRNT
      RETURN                                                            PRNT
    2 WRITE(21,300) XLAST,DELX,SGPY,SGLY,SGSY,SGPZ,SGLZ,SGSZ,           PRNT
     &CGW,PH,CSS,T,NCX,NCAL,NITN,                                       PRNT
     &RTT,RTOH,RTOZ,RTO,G(1,1),G(1,2),G(2,1),G(2,2)                     PRNT
      WRITE(21,325) C4,C6,COZ,COH,CC,CN,CW                              PRNT
      WRITE(21,340) PN,PC,PS                                            PRNT
      IF(CGW.GT.0.0) GO TO 21                                           PRNT
      WRITE(21,348)                                                     PRNT
   21 WRITE(21,350) CMN,CM1N,CMC,CM1C,CM2C,CMS,CM1S,CM2S,CM3S,CM4S      PRNT
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100 FORMAT(1H1,'SULFUR CHEMISTRY IN A GAUSSIAN PLUME'////              PRNT
   &1X,'  WPCTC   WPCTH   WPCTS   QCCAL   FCTS6   EXAIR',              PRNT
   &'     FCON       H      TCP NSC NRL       UX      VDG',            PRNT
   &'     VDP      TCA'/                                               PRNT
   &1X,F7.2,8F8.2,2I4,4F8.2/)                                          PRNT
125 FORMAT(                                                            PRNT
   &1X,'      AC4      AC6      AOZ      AOH      ACC      ACN',       PRNT
   &'       ACW'/1X,1P7E9.2///)                                        PRNT
150 FORMAT(1X,'  ERRR     SG0  '/1X,1PE8.1,0PF8.2/)                    PRNT
300 FORMAT(                                                            PRNT
   &21X,'      X    DELX    SGPY    SGLY    SGSY    SGPZ',             PRNT
   &'    SGLZ    SGSZ'/21X,F7.1,7F8.2,//                               PRNT
   &21X,'      CGW       PH     CSS       T   NOX   NCL   NITN'/       PRNT
   &21X,1PE9.2,0P2F8.4,F8.2,2I6,I7//                                   PRNT
   &21X,'      RTT     RTOH     RTOZ      RTO       GH',               PRNT
   &'      GN      GHS      GS'/21X,1P4E9.2,0P4F8.4/)                  PRNT
325 FORMAT(                                                            PRNT
   &11X,'       C4       C6      COZ      CCH       CC       CN',      PRNT
   &'       CW'/11X,1P7E9.2/)                                          PRNT
340 FORMAT(                                                            PRNT
   &11X,'      PN      PC      PS'/11X,1P3E8.1/)                       PRNT
348 FORMAT(1X,'DROPLETS HAVE DRIED UP, LAST SCLN. COMP. WAS:'/)        PRNT
350 FORMAT(                                                            PRNT
   &1X,'        CMN       CM1N        CMC       CM1C       CM2C',      PRNT
   &'        CMS       CM1S       CM2S       CM3S       CM4S'/         PRNT
   &1X,1P10E12.4//)                                                    PRNT
    RETURN                                                             PRNT
    END                                                                PRNT
```

3. Sample Input and Output

The following input values, used in the reference case (Table V), were read by the indicated READ statements in M. SULCAL:

```
[READ(20, 100)  WPCTC,WPCTH,QCOAL,FCTS6,EXAIR,FCON,TCP,H]
 82.57      6.93      100.0      0.02      0.25      5.0      177.0
 400.0

[READ(20, 100)  NSC,NRL,UX,VDG,VDP,(A(I), I=1, 7),TCA,WPCTS]
     3         5        2.0      0.01      0.01      0.004      0.0
0.0032     2.0E-8     12.26    6.0E-4     929.7     21.11      1.0

[READ(20, 100)  XNEXT,DELX,ERRR]
 300.0        0.1  0.000003

[READ(20, 100)  NX,(XINCR(I), I=1,NX)]
     4      700.0     4000.0     5000.0    15000.0
[100 FORMAT (7G 10.0)]
```

The output produced is shown on the next two pages. The first three rows of values, mostly input, are independent of x. In row 2 are the ambient concentrations of the seven components S(IV), S(VI), O_3, OH, CO_2, NH_3, and H_2O. Rows 4 through 9 are repeated for each specified value of x. Row 4 includes the current value of the increment in x (DELX) in S. KUTTA. In row 5, NOX, NCL and NITN are, respectively, the accumulated entries into S. RATE, S. EVAL and S. GAMAW. Row 6 includes the oxidation rates: total, by OH, by O_3, and by oxygen; and the activity coefficients of the aqueous ions H^+, NH_4^+, X^-, and X^{2-}. In row 7 are the effective concentrations of components in the plume. Row 8 includes the partial pressures of NH_3, CO_2 and SO_2 gases. Finally in row 9 are the concentrations of the aqueous species NH_3, NH_4^+, H_2CO_3, HCO_3^-, CO_3^{2-}, H_2SO_3, HSO_3^-, SO_3^{2-}, HSO_4^- and SO_4^{2-}.

