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PHYSICS AND CHEMISTRY OF E-BEAM STACK GAS PROCESSING

Final Report for the Period September 20, 1982—January 14, 1984

By
Richard Slater

October 1983

Work Performed Under Contract No. AC22-82FE60088

AVCO Everett Research Laboratory, Inc.
Everett, Massachusetts

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20 September 1982 - 14 January 1984

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Division of Energy Technology
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I. INTRODUCTION

The purpose of this program is to investigate some of the basic physics and chemistry of the electron beam induced NO_x and SO_x removal process. The program involves both kinetic modelling and diagnostic development. The development of an adequate kinetic model is necessary in order to scale the laboratory results, which are currently available, to process conditions closer to those that will be encountered at full scale operation. It is also necessary in order to place the laboratory data on a firm theoretical foundation. The development of a kinetic model that can predict NO_x/SO_x removal under a wide variety of conditions could go a long way towards achieving this goal. The development of real time optical diagnostics is a necessary supporting task for these goals in order to obtain kinetic data on some of the myriad of species that are present in this hostile environment (X-rays present; hot, acidic gas) which is difficult to access by conventional methods.

This particular NO_x/SO_x removal process, which involves the irradiation of combustion products at temperatures around 100°C with a beam of high energy electrons has been studied by groups in both Japan and the U.S. [1-17,37]. Much of the Japanese work has attempted to elucidate some aspects of the SO_x/NO_x removal mechanism [6-17,37]. These papers have identified the neutral homogeneous gas phase reactions of radical and atomic species with SO_x and NO_x as being the primary removal processes. The radicals and atoms are generated by the impact of high energy electrons upon the main chemical components of the stack (or flue) gas: N_2 , O_2 , CO_2 , H_2O . These conclusions were somewhat qualitative in nature; the quantitative prediction of SO_x and NO_x removal as a function of various parameters, e.g., dose, temperature, added gases, etc., was not attempted.

The current study expands upon the mechanistic studies published by the Japanese. A detailed kinetic model is described which includes all the necessary assumptions that enter in order to take the very large number of possible processes that occur in e-beam irradiated mixtures and reduce them to

some tractable number. Quantitative comparisons are then made between the kinetic model and experimental data.

Another phase of this program is the development of laser diagnostics to probe various species in the irradiated flue gas. The extensive involvement of AERL in excimer laser technology has led us to consider ultraviolet rare gas halide laser pumping to follow the concentrations of SO_2 and OH by their characteristic laser induced fluorescence. It turns out that there are a sufficient number of accidental coincidences of SO_2 with the KrCl laser and OH with the XeCl laser that pumping with fixed frequency excimers is possible. This is especially useful for the spectral region below 250 nm where the energy output of alternative laser pump sources, such as doubled dye lasers, is quite low.

In the following sections the experimental phase of program is first described including a discussion of our e-beam facility and the methods used to accurately measure energy deposition. A description of the laser diagnostics follows along with a discussion of the results obtained with those diagnostics. The discussion of the kinetics model and comparisons with data complete this report.

II. EXPERIMENT

A. E-BEAM FACILITY

The e-beam source used in this program is depicted in the schematic in Figure 1. The gun is a triode structure which utilizes heated tungsten filaments as an electron source, a negatively biased grid to control electron current, and a foil plate holder which accelerates the electrons to 90 KeV. The grid filament region is run in a space charge limited mode with the grid biased up to 2 KeV with respect to the filament. E-beam currents up to 7×10^{-3} amps can be obtained. The gun is housed in a high-vacuum diffusion pumped chamber and operates at a pressure of 2×10^{-6} torr. The vacuum is separated from the flue gas sample by a thin electron window made of $12.5 \mu\text{m}$ aluminum. The cross sectional area of the electron beam is nominally 25 cm^2 .

The electron beam dose delivered to the non-flowing flue gas is accurately controlled by pulsing the grid between ground and 1.5 keV using the circuit schematic indicated in Figure 2. A light controlled Jennings switch was constructed to switch the grid bias on and off for any time interval ≥ 30 msec. Two separate UV light pulses were used. The light from UV flashtube #1 is used to trigger the gate in a light activated SCR allowing current to energize the solenoid and thus close the Jennings switch. At an appropriate later time determined by the desired e-beam dose and current, a second UV flashtube fires which dumps the solenoid power and releases the switch into the nominally open position. The delay time between lamp firings as well as the triggering of the excimer laser with respect to the e-beam pulse are controlled by several pulse and delay generators.

B. ENERGY DEPOSITION

An important experimental parameter in electron beam radiation measurements is the energy deposition into the medium. This quantity ultimately determines the ionization and dissociation rates in molecular systems such as flue gas mixtures. The energy deposition in the present experiments was

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Figure 1 Schematic of High Energy Electron Beam Facility

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Figure 2 Circuit Schematic for Pulsed Electron Beam Operation

accurately measured and checked using two independent measurement techniques, calorimetry and C_2H_4 dosimetry, and a one dimensional calculation of the relative electron beam dose profile.

The calorimetry measurements were obtained by interposing a large area aluminum calorimeter in the path of the electron beam and measuring the energy deposited in the calorimeter as a function of the distance from the edge of the foil support plate. The calorimeter area was $45 \times 30 \text{ cm}^2$ which is much larger than the nominal cross-sectional area of the electron beam and insured that all the electron beam dose was collected. These measurements were performed in air (80% N_2 , 20% O_2) and these results, depicted in Figure 3 differ insignificantly from those expected in typical flue gas mixtures (3% O_2 , 1% H_2O , 12% CO_2 , 80% N_2). The percent of the electron beam that gets transmitted through the foil and support structure is only about 5% of the incident energy due mainly to large losses in the support structure. The transmitted power is a nearly linear function of the distance, D , away from the support plate out to about $D = 3.5 \text{ cm}$. At the location of the KrCl laser probe, $D = 1.8 \text{ cm}$, the e-beam power has dropped to 3% of the incident value.