```
SULFUR CHEMISTRY IN A GAUSSIAN PLUME


 WPCTC    WPCTH    WPCTS   QCOAL    FCTS6    EXAIR     FCON       H     TCP NSC NRL      UX      VDG      VDP     TCA
 82.57     6.93     1.00  100.00     0.02     0.25     5.00  400.00  177.00   3   5    2.00     0.01     0.01   21.11

      AC4       AC6       AOZ       AOH       ACC       ACN       ACW
4.00D-03 0.0      3.20D-03 2.00D-08 1.23D 01 6.00D-04 9.30D 02


 FRRR      SG0
3.0D-06    8.84

                                   X     DELX    SGPY     SGLY    SGSY     SGPZ     SGLZ    SGSZ
                              300.0     0.10   28.94    37.78   15.73    29.31    38.15   15.82

                                 CGW        PH       CSS        T   NOX    NCL   NITN
                              6.39D-03 -1.2005  0.0      330.21     2      5     24

                                 RTT      RTOH     RTOZ      RTO       GH       GN      GHS       GS
                              3.00D-05 3.00D-05 5.27D-16 1.32D-18 49.3771  0.3923 59.5242  0.0157

                       C4        C6      COZ      COH       CC       CN       CW
                  4.89D 00 9.98D-02 2.19D-03 1.37D-08 1.11D 03 4.11D-04 1.19D 03

                      PN       PC       PS
                  9.4D-15 3.0D-02 1.3D-04

           CMN         CM1N          CMC         CM1C         CM2C          CMS         CM1S         CM2S         CM3S         CM4S
  1.3990D-13  6.4383D-02  3.6043D-05  1.0670D-15  4.3346D-25  1.0746D-05  2.0027D-12  4.0459D-19  1.5294D 01  3.1787D-01


                                   X     DELX    SGPY     SGLY    SGSY     SGPZ     SGLZ    SGSZ
                             1000.0    12.80   77.41    86.25   27.26    75.91    84.75   26.90

                                 CGW        PH       CSS        T   NOX    NCL   NITN
                              4.47D-03 -0.9559  0.0      305.47   595   2973  16466

                                 RTT      RTOH     RTOZ      RTO       GH       GN      GHS       GS
                              1.32D-05 1.32D-05 1.41D-14 2.28D-17  6.0477  0.4091  9.8348  0.0165

                       C4        C6      COZ      COH       CC       CN       CW
                  1.65D 00 3.79D-02 2.86D-03 1.79D-08 3.82D 02 5.36D-04 1.02D 03

                      PN       PC       PS
                  2.0D-14 9.6D-03 4.1D-05

           CMN         CM1N          CMC         CM1C         CM2C          CMS         CM1S         CM2S         CM3S         CM4S
  8.3464D-13  1.2014D-01  1.4468D-04  1.2400D-13  7.3285D-23  2.1002D-05  5.6631D-10  3.3968D-16  7.7830D 00  6.9631D-01


                                   X     DELX    SGPY     SGLY    SGSY     SGPZ     SGLZ    SGSZ
                             5000.0   102.40  223.19   232.03   61.94   236.07   244.92   65.00

                                 CGW        PH       CSS        T   NOX    NCL   NITN
                              3.20D-03 -0.6334  0.0      296.23  1160   5805  35040

                                 RTT      RTOH     RTOZ      RTO       GH       GN      GHS       GS
                              2.60D-06 2.60D-06 3.84D-14 9.02D-17  1.4106  0.4276  2.7777  0.0196

                       C4        C6      COZ      COH       CC       CN       CW
```

```
         2.97D-01 1.20D-02 3.14D-03 1.96D-08 7.93D 01 5.88D-04 9.45D 02

              PN      PC      PS
         1.0D-13 1.9D-03 7.2D-06

       CMN        CM1N         CMC        CM1C        CM2C         CMS        CM1S        CM2S        CM3S        CM4S
6.3393D-12  1.8356D-01  5.7870D-05  1.4439D-12  1.5260D-21  7.8317D-06  8.3611D-09  1.2068D-14  2.9836D 00  7.4973D-01


                        X    DELX    SGPY    SGLY    SGSY    SGPZ    SGLZ    SGSZ
                  10000.0  204.80  329.80  338.65   87.30  355.37  364.22   93.39

                        CGW      PH     CSS       T   NOX   NCL   NITN
                   3.04D-03 -0.5419  0.0     295.23  1340  6705  40674

                        RTT     RTOH     RTOZ      RTO      GH      GN     GHS     GS
                   1.28D-06 1.28D-06 2.97D-14 7.95D-17  1.1468  0.4362  2.2439  0.0211

               C4       C6      COZ      COH      CC       CN       CW
         1.45D-01 9.11D-03 3.17D-03 1.98D-08 4.54D 01 5.93D-04 9.37D 02

              PN      PC      PS
         1.5D-13 1.1D-03 3.5D-06

       CMN        CM1N         CMC        CM1C        CM2C         CMS        CM1S        CM2S        CM3S        CM4S
9.7110D-12  1.9500D-01  3.5642D-05  1.6543D-12  1.9528D-21  4.1551D-06  8.5414D-09  1.4235D-14  2.3121D 00  6.8261D-01


                        X    DELX    SGPY    SGLY    SGSY    SGPZ    SGLZ    SGSZ
                  25000.0  819.20  534.71  543.56  136.05  552.64  561.49  140.32

                        CGW      PH     CSS       T   NOX   NCL   NITN
                   3.10D-03 -0.4734  0.0     294.67  1540  7707  46631

                        RTT     RTOH     RTOZ      RTO      GH      GN     GHS     GS
                   5.30D-07 5.30D-07 1.73D-14 5.09D-17  1.0142  0.4435  1.9694  0.0224

               C4       C6      COZ      COH      CC       CN       CW
         5.95D-02 7.87D-03 3.19D-03 1.99D-08 2.63D 01 5.94D-04 9.33D 02