The results of the one-dimensional deposition calculation are also shown in Figure 3. This calculation is normalized to the data at $D = 0$ because it can only account for deposition in the foil and the gas and cannot account for the losses in the foil support structure. The cross hatched region indicates the uncertainty in the calculation due to uncertainties in the foil thickness (10% and electron beam voltage (3%). The code is in fairly good agreement with the measurements near the laser probe region.

The calorimeter measurements were verified by using chemical dosimetry and measuring the production of H_2 via the reaction:

for which the $G(H_2)$ values has been measured to be 1.31 [18]. The absolute H_2 production was measured using mass spectrometry at $m/e = 2$. This peak was calibrated absolutely using premixed samples containing H_2 in N_2 at known concentrations close to that obtained for C_2H_4 irradiation, ~ 1000-2000 ppmV. A special low dead volume irradiation cell was used to

Figure 3 Comparison of Measured and Calculated One-Dimensional E-beam Deposition Profiles

insure that all the dosimetry gas was irradiated. The irradiated gas samples were diluted with N_2 and trapped at $-195^\circ C$ in order to eliminate the contribution to the $m/e = 2$ signal from higher boiling point hydrocarbons and to insure that the signal from the irradiation sample was measured under conditions nominally identical to those used for the calibration samples.

The average dose in N_2 , $\langle D(N_2) \rangle$, can be obtained from the H_2 yield by the relation:

$$\langle D(N_2) \rangle = \left(\frac{n_{H_2} V}{G(H_2)} \right) \left(\frac{S(N_2)}{S(C_2H_4)} \right) \quad (2)$$

where n_{H_2} is the absolute density of H_2 produced, V is the volume of the irradiation cell (65 cm^3). $S(N_2)$ and $S(C_2H_4)$ are the stopping powers of the N_2 and C_2H_4 , respectively, at an electron energy of 52 keV, which is the code calculated energy of the beam electrons as they exit the foil [19].

A comparison of the average dose obtained by the two methods is given in Figure 4 where the subscripts C and D denote measurements from calorimetry and dosimetry, respectively. The fractional difference in the measurements are plotted versus electron beam current. The cross-hatched area represents the uncertainty in the measurements. This comparison indicates that the two methods agree to within the experimental uncertainty of $\sim 18\%$.

C. DIAGNOSTICS

The development of rare gas halide excimer laser technology has led to powerful ultraviolet (UV) light sources in the wavelength region 190-350 nm. Commercial discharge pumped exciplex lasers are available for which the following discrete wavelengths can be obtained by a simple change of laser gas mixture without a change in the laser optics.

$\lambda(\text{nm})$	Excimer	Rare gas/halogen mix
193	ArF	He/Ar/ F_2
222	KrCl	He/Kr/HCl
248	KrF	He/Kr/ F_2
288	XeBr	He/Xe/HBr
308	XeCl	He/Xe/HCl
351	XeF	He/Xe/ F_2

Figure 4 Comparison of Average Absolute E-Beam Deposition Using Calorimetric and Dosimetric Methods

With the additional capability of raman shifting using high pressure gas cells containing H_2 , CH_4 , N_2 , etc. the gaps between these wavelengths can be filled in to provide a much broader range of tuning. Typical output energies of commercial discharge pumped excimer lasers are in the range 30-300 mJ depending upon the laser mix.

Early in this program it was decided that we would use one of our existing commercial discharge pumped excimer lasers as an excitation source for laser induced fluorescence detection of SO_2 and OH. Another alternative laser pump source, doubled dye laser excitation, was not considered because the significant expense and added complexity associated with tuning the doubling crystal did not justify the one added advantage, continuous tunability, associated with the dye laser source. With discharge pumped excimer lasers, the spectral bandwidths are sufficiently broad (0.1-0.5 nm) that we expect a number of fortuitous accidental overlaps of the excimer wavelength band with the SO_2 and OH electronic absorption bands. This expectation obviated the need to consider doubled dye lasers. Experience in this program has indicated that this expectation was completely borne out for the SO_2 case, but was only partially borne out for the OH case as will be indicated below.

1. SO_2 Diagnostic

A partial energy level diagram of some of the electronic levels of SO_2 is depicted in Figure 5. The important point to note for this SO_2 diagnostic application is the relative isolation of the $C(^1B_2)$ state with respect to its proximity to the other lower-lying electronic levels. This isolation leads, in part, to a short radiative lifetime and a simple photochemistry subsequent to photoexcitation. These molecular properties are needed to insure the generation of a reliable diagnostic. This situation is to be contrasted with photoexcitation of the lower lying $A(^1B_1)$ state which leads to a relatively longer radiative lifetime ($> 10^{-5}$ seconds) and a complex set of photochemical processes generated by intersystem crossing and collisional mixing of the $A(^1B_1)$ state with the nearby triplet levels. These differences have led to the suggestion that excitation of the $C(^1B_2)$ state is preferred as a method for UV detection of SO_2 and is also the basis for at least one commercial SO_2 analyzer [20].

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Figure 5 Partial Energy Level Diagram of SO_2 Electronic Levels

The low resolution absorption spectrum of the dipole allowed ($C \leftarrow X$) transition is shown in Figure 6 [21]. This band is seen to contain discrete transitions overlaying a broad continuum absorption. The vibronic transitions have been definitely assigned only over the spectral region from the band origin near 234.8 nm down to 224.7 nm. At shorter wavelengths (energies $\sim 2000 \text{ cm}^{-1}$ above the origin), the vibrational levels are strongly coupled and single vibrational configuration assignments are inappropriate. For the purpose of reference only, two bands are indicated using the assignments of Rosen, et. al [22]. At 2190 Å, Figure 6 indicates the thermochemical threshold for photodissociation ($D_0 = 5.65 \text{ eV}$) via:

Excitation at wavelengths shorter than this is to be avoided in fluorescence detection due to the significant loss in fluorescence efficiency caused by process (3). The radiative lifetimes and fluorescence yields for various transitions in this band have been measured down to 242 Å. The radiative lifetimes are generally in the range 20-30 nsec and the fluorescence yields (relative to benzene at 259.0 nm) are between 0.5 - 1.0 for $\lambda > 220.0 \text{ nm}$ monotonically falling at short wavelengths down to 0.03 at 215.24 nm [23].

Also indicated in Figure 6 are excimer laser pump wavelengths that provide excitation within the $C \leftarrow X$ band in SO_2 . The notation KrF/H_2 indicates the wavelength corresponding to raman shifted KrF using an H_2 shifter. A consideration of the expected output energies and experimental complexity obtainable using either KrCl or raman shifted KrF led us to choose KrCl as the SO_2 pump source. According to Figure 6, the KrCl pump is in the valley between the peak of the $\alpha_2(0,2)$ and $\alpha(0,3)$ vibronic transitions. This is a part of the $C \leftarrow X$ absorption band for which vibrational and rotational assignments are unavailable. Nevertheless, we will show that excitation is strong enough to generate single shot fluorescence signals down to about 50 ppmV SO_2 .

Figure 6 SO_2 Absorption Spectrum (see Ref. 21)

The fluorescence spectrum generated by excitation in the 210-220 nm spectral region extends from the pump wavelength out into the violet to around 400 nm [24]. This complex spectrum will be a reasonably smooth continuum emission with a peak near 340 nm under flue gas conditions at near atmospheric density and elevated temperature. The quantum efficiency for undispersed fluorescence is expected to be ~ 0.06 based upon an average spontaneous emission rate from SO_2 (α_2 (0,2) and α_2 (0,3)) of $1.63 \times 10^7 \text{ sec}^{-1}$ and a quenching rate of $2.45 \times 10^8 \text{ sec}^{-1}$ based upon the dominant N_2 quenching via

at atmospheric density.

The laser induced fluorescence set-up used to detect low concentrations of SO_2 is shown in Figure 7. The KrCl laser (Lumonics Model 261) generated about 10 mJ of energy in a 6 nsec pulse at 222.1 nm with a nominal 0.3 nm bandwidth. The laser mix consisted of 0.15% HCl/10% Kr/balance He at 2 atmospheres total pressure. Neutral density filters were used to reduce the laser beam energy to the desired value, typically a 100X reduction. Before entering the cell, a small portion of the beam was reflected from a quartz beam splitter onto the surface of a fast photodiode. This signal was used as a fiducial time mark and indicated relative variations in the laser beam energy. The laser beam was then focussed into the center of the electron beam irradiation cell by means of a 25 cm focal length cylindrical quartz lens. The dimensions of the focal volume were $\sim 0.3 \times 1.0 \times 1.0 \text{ cm}$.

SO_2 fluorescence emanating from the focal volume was detected at a right angle to the incident laser beam using a dielectric filter ($\lambda_0 = 351 \text{ nm}$, $\Delta\lambda = 20 \text{ nm FWHM}$) and fast response photomultiplier (S-5 photocathode response, 10 nsec rise time). A glass collecting lens was used to focus the SO_2 fluorescence onto the photocathode surface and to reject scattered laser light, and adjustable apertures were used to define the focal volume.

A typical oscilloscope recording of the SO_2 fluorescence and KrCl laser pulse shapes are shown in Figure 8. The temporal width of the fluorescence pulse is limited by the photomultiplier bandwidth. The delay between

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Figure 7 Schematic of Laser Induced Fluorescence (LIF) Apparatus

Figure 8 SO₂ LIF Signal

the laser and fluorescence pulses is due to the electron transit time typical of venetian blind type photomultiplier tubes. It was shown that no fluorescence signal appears when SO_2 is eliminated from the mix.

The signal to noise ratio, S/N, in these experiments is limited by a background luminescence generated by the powerful laser beam as it strikes the cell entrance window. The luminescence is temporally and spectrally coincident with the SO_2 fluorescence signal. The only way to reduce the luminescence signal and thereby increase S/N is to reduce the solid angle of the luminescence as seen by the detector. This was accomplished by mounting the entrance window on a 10 cm extension tube that contained collimating apertures designed to pass the laser beam, but reject wide angle luminescence. The laser exit window was replaced by a Wood's horn that provided a non-luminescent beam dump.

Using these cell modifications, the S/N was shown to be laser intensity, I , dependent. A significant reduction in I was required for optimization of S/N. The S/N varies as $I^{-0.5}$ because the SO_2 fluorescence signal is partially saturated varying as $I^{0.5}$ (see Figure 9) while the luminescence is unsaturated varying as I . A 100X reduction in I was required to optimize S/N at a value of 6 for a 1000 ppm SO_2 sample. A further reduction in I did not improve S/N because the total noise level is limited by the electrical discharge noise from the laser at low I .

The SO_2 fluorescence signal was calibrated using premixed SO_2 samples at variable concentrations. This calibration method obviates the need to know the absolute efficiency of the detector optics, the absolute SO_2 fluorescence efficiency and absolute laser absorption. However, this method does require that the experimental conditions during the e-beam induced SO_2 removal measurements be nearly identical to those used during the calibration measurements when the e-beam is off. The only potential differences between the e-beam and calibration runs are: 1) the absorption lengths between entrance window and focal region and between focal region and detector, and, 2) the effects of acid mist on SO_2 fluorescence. The former were shown to be negligible based upon our measured SO_2 absorption coefficient using KrCl at 222.1 nm. The latter visibility issue is discussed below.

Figure 10 displays the SO_2 calibration measurements in both wet (1.2% H_2O , 3% O_2 , 13% CO_2 and bal N_2) and dry (1000 ppmV H_2O , 3% O_2 , 13% CO_2 , bal N_2) flue gas mixtures. The best straight line through the data yields an empirical relation

Figure 9 Laser Intensity Dependence of SO₂ LIF Fluorescence Signal

Figure 10 Calibration of SO_2 LIF Signal

$$S \propto [SO_2]^{0.60 \pm 0.03} \quad (5)$$

There appears to be no difference between wet and dry calibration runs.