              PN      PC      PS
         1.8D-13 6.4D-04 1.4D-06

       CMN        CM1N         CMC        CM1C        CM2C         CMS        CM1S        CM2S        CM3S        CM4S
1.2339D-11  1.9167D-01  2.1560D-05  1.5005D-12  1.9100D-21  1.7838D-06  5.6055D-09  1.0265D-14  1.9130D 00  6.2662D-01
```

APPENDIX B

EFFECTIVE VOLUME OF FREE PLUME

The reactions in a plume are complicated by the situation that the reaction rates vary across and down the plume because of variations in concentration, temperature and mixing. The detailed treatment of these varying conditions is beyond the scope of this investigation. We want to use an idealized model for this study and yet relate the result to the conditions which are obtained in the open environment. The dispersion of effluents in the atmosphere has been successfully modeled by a Gaussian distribution in which the variance or dispersion σ follows empirically determined relations that are functions of time, distance from source, and the prevailing meteorological and topographical conditions. We will show that when modeling reaction rates it is possible to use a simple uniform model which can yield the same reaction rates as a well mixed Gaussian distribution.

In the following treatment, let q_i be the total amount of reactant i, in a unit length of the plume in the x direction, let C_i be the density or concentration of reactant i, and let R be the total rate of production of the reaction product. Consider a binary reaction

$$\frac{\text{Rate}}{\text{Volume}} = kC_1^{\alpha_1} C_2^{\alpha_2} , \qquad (1)$$

then

$$R = k \int_V C_1^{\alpha_1} C_2^{\alpha_2} \, dv . \qquad (2)$$

Let

$$C_i = \frac{q_i}{2\pi\sigma_y\sigma_z} e^{-y^2/2\sigma_y} e^{-z^2/2\sigma_z} . \qquad (3)$$

Then the rate of reaction in a volume of unit length in the x-direction and infinite in extent in the y and z direction is

$$R = \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \; k \, C_1^{\alpha_1} \; C_2^{\alpha_2}$$

$$= \frac{k \; q_1^{\alpha_1} \; q_2^{\alpha_2}}{2\pi\sigma_y\sigma_z} \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \; e^{-(\alpha_1+\alpha_2)y^2/2\sigma_y^2} \; e^{-(\alpha_1+\alpha_2)z^2/2\sigma_z^2}$$

$$= \frac{k \, q_1^{\alpha_1} \, q_2^{\alpha_2}}{(2\pi\sigma_y\sigma_z)^{\alpha_1+\alpha_2}} \; (2\pi\sigma_y\sigma_z) \cdot \frac{1}{\alpha_1 + \alpha_2}$$

$$\equiv \frac{k \cdot q_1^{\alpha_1} q_2^{\alpha_2}}{(4\pi\sigma_y\sigma_z)^{\alpha_1 + \alpha_2}} \; (4\pi \; \sigma_y\sigma_z) \left(\frac{2^{\alpha_1+\alpha_2-1}}{\alpha_1 + \alpha_2}\right), \tag{4}$$

where we have assumed a uniform or effective temperature. Now suppose the same amounts of reactants were spread uniformly through a volume V such that

$$\bar{C}_i = q_i/V. \tag{5}$$

Then

$$\bar{R} = k \int_V \bar{C}_1^{\alpha_1} \bar{C}_2^{\alpha_2} \, dv = \frac{k q_1^{\alpha_1} q_2^{\alpha_2}}{V^{\alpha_1+\alpha_2}} \cdot V \quad . \tag{6}$$

Now if we choose as a control volume $V = 4\pi\sigma_y\sigma_z$ then

$$\bar{R} = \frac{\alpha_1 + \alpha_2}{2^{\alpha_1+\alpha_2-1}} \; R = F \; R \; . \tag{7}$$

The choice $V = 4\pi\sigma_y\sigma_z$ yields reaction rates which are correct through second order. Note this includes the case $\alpha_1 = 0$ with $\alpha_2 = 1$ or 2.