This scaling can be understood qualitatively in terms of the competition between quenching rates and the radiative rate. A accurate quantitative result is not possible because some of the quenching rates are not known.

Consider the mechanism:

where $SO_2(C)$ and $SO_2(X)$ denote the C and ground state populations, respectively and σ_u and σ_d denotes the absorption and emission cross sections for the C $\leftrightarrow$ X transition. Solving these kinetic equations for the steady state C population yields:

$$SO_2(C)_{s.s.} = \frac{[SO_2] \sigma_u \phi}{k_6 + \sigma_d \phi + \sum_{i=7} k_i [x_i] + k_{11} [SO_2]} \quad (13)$$

where $[SO_2]$ denotes the total $[SO_2]$ density, ϕ denotes the laser intensity ($\text{cm}^{-2} \text{sec}^{-1}$) and the summation term denotes the N_2 , O_2 , H_2O and CO_2 quenching rates, all of which have not been measured as far as we know.

If we let $k_6 + \sigma_d \phi + \sum_i k_i [M] = K$, then the C state population dependence on $[SO_2]$ will depend upon the relative magnitudes of k_2 and K . The latter quantity is a constant in the calibration measurements. For $K \gg k_2 [SO_2]$, the C state population is linear in $[SO_2]$ while, for $k_2 [SO_2] \ll K$, the population is independent of $[SO_2]$. The $[SO_2]^{0.6}$ scaling suggests an intermediate regime where $k_2 [SO_2] \approx K$. For $k_2 = 1.4 \times 10^{-9} \text{ cm}^3/\text{sec}$, we get $K \sim 4 \times 10^6 - 4 \times 10^7 \text{ sec}^{-1}$. Since $k_6 = 1.6 \times 10^7 \text{ sec}^{-1}$, K is probably closer to the higher of the above values.

2. SO₂ Room Temperature Removal Experiments

SO₂ removal was measured as a function of electron beam energy deposition (dose) at room temperature. SO₂ removal was measured by ratioing the peak height of the fluorescence signal with the e-beam on to the peak height of the signal with the e-beam off. A typical comparison of e-beam on and off signals is shown in Figure 11 for a mixture of 1600 ppm SO₂, 1.3% H₂O, 3% O₂, 13% CO₂ and balance N₂ at 1 atmosphere density. The dose level is about 0.9 Mrad (1 Mrad = 10 J/gram) for this data. The dose dependence of the SO₂ removal for this flue gas mixture is shown in Figure 12 as the solid circles. Two processes are evident; a fast removal at dose levels less than about 1 Mrad followed by a slower removal at higher dose levels. The $G(-SO_2)$ values for the fast process is about 22 while $G(-SO_2)$ is about 5.5 for the slow process.

Using the same gas mixture as above, the dose dependence of the SO₂ removal was also measured using a calibrated commercial SO₂ analyzer (Thermoelectron Corp. Model 40). This analyzer was located downstream of the e-beam irradiation cell and was connected to the cell by a short length of tubing. This analyzer detects SO₂ concentration via C ← X fluorescence using a repetitively pulsed flashlamp rather than a laser. The results of these analyzer measurements are shown in Figure 12 as the open circles. Variable dose was obtained by varying electron beam current and flue gas flow rate. The two sets of measurements are in good agreement with each other (to within experimental error) over the whole dose range investigated.

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Figure 11 SO₂ LIF Signal With and Without E-Beam Irradiation

Figure 12 Dose Dependence of SO₂ Removal at Room Temperature. Data: open and solid circles. Solid line is code result.

These experimental results are, however, not in agreement with the SO_x kinetics code predictions as indicated in Figure 12. This result is surprising in light of the good agreement between code and experiment at elevated temperatures. The SO_x code model and comparison with experimental data are discussed in more detail in Section III.

One possible explanation for the code's inability to predict the low temperature SO_x removal is the absence of acid mist in the kinetics code and its effects on the apparent SO_2 removal rate. The code considers only homogeneous gas phase chemistry and does not consider either particulate growth by nucleation phenomena nor heterogeneous gas-particulate interactions that could perturb SO_2 removal. We suggest that the particulates are present in these room temperature studies, but they are not present at the elevated temperatures of previous studies ($> 100^\circ\text{C}$) [6-17]. Under the latter conditions, the gas phase chemistry of the SO_x code is adequate to predict experimental results.

Observations of an acidic coating on the inside bottom wall of the electron beam chamber subsequent to electron beam irradiation are consistent with the notion of H_2SO_4 formation. The production of H_2SO_4 was firmly established by the Japanese who measured H_2SO_4 and HNO_3 yields in NH_3 free e-beam irradiated flue gas [25]. The vapor pressure of H_2SO_4 at 20°C is much less than 0.001 torr [26]. If we assume 50% conversion of SO_2 to H_2SO_4 at an initial SO_2 concentration of 1600 ppmV at 1 atmosphere total density, then the H_2SO_4 vapor created by the e-beam will be super-saturated by several orders of magnitude. There is sufficient time between the e-beam irradiation and our visual inspection of the cell (several minutes) for the vapor to nucleate and rain out on the lower cell walls. It is also reasonable to assume that nucleation can occur during the e-beam irradiation period (several seconds).

The presence of particulates at $\geq 100^\circ\text{C}$ is not clear. The H_2SO_4 vapor pressure at this temperature is comparable to the potential amount that could be created by the electron beam irradiation (approximately few tenths of a torr). However, the good agreement between code and experiments at elevated temperatures suggests that the acidic mist production is low.

There are several ways that an acid mist could perturb the SO_2 measurements. The particulates could obscure either the laser pump beam or the SO_2 fluorescence signal. For our conditions we roughly estimate that there are enough 1 micron radius droplets to attenuate the signal by 50 %. The droplet size distribution is not known for our conditions. In addition, there is also the potential effect of heterogeneous gas-particulate chemistry on the SO_2 removal.

3. SO_x Removal in O_2 Free Mixtures

We found anomalously high SO_2 removal rates in O_2 free mixtures using our KrCl based laser diagnostic. The SO_x removal was remeasured using gas chromatography (GC) with a Poropak P column at 45°C and thermal conductivity detector. The GC results are indicated in Figure 13. These data are consistent with previous results in mixtures containing 3% O_2 (see Figure 12). A comparison of the data in Figure 12 and 13 suggests that the O_2 dependence on room temperature SO_2 removal is negligible. The fact still remains, however, that neither of these data are adequately explained in terms of the room temperature SO_x removal code.

4. OH Diagnostics

The XeCl rare gas halide laser generates two laser lines at 308.0 nm and 308.2 corresponding to the $1\leftarrow 0$, $2\leftarrow 0$ bands in the $\text{B}\rightarrow\text{X}$ system in XeCl [27]. These lines lie within the $0\leftarrow 0$ band in the $^2\Sigma^+ \rightarrow ^2\Pi$ system in OH [28]. This suggests using the XeCl excimer as a pump source for laser induced fluorescence detection OH. Pumping in the $0\leftarrow 0$ band in OH leads to a fluorescence spectrum that extends from the pump wavelength to $\sim 314 - 315$ nm [28]. This small wavelength difference between the pump and fluorescence leads to a stringent requirement on the ability of the detection system to reject scattered laser light. This is contrasted with KrCl pumping of SO_2 where the peak of the fluorescence band is about 130 nm to the red of the pump wavelength and can be easily rejected by plate glass.

The OH fluorescence power is expected to be low for XeCl pumping of e-beam irradiated flue gas. Closer examination of the OH $^2\Sigma^+ \rightarrow ^2\Pi$ system indicates several accidental rovibronic coincidence that lie within the

Figure 13 Dose Dependence of Room Temperature SO₂ Removal Without O₂ Present

0.1 nm bandwidth of each of the XeCl lines: $Q_1(2)$, $Q_1(2')$, $R_2(2)$, $Q_1(3)$, $Q_1(3')$, $R_2(18)$, $R_1(19)$, $R_1(19')$. However, these line-widths (~ 0.001 nm) are small (due to Doppler Broadening) relative to the laser bandwidth leading to about 4% overlap of each laser line and the OH absorbing lines. The estimated maximum number of OH absorbers expected for e-beam irradiated flue gas is only about 10^{13} cm^{-3} in the absence of both NO_x and SO_x as calculated from our kinetic model. In addition, only a small fraction of the absorbed energy appears as fluorescence power due to a low quantum yield. The radiative lifetime is about $0.7 \text{ } \mu\text{sec}$ as compared to an estimated collisional lifetime of about 1 nsec at 1 atmosphere of flue gas indicating a quantum yield $\sim 1/700$. Using f/10 optics, an optics transmission factor of 0.1 and a 1 cm^3 focal volume yields a total fluorescence signal [25],

$$(5 \times 10^{12} \text{ cm}^{-3})(1 \text{ cm}^3)(0.04)(1/700)(0.01)(0.1) = 3 \times 10^5 \text{ photon/pulse}$$

Given that each laser pulse contains about 10^{17} photons means that a rejection ratio of about $\sim 10^{-12}$ is required to eliminate scattered light.

The apparatus that was used for OH fluorescence detection is basically the same as that depicted in Figure 7 to study SO_2 detection. The only changes that were made include: using an XeCl gas mix that generates about 50 mJ of energy, using a 2 m focal length lens to focus the laser beam into the cell in order to avoid hitting the walls of the cell, eliminating both the neutral density filters to exploit the full laser beam energy and the front window on the cell in order to try to reduce the broad band luminescence signal (see SO_2 diagnostic section) and using a two series dielectric cut-on filters in the detection optics ($\lambda_{\text{max}} = 320 \text{ nm}$; $\Delta\lambda = 250 \text{ nm}$; transmission at $300 \text{ nm} \approx 0.03$; transmission at $313 \text{ nm} \approx 0.5$) to reject the laser light and pass as much fluorescence power as possible. By eliminating the entrance window to the cell, we were forced into exhausting the contents of the cell into the room and, therefore, for safety considerations, only mixtures of H_2O and N_2 without SO_2 present could be investigated.

We were unable to observe any OH signal above a persistent background signal that occurred even in the absence of e-beam power. The background signal

has contributions from several sources: direct scattered laser light at 308 nm, the ubiquitous "blue" luminescence signal, and spontaneous Raman scattering signal from N_2 . The latter contribution arises because the first vibration level in N_2 at 2300 cm^{-1} will cause the incident photon at 308 nm to be red shifted by inelastic scattering into the peak of the detection bandpass around 330 nm. This signal was eliminated by going to H_2O/Ar mixes for which there are no Raman processes allowed at this pump wavelength. However, the other two contributors to the background signal could not be eliminated although it is apparent that the luminescence signal is still the major contributor. This conclusion is based on our observation that the background only increases by about a factor of four when both dielectric filters are removed, a change that is inconsistent (too small) with the net transmission factor for the filters at 308 nm, $\sim (0.03)^2$.

5. Absolute OH Measurements

In this section we propose a new method for the absolute measurement of OH concentration. The method has not been applied to the present case of electron beam irradiated flue gas due to the poor signal to noise ratio as mentioned above. The proposed method utilizes the laser induced fluorescence detection method, but obviates the need to know accurate quenching rate constants, solid angle factors, and transmission factors as is required in typical laser induced fluorescence techniques. These experimental parameters are not needed because the method relies on the laser induced generation of a calibrated amount of OH which can be subsequently detected by standard laser induced fluorescence techniques using a second detection laser at a different color. This relative fluorescence signal can be placed on an absolute scale of OH concentration provided that the same detection optics is used for both unknown and calibrated samples.