Other cases can be handled by scaling the rate constants by the relation

$$\bar{k} = k \cdot \frac{2^{\alpha_1+\alpha_2-1}}{\alpha_1+\alpha_2} , \tag{8}$$

where $\bar{k}$ is the effective rate constant. Similar results may be obtained for equilibria, and they may be extended to reactions and equilibria of the form $kC_1^{\alpha_1} C_2^{\alpha_2} \ldots C_n^{\alpha_n}$ by replacing $(\alpha_1 + \alpha_2)$ in the equations above by $(\alpha_1+\alpha_2+\ldots+\alpha_n)$.

1. Mean Concentration When Plume Touches the Ground

The forgoing discussion assumes a free plume and neglects interactions with the surface. An effect of the ground is to limit the downward spread of the plume and to restrict the dilution of the effluents near the land surface. This has been successfully modeled by assuming an "image plume", i.e., a "reflection" of the plume at the ground. The effect of the "image plume" is included in the present treatment as follows:

Consider the total reaction rate

$$R = k \int_V C_1 C_2 \, dv , \tag{9}$$

where the concentrations C_i have the distribution

$$C_i(x,y,z) = \frac{q_i}{2\pi\sigma_y\sigma_z} e^{-y^2/2\sigma_y} \left[e^{-(z-h)^2/2\sigma_z^2} + e^{-(z+h)^2/2\sigma_z^2} \right] , \tag{10}$$

where q_i is the total amount of material available to react in a unit length of plume. Then

$$R = \frac{kq_1 q_2}{(2\pi\sigma_y\sigma_z)^2} \int_{-\infty}^{\infty} e^{-2y^2/2\sigma_y^2}\, dy \int_{-\infty}^{\infty} \left(e^{-(z-h)^2/2\sigma_z^2} + e^{-(z+h)^2/2\sigma_z^2}\right)^2 dz$$

$$= \frac{kq_1 q_2}{(2\pi\sigma_y\sigma_z)^2} \cdot \sqrt{2\pi}\,\sigma_y \int_0^{\infty} dz \Bigg[\Big(e^{-2(z-h)^2/2\sigma_z}$$

$$+ e^{-(z+h)^2/2\sigma_z}\Big) + 2e^{-\frac{(z-h)^2}{2\sigma_z}}\, e^{-\frac{(z+h)^2}{2\sigma_z}}\Bigg]$$

$$= \frac{kq_1 q_2}{(2\pi\sigma_y\sigma_z)^2} \left[\frac{2\pi\sigma_y\sigma_z}{2} + \sqrt{2\pi}\,\sigma_y\, 2\int_0^{\infty} e^{-(z^2-2hz+h^2+z^2+2hz+h^2)/2\sigma_z}\, dz\right]$$

$$= \frac{kq_1 q_2}{(2\pi\sigma_y\sigma_z)^2} \left[\frac{2\pi\sigma_y\sigma_z}{2} + \sqrt{2\pi}\,\sigma_y\, e^{-h^2/\sigma_z^2}\, 2\int_0^{\infty} e^{-2z^2/2\sigma_z^2}\, dz\right]$$

$$= \frac{kq_1 q_2}{(4\pi\sigma_y\sigma_z)^2} \cdot (4\pi\sigma_y\sigma_z) \left[1 + \frac{e^{-h^2/\sigma_z^2}}{\sqrt{2}}\right] = k\left(\frac{q_1}{\beta V}\right)\left(\frac{q_2}{\beta V}\right)\left(\beta V\right)\beta\left[1 + \frac{e^{-h^2/\sigma_z^2}}{\sqrt{2}}\right], \tag{11}$$

where $V = 4\pi\sigma_y\sigma_z$. To give the same reaction rate assuming $\bar{C} = Q/V$ we must choose

$$\beta = \frac{1}{1 + \exp\left(-h^2/\sigma^2\right)/\sqrt{2}} \quad . \tag{12}$$

Note for <u>point</u> source, $\beta(x=0) = 1$, $\beta(x=\infty) = \frac{\sqrt{2}}{1+\sqrt{2}} = .586$.

2. Plume Depletion Due to Washout

According to the washout concept, the depletion from the box of the chemical model is expressed in terms of the washout coefficient Λ as,

$$\Delta m = \Lambda \, m \, \Delta t \quad , \tag{13}$$

where m is the amount of (aerosol or water soluble) material in the box. But in terms of the volume V of the box, $C = m/V$, hence

$$\left(\frac{dC}{dt}\right)_{\text{washout}} = -\Lambda C \quad . \tag{14}$$

Washout occurs under conditions of higher than normal ambient humidity. Washout is not included in the present model.