The calibrated OH concentration is generated by laser induced photolysis of N_2O via:

at wavelengths short enough to photodissociate N_2O followed by reaction with H_2O to form OH in a known amount via:

The quantum yield for process (15) as well as the quenching rate constants for the processes:

are all known as is the absolute photolysis cross section, σ^P , for process (14) so that the absolute OH density is given by:

$$OH = 2F\sigma^P [N_2O]\phi(^1D) k_{15} [H_2O] / (k_{15} [H_2O] + k_{16} [N_2O] + k_{17}[He]) \quad (18)$$

where F is the laser fluence at the photolysis wavelength (in photons/cm²), k_i are the rate constants for the various processes, $\phi(^1D)$ is the quantum yield for process (14) and $[He]$, $[H_2O]$ and $[N_2O]$ are the respective densities.

It is well known that process (14) will produce $O(^1D)$ with near unit quantum efficiency at wavelengths shorter than ~ 200 nm [29]. This suggests using the ArF excimer laser at 193 nm as a laser photolysis source. Neither H_2O nor He absorb significantly at this wavelength [29]. The cross section for process (14) at 193 nm has been measured to be $\approx 1 \times 10^{-19}$ cm² [29]. The bound-free nature of this process insures that all photons within the entire laser linewidth can be utilized for photodissociation. Typical fluences for commercial discharge pumped excimers running on ArF mixes are about 10^{17} photons/cm².

The concentrations of the various species and the photolysis laser energy can be adjusted to yield the appropriate amount of OH. The rate constant for process (15) is only ~ 1.5 times faster than process (16) so that $[H_2O] > 10 [N_2O]$ in order to insure that most of the $O(^1D)$ will react

rather than quench [30]. If we wish to generate $\text{OH} \approx 10^{13} \text{ cm}^{-3}$, we need $(\text{N}_2\text{O}) \approx (10^{13} \text{ cm}^{-3}) / (10^{-19} \text{ cm}^2) (10^{17} \text{ cm}^{-2}) \approx 10^{15} \text{ cm}^{-3}$. The required $[\text{H}_2\text{O}]$ is in excess of 10^{16} cm^{-3} , about 1/3 torr, which is much below the dew point at room temperature.

The reaction (15) is sufficiently exothermic ($\Delta H_R^\circ = 28.4 \text{ kcal/mole}$) to yield OH in excited vibrational levels (up to $v=2$) for either product. Measurements of the nascent vibrational distribution of the OH product indicate $\text{OH}(v=1)/\text{OH}(v=0) \approx 0.4$ and, if a Boltzmann distribution is assumed, $\text{OH}(v=2)/\text{OH}(v=0) = 0.16$ [31]. As much as one-half of the total OH produced by reaction (15) could be unaccounted for if the vibrational distribution is not relaxed. We suggest that the distribution could be relaxed prior to laser induced fluorescence detection of OH by diluting the $\text{N}_2\text{O}/\text{H}_2\text{O}$ mix with enough helium to relax the $v=1$ level and delaying firing the detection laser by an appropriate amount. The rate constants for the processes

are, respectively $< 3 \times 10^{-16} \text{ cm}^3/\text{sec}$ and $\approx 10^{-12} \text{ cm}^3/\text{sec}$ [30]. At $[\text{He}] = 10^{19} \text{ cm}^{-3}$, vibrational relaxation would be about 90% complete in 200-300 nsec compared with a 90% complete reaction time for process (15) of $\sim 1\text{-}2 \text{ } \mu\text{sec}$. This helium density would have a negligible effect on the $\text{O}(^1\text{D})$ quantum yield.

III. KINETICS MODEL

In this section we will describe the details of a kinetics model that has been developed to understand the mechanism of electron beam initiated SO_x/NO_x removal. In order to better understand these processes, two separate models have been used: a SO_x removal model and a NO_x removal model. This differentiation is necessary because of fundamental differences between the two mechanisms, e.g., e-beam initiated NO_x removal does not require the presence of water vapor whereas SO_x e-beam initiated removal does. The discussion below begins with a description of the SO_x mechanism and a comparison of model predictions with experimental data. This is followed by the NO_x removal model description and a comparison of model predictions with experiment. The experimental data that is used for comparison here was published several years ago by two groups active in this area: Ebara Corp. and the Japan Atomic Energy Research Institute (JAERI).

A. SO_x REMOVAL MECHANISM

The chemical kinetics in electron beam irradiated flue gas is quite complex due to the non-selective nature of the high energy electron beam irradiation. A wide variety of chemical processes can occur including ion chemistry, excited state chemistry and neutral chemistry. We have discovered that, at least in the case of the SO_x removal kinetics, the problem can be greatly simplified by decoupling the ion chemistry from the neutral chemistry and ignoring the excited state chemistry entirely. We will show that the dominant SO_2 removal mechanism basically involves neutral chemistry between SO_2 and radicals produced by the electron beam induced fragmentation of the main chemical components of flue gas. The ion chemistry can be considered as a transfer mechanism to convert each ion pair formed by the electron beam induced ionization into one H, OH pair. By treating the ion chemistry in this global fashion, we can ignore the details of the charge transfer, ion-molecule, attachment and detachment, association and recombination processes.

1. Energy Deposition

At the primary electron beam energies envisioned for SO_x/NO_x removal (approximately several hundred keV), the energy deposition depends mainly upon the atomic properties of the gas and only very little upon its chemical properties. The fundamental atomic property that describes the energy deposition is the stopping power, S , of the gas. These quantities are tabled in the monograph by Berger and Seltzer[29]. For a mixture of gases such as flue gas, the total stopping power, S_T , can be approximated by

$$S_T = \frac{JN}{e} \sum_i S_i \psi_i M_w(i) \quad (20)$$

where the sum extends over the various major gas components (N_2 , CO_2 , H_2O , O_2), S_i is the stopping power of the i th component, ψ_i is the mole fraction of the i th component, $M_w(i)$ is the molecular weight of the i th component, J is the current flux (in amps/m²), e is the charge on the electron, and N is the total gas density (in m⁻³). The values of the S_i and molecular weights are found in Table 1 for the main components of flue gas at a nominal electron energy of 100 keV. Note that the S_i for N_2 , O_2 and CO_2 differ by less than 1% indicative of the fact that these compounds are composed of atoms of comparable atomic number. The quantities S_i^{rel} indicate the fraction of the total electron beam energy absorbed by each species assuming $\psi_i = \psi_j$ (for all j). It is given by:

$$S_i^{\text{rel}} = \frac{S_i M_w(i)}{\sum_j S_j M_w(j)} \quad (21)$$

At the several hundred keV primary electron energy, the stopping power of the flue gas is dominated by collisional energy loss while the radiative loss, "bremsstrahlung" loss, is negligible. The collisional losses produce ionization, dissociation, electronically excited states and a small amount of rotational and vibrational excitation. It is usually found that ionization

TABLE 1
STOPPING POWERS OF FLUE GAS COMPONENTS

<u>i</u>	<u>M.W. (gr/gr-mole)</u>	<u>S_i (MeV-M²/gr x 10⁻⁴)</u>	<u>S_i rel</u>
N ₂	28	3.642	0.225
O ₂	32	3.621	0.256
CO ₂	44	3.638	0.353
H ₂ O	18	4.197	0.167

and dissociation processes dominate the electron beam energy loss and, therefore, we generally ignore (except for $O(^1D)$, see below) excited state chemistry.

2. Electron Cooling Processes

The secondary electrons, e_s , produced by the ionization by the primary beam electrons, e_p , via processes such as

are generated with significant excess kinetic energy. The average energy required to create an electron-ion pair (such as N_2^+/e) via process (22) is in the range 30-40 eV for flue gas components. The average excess kinetic energy is about 15-28 eV because the ionization potential is about 12-15 eV.

Since there is no applied electric field in the e-beam irradiation process, the electrons will eventually cool down to the gas temperature (300-500°K). The question arises as to the rate of cooling and a comparison of this rate with the chemical rates of interest in the SO_x removal mechanism. The comparison is important because some chemical processes such as dissociative attachment, e.g.,

have a very significant electron energy dependence. The time for which the energy distribution overlaps the peak in the dissociative attachment cross section compared to the time constant for process (23) determines its contribution to the overall kinetics.

In principle, the time dependence of the electron energy distribution can be obtained from the transient solution to the Boltzmann transport equation by including all the elastic and inelastic processes that describe the rate of electron energy loss (momentum transfer, rotational, vibrational and electronic excitation and ionization) by collision with flue gas. However, this calculation is beyond the scope of this work. Instead, simple estimates could be obtained from a knowledge of the maximum cross sections for the various cooling processes, the electron energy and the density of the colliding gas. It was found that the electron cooling time in a gas comprised of 67%

N_2 , 21% CO_2 , 10% H_2O and 2% O_2 at a total density of 0.8 amagat ($1.96 \times 10^{25} M^{-3}$) was in the range 1-10 nsec. This rapid cooling should be expected given the high gas density and the large cross sections for vibrational excitation in N_2 and CO_2 and the overall large density of states available to soak up the electron energy.

The $10^8 - 10^9 \text{ sec}^{-1}$ cooling rate is much faster than most of the chemical reactions included in the model. It is safe to assume that the electron energy is at the gas temperature in this model.

3. Positive Ion Chemistry

The various flue gas components are ionized to an extent that is proportional to their mole fraction:

etc.

The ionization G values (# produced per 100 eV deposited) for the major components of flue gas are listed in Table 2. The total ionization rate is then given by I:

$$I = \frac{NJ}{e} \sum_i \sum_j S_i \psi_i G_i(j) M_w(i) \quad (27)$$

where the index j extends over all ion fragments of a given flue gas component, i.

TABLE 2
G-VALUES FOR IONIZATION

<u>Species</u>	<u>G-Value</u>			
N ₂	G(N ₂ ⁺)=2.2	G(N ⁺)=0.7		
O ₂	G(O ₂ ⁺)=2.07	G(O ⁺)=1.23		
CO ₂	G(CO ₂ ⁺)=2.23	G(O ⁺)=0.21	G(CO ⁺)=0.51	
H ₂ O	G(H ₂ O ⁺)=1.99	G(O ⁺)=0.06	G(OH ⁺)=0.57	G(H ⁺)=0.67

Subsequent to the initial ionization by primary electrons, a complex set of ion-molecule reactions occurs on a rapid time scale during which the initial positive charge is believed to flow down to the species with the lowest ionization potential. A schematic diagram of the positive charge flow is shown in Figure 14. In this diagram the lowest ionization potential species is at the bottom of the page and, therefore, the charge is expected to flow from top to bottom. The various intermediate ions that convey the charge are indicated by circles and squares, but the collision partners needed for chemical transformation are not explicitly shown. It should also be noted that Figure 14 is not to scale.

In dry flue gas the positive charge would reside on the O_2^+ (or O_4^+) ion via charge transfer processes such as

The chemistry in the more realistic wet flue gas environment is somewhat more complicated due to the ability of the polar water molecule to cluster around bare ions forming clusters via processes such as,

etc.

As indicated in Figure 14 the water cluster ions are expected to be the sink for the residual positive charge.

K8943

Figure 14 Model of Positive Ion Chemistry in E-Beam Irradiated Stack Gas

4. Negative Ion Chemistry

The electrons produced by the ionization processes can be lost either by recombination with positive ions, e.g.,

or attachment via two or three body processes, e.g.,

The electron loss rate in flue gas is expected to be dominated by attachment processes because the electron density is low ($N_e \sim 10^{10} \text{ cm}^{-3}$) and the recombination rate is quadratic in the electron density.