3. Plume Depletion Due to Dry Deposition

The ground level concentration according to the Gaussian plume model is given by

$$C(x,y,0) = \frac{Q(x)}{2\pi\sigma_y\sigma_z u_x} e^{-y^2/2\sigma_y} \, 2e^{-h^2/2\sigma_z^2} \quad . \tag{15}$$

In terms of the concentration $\bar{C}$ of the chemical box model

$$\bar{C}(x) = Q(x)/4\pi\sigma'_y\sigma'_z u_x \quad , \tag{16}$$

or

$$C(x,y,0) = 4\bar{C}\, e^{-y^2/2\sigma_y^2}\, e^{-h^2/2\sigma_z} \quad . \tag{17}$$

The dry deposition in time Δt at a distance x is

$$\Delta m = \int_{-\infty}^{\infty} dy \int_{x-1/2}^{x+1/2} dx\; C(x,y,0)\, V_d\, \Delta t = 4\bar{C}\, V_d\, \Delta t\, \sqrt{2\pi}\; \sigma_y u_x e^{-h^2/2\sigma_z^2}$$

$$= -\left(\frac{d\bar{C}}{dt}\right)_{dep} (4\pi\sigma'_y\sigma'_z u_x)\; \Delta t \;, \tag{18}$$

where V_d is the deposition "velocity".

Hence

$$\left(\frac{dC}{dt}\right)_{dep} = -\, \bar{C}\, 2V_d \left(\frac{e^{-h^2/2\sigma_z^2}}{\sqrt{2\pi}\;\sigma_z}\right) . \tag{19}$$

4. Choice of Sigma

The behavior of a natural plume is far more complicated than the idealized case we have considered so far. Over a period of time convection cells move, the plume may wander, fan, fumigate, etc., so that the volume swept out is considerably larger than that which obtains in any instant. It is the larger volume which is described by the dispersion coefficients of Pasquill-Gifford and Briggs-Smith, which are defined for a point source. For the shorter distances at least, the instantaneous plume will be considerably smaller. At very short distances a "concentration catastrophy" arises if the plume dimensions are allowed to shrink to zero. Two artifices are used to avoid this crisis. One is the concept of a "virtual (point) source" behind the stack, i.e. the distances along the plume are measured from a point behind the stack and can not go to zero. The second artifice (which we use) involves adding a constant such that $4\pi\sigma_y\sigma_z u_x$ reduces to the initial plume volume flow rate V_p° at $x = 0$. At small distances the additive term σ° dominates while at large distances it can be neglected.

In defining the various dispersion coefficients below we use an asterisk to denote a point source, a subscript ℓ for long-time (larger) σ's and a subscript s for short-time (smaller) σ's. We assume that large scale effects such as deposition are governed by these coefficients given by

$$\sigma_\ell = \overset{*}{\sigma_\ell} + \sigma^\circ \quad . \tag{20}$$

The instantaneous dispersion coefficients used in determing the size of the "box" we define by

$$\sigma_s = f\overset{*}{\sigma_\ell} + \sigma^\circ \quad , \tag{21}$$

where f is a function of the distance x, $f < 1$ and f approaches unity at large distances. The exact form of f is not crucial and we have elected to use a form due to Scriven,[12] which we write in the form

$$f = \sqrt{\frac{x}{x+50L}} \quad , \tag{22}$$

where L is given in the table below.

Stability Class	L (meters)
A	500
B	250*
C	100
D	50*
E	20*
F	10

---

*Interpolated values.

APPENDIX C

ACTIVITY COEFFICIENTS, THE WATER ACTIVITY, AND INITIAL VALUES

1. The Estimation of Ion Activity Coefficients and the Osmotic Coefficient

For an ideal solution, the activity coefficients of ions are unity and the activity of water is given by its mole fraction,

$$a_w = \frac{n_w}{n_w + \sum_i n_i + \sum_j n_j} = \frac{55.51}{55.51 + \sum_i [i] + \sum_j [j]} \qquad (1)$$

(here i and j refer to cations and anions, respectively). Such behavior is approached as solutions become more and more dilute. The aerosol droplets in the atmosphere often are quite concentrated, however, and the deviations from ideal behavior can be considerable (Fig.4). Hence it is necessary to estimate the values of ion activity coefficients for use in the equilibrium constant expressions (Table I) and in the calculation of the activity of water. The following is based on the treatments of Pitzer and Brewer[13] and Pitzer.[14]

The activity coefficients of ions g_i and g_j in a solution and the activity of water (a_w) are related by the Gibbs-Duhem equation,

$$\sum_i [i] d\ln([i]g_i) + \sum_j [j] d\ln([j]g_i) = -55.51 \, d\ln a_w \, . \qquad (2)$$

The activity of water is usually expressed in terms of the osmotic coefficient ϕ,

$$\ln a_w = -0.018(\sum_i [i] + \sum_j [j])\phi \, . \qquad (3)$$

The relationship between the osmotic coefficient and the activity coefficient is obtained by combining Eqs. 2 and 3 and integrating,

$$\phi = 1 + \frac{\sum_i \int [i] d \ln g_i + \sum_j \int [j] d \ln g_j}{\sum_i [i] + \sum_j [j]} \, . \qquad (4)$$

The integrations are from 0 concentration to the individual ion concentrations in the solution for which ϕ is desired.

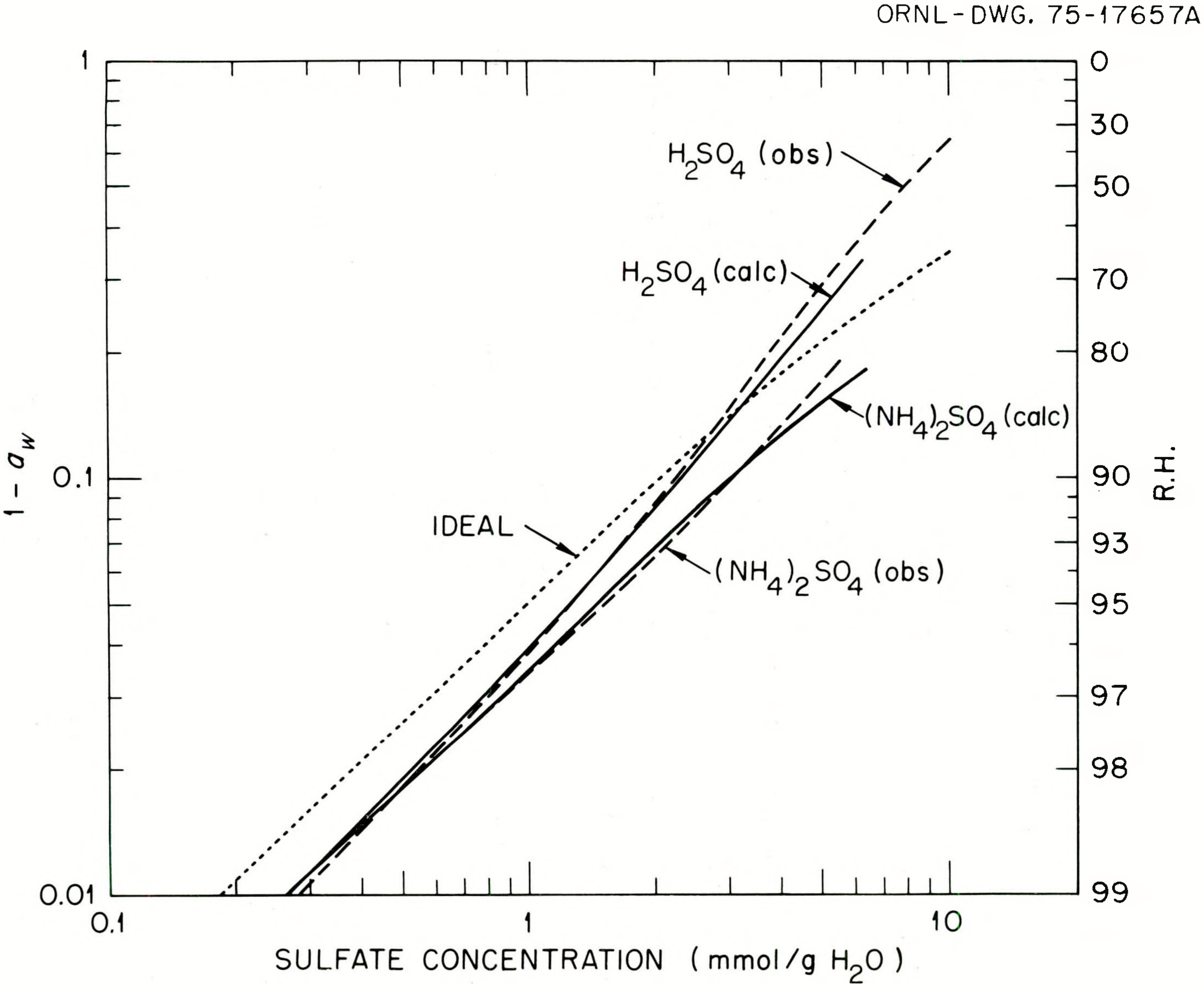

Fig. 4 Variation of the concentration of aerosol droplets with the activity of water a_w (the relative humidity/100) at 25°C.

The following expressions are assumed for the individual ionic activity coefficients;

$$\ln g_i = \frac{-Z_i^2 S\, I^{1/2}}{1 + I^{1/2}} + \sum_j B_{ij}^{g}[j] \,, \tag{5a}$$

$$\ln g_j = \frac{-Z_j^2 S\, I^{1/2}}{1 + I^{1/2}} + \sum_i B_{ij}^{g}[i] \,, \tag{5b}$$

wherein Z_i and Z_j are the ion charges, I is the ionic strength

$$I = \frac{1}{2}\left(\sum_i Z_i^2[i] + \sum_j Z_j^2[j]\right) \,, \tag{6}$$

and S is the Debye-Hückel constant, a theoretical quantity which depends only on the density and dielectric constant of the solvent and on the temperature. It is given with adequate accuracy for present purposes by the approximate expression

$$S = 1.1305 + 0.01842\, t(°C) \tag{7}$$

The coefficients B_{ij}^{g}, one for each pairwise combination of cations and anions is assumed to be a function only of I.

$$B_{ij}^{g}(I) = B_{ij}^{\circ} + B_{ij}^{1}F(I) \tag{8}$$

$$F(I) = [1 - (1 + 2I^{1/2} - 2I)\cdot \exp(-2I^{1/2})]/4I \,. \tag{8a}$$

B_{ij}° and B_{ij}^{1} are adjustable constants.

The above expressions for g_i and g_j (eqs 5-8) when introduced into eq 4 give the following expression for ϕ

$$\phi = 1.0 + \frac{-2SG(I) + \sum_i \sum_j B_{ij}^{\phi}[i][j]}{\sum_i [i] + \sum_j [j]} \,, \tag{9}$$

$$G(I) = (1 + I^{1/2}) - \frac{1}{(1 + I^{1/2})} - 2\ln(1 + I^{1/2}) \,, \tag{9a}$$

$$B^{\phi}_{ij} = B^{\circ}_{ij} + B^{1}_{ij} \exp(-2I^{1/2}) \qquad (9b)$$

Since four kinds of ions are distinguished, two cations (H^+ and NH_4^+) and two anions (X^- and X^{2-}), there are four pairwise combinations of cations with anions and 8 adjustable parameters. Six of the following values were assigned by fitting the appropriate expressions above to the known osmotic and activity coefficients of pure H_2SO_4 and $(NH_4)_2SO_4$ solutions given by Robinson and Stokes[15] (Fig. 4), and the observed dissociation of HSO_4^- ion in pure sulfuric acid solutions (Young et al[16]).

i	j	B°_{ij}	B^{1}_{ij}
H^+	x^-	0.272	3.080
H^+	x^{2-}	0.050	-4.005
NH_4^+	x^-	0.0*	0.319*
NH_4^+	x^{2-}	-0.049	-1.186

The remaining two (with asterisks) were adjusted to give approximately the observed solubility of $(NH_4)_2SO_4$ in H_2SO_4 solutions (Seidell,[17] Vol. II p. 756), Fig. 5.

2. Initial Estimate of Quantities Needed for the Calculation of the Plume Composition

The initial estimates of the amount of condensed water g_W and of the ion concentrations $[H^+]$, $[NH_4^+]$, $[x^2]$ and $[x^{2-}]$ are made by assuming that the only ions present in solution are H^+, NH_4^+, HSO_4^-, and SO_4^{2-} and that all the NH_3 is present as NH_4^+. The following expressions then apply;

$$[NH_4^+] = C(NH_3)/g_W \ , \qquad (10)$$

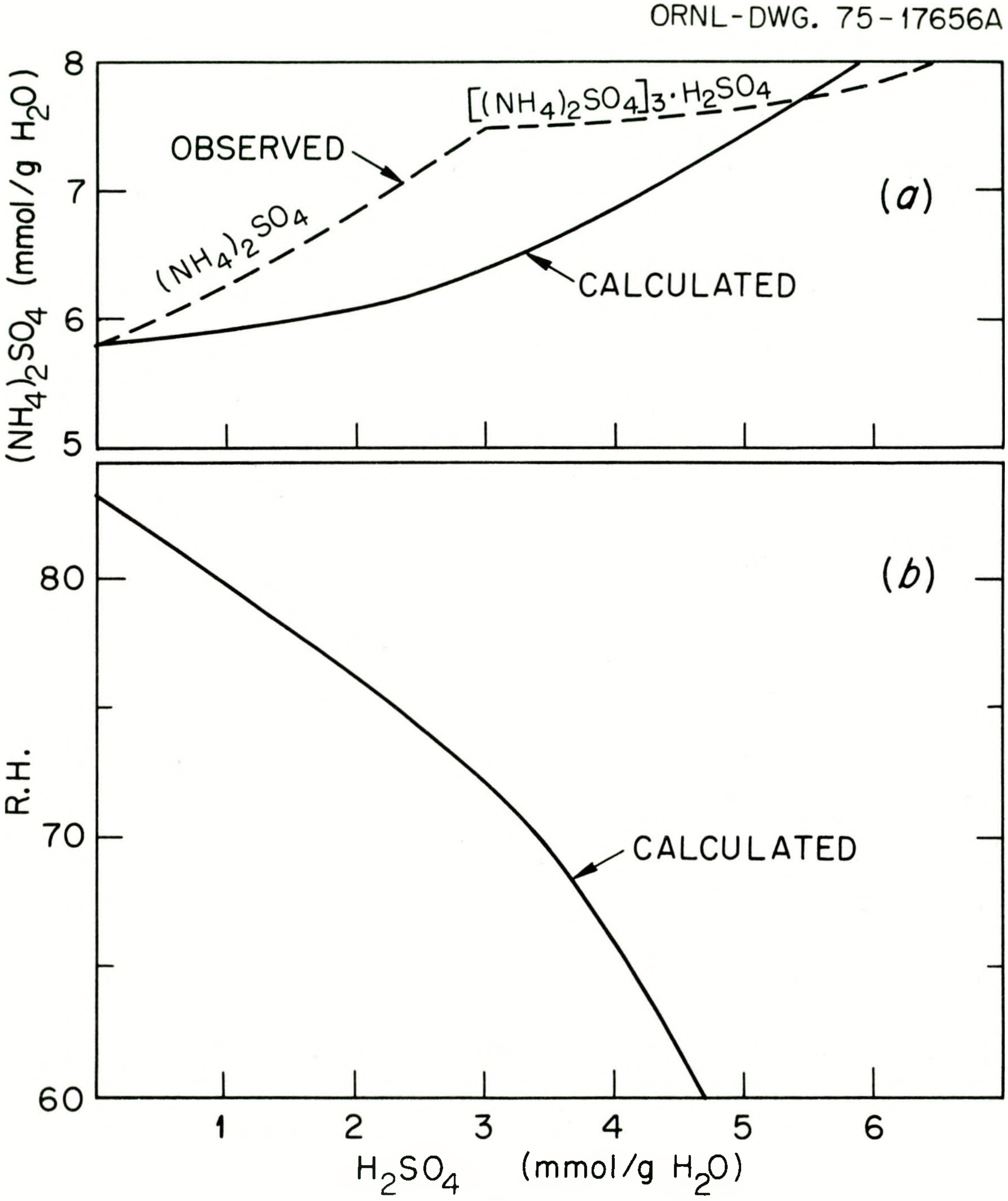

Fig. 5 The sulfuric acid - ammonium sulfate - water system at 25°C.

$$[X^-] = [HSO_4^-] = \frac{[H^+]}{[H^+] + Q_4} \cdot \frac{C(S(VI))}{g_w} , \tag{11}$$

$$[X^{2-}] = [SO_4^{2-}] = \frac{Q_4}{[H^+] + Q_4} \cdot \frac{C(S(VI))}{g_w} , \tag{12}$$

where Q_4 is the concentration quotient from K_4 (Table I),

$$Q_4 = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = K_4 \cdot \frac{g_{X^-}}{g_{H^+} g_{X^{2-}}} . \tag{13}$$

Introducing Eqs. 10 to 13 into the charge balance equation

$$[H^+] + [NH_4^+] = [HSO_4^-] + 2[SO_4^{2-}] , \tag{14}$$

a quadratic in $[H^+]$ is obtained with the solution

$$[H^+] = - B + \left(B^2 - C\right)^{1/2} , \tag{15}$$

wherein

$$B = \left[Q_4 + [C(NH_3) - C(S(VI))]/g_w\right]/2 , \tag{15a}$$

$$C = Q_4[C(NH_3) - 2C(S(VI))]/g_w . \tag{15b}$$

The only unknowns are g_w and the ion activity coefficients.

The calculation begins by solving the following equation for g_w,

$$[C(H_2O) - g_w/0.018] \frac{RT}{P_w^\circ} = \frac{g_w}{g_w + 3 \cdot C(S(VI)) \cdot 0.018} . \tag{16}$$

Each side is an expression of the activity of water, the right side being an approximation of the mole fraction of water in solution assuming three moles of ions are produced by a mole of S(VI). The solution for g_w is

$$g_w = [-B' + (B'^2 - C')^{1/2}] \cdot 0.018 , \tag{17}$$

$$B' = [P_{w^\circ}/RT - C(H_2O) + 3\ C(S(VI))]/2 , \tag{17a}$$

$$C' = -3\ C(S(VI)) \cdot C(H_2O) . \tag{17b}$$

The activity coefficients are set initially at unity. The ion concentrations thus obtained from Eqs. 10-15 are used to estimate activity coefficients in S. GAMAW, and the calculation is repeated by cycling between S. EVAL AND S. GAMAW until the activity coefficients become constant (only a few interactions are needed). Then the water activity given by S. GAMAW is compared with that given by the amount of gaseous water,

$$a_w = [C(H_2O) - g_w/0.018]RT/P_w^\circ \qquad (18)$$

and g_w is adjusted by repeated cycling between S. NONLIN and S. EVAL until a good estimate of g_w (and ion concentrations and activity coefficients) is obtained.

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