It is also expected that three body attachment to O_2 is the dominant attachment process. Two body attachment can occur in many oxygenated species, e.g., O_2 , CO_2 , H_2O , NO , NO_2 , SO_2 , etc.. These processes usually possess a high energy threshold of several eV (because chemical bonds are stronger than the oxygen electron affinity). However, the secondary electron energy cooling rate is so rapid in flue gas at atmospheric density that the secondaries do not spend enough time at energies above the dissociative attachment threshold to allow the two body process to occur efficiently. On the other hand, three body processes possess no energy threshold and can occur down to thermal electron energies provided that the third body can effectively remove all the kinetic energy of the electron and stabilize the parent negative ion. Three body processes have been observed for all the oxygenated species listed above except for H_2O and CO_2 . This implies that O_2 is the main three body attaching species since the NO_x and SO_x species are in minor concentrations relative to O_2 .

The O_2^- ion will cluster H_2O molecules around itself via the association reaction.

etc.

in a manner analogous to positive ion clustering. The number of cluster ligands can reach 4-5 under flue gas conditions. The energy of the cluster is in the range 1-3 eV and therefore, these clusters are stable at the elevated flue gas temperatures.

5. Radical and Atom Formation

The SO_x removal model considers three contributions to the formation of radicals and atoms: products of ion-ion recombination processes, products of primary electron impact on the major flue gas components, and products of the $O(^1D)$ reaction with water vapor. Each of the three contributions is discussed below.

The product of the recombination of the positive and negative water clusters, $H_3O^+(H_2O)_N$ and $O_2^-(H_2O)_M$ is expected to be one H atom via the neutralization process

In order to conserve mass, one OH radical must also be generated for each H atom given that the H atom originated from a water molecule. The rate of generation of the H, OH pair is given by the ionization rate, equation 27. It should be noted that we are assuming that neither SO_x nor NO_x play any role in the ion chemistry.

The primary electron impact upon molecular flue gases (N_2 , CO_2 , H_2O , O_2) can generate atoms or radicals directly through either dissociative ionization or neutral dissociation processes, e.g.,

The atom and radical yields (G^R values) from the e-beam radiolysis literature have been reviewed in Reference 32, and are listed in Table 3. G^R values have been obtained for one component system. We assume in our model that these values also apply to the mixtures of interest here. An additional assumption that we make in our model is to sum the excited and ground state G^R values together to generate a G^R value for total atom or radical production. The only excited state that is separately accounted for in the code is $O(^1D)$ production from neutral dissociation and dissociative ionization of CO_2 . The values in Table 3 also include the contributions from atomic ions such as N^+ assuming that a neutral atom is produced subsequent to charge transfer.

As indicated above, the $O(^1D)$ production from primary electron impact upon CO_2 is significant and, therefore, it is directly counted. The production of $O(^1D)$ is favored over ground state $O(^3P)$ during CO_2 dissociation in order to satisfy spin conservation. The main impact of $O(^1D)$ production is the production of OH via the rapid process:

6. Radical/Atom - Molecule Reactions

The SO_x kinetics code then reduces to a set of neutral reactions involving atoms, radicals, NO_x , and SO_x with driving terms for atom and radical production given by the appropriate contributions from one or all of the three contributors listed in the previous section.

The current SO_x kinetics code contains 27 neutral species and 49 reactions. Not all of these species or reactions are of equal importance. However, only reactions that can proceed with rate constants $\geq 10^{-18} \text{ cm}^3/\text{sec}$ were considered for the temperature range of interest here (300-500°K). A list of species can be found in Table 4 and a list of reactions and their associated rate constants at three temperatures can be found in Table 5. In Table 5, M indicates a third body. Forty-eight of the forty-nine rate constants have been critically reviewed in the literature and the best current values were used in this study [33,34]. The only reaction that was not critically reviewed is k_{54}

TABLE 3
G^R-VALUES FOR ATOM AND RADICAL PRODUCTION

<u>SPECIES</u>	<u>G VALUE</u>			
N ₂	G(N) = 6.1			
O ₂	G(O) = 2.82			
CO ₂	G(C) = 0.07	G(O(¹ O)) = 4.51	G(O) = 0.79	G(CO) = 5.02
H ₂ O	G(O) = 0.52	G(H) = 4.82	G(OH) = 4.82	G(H ₂) = 0.52

G^R in # produced per 100eV deposited.

TABLE 4
LIST OF SPECIES IN CODE

1 - N2	11 - H02	21 - HS03
2 - C02	12 - N02	22 - H2S04
3 - H20	13 - N03	23 - C
4 - 02	14 - HN0	24 - H2
5 - S02	15 - H02N02	25 - C0
6 - N0	16 - N20	26 - H202
7 - H	17 - HN02	27 - HS03.H20
8 - N	18 - HN03	
9 - 0	19 - S03	
10 - OH	20 - 03	

TABLE 5
SO_x CODE PROCESSES

<u>NO.</u>	<u>REACTION</u>	<u>k(298°K)</u>	<u>k(373°K)</u>	<u>k(473°K)</u>
39.	SO ₂ + OH + M > HSO ₃ + M	2.000D-12	1.500D-12	7.040D-13
40.	SO ₂ + O + M > SO ₃ + M	1.320D-33	3.200D-33	4.830D-33
41.	SO ₂ + HO ₂ > SO ₃ + OH	1.000D-18	1.000D-18	1.000D-18
42.	SO ₂ + NO ₂ > SO ₃ + NO	2.000D-24	2.000D-24	2.000D-24
43.	NO + HO ₂ > NO ₂ + OH	8.500D-12	7.100D-12	6.600D-12
44.	NO + O + M > NO ₂ + M	1.000D-31	7.200D-32	5.240D-32
45.	NO + OH + M > HNO ₂ + M	9.600D-12	4.500D-12	2.460D-12
46.	NO + H + M > HNO + M	4.200D-32	3.300D-32	2.800D-32
47.	NO + NO ₃ > 2NO ₂	1.900D-11	1.900D-11	1.900D-11
48.	NO + O ₃ > NO ₂ + O ₂	1.640D-14	4.700D-14	1.070D-13
49.	NO + N > N ₂ + O	3.400D-11	3.400D-11	2.700D-11
50.	H + O ₂ + M > HO ₂ + M	5.700D-32	4.100D-32	2.900D-32
51.	H + OH + M > H ₂ O + M	5.310D-31	2.800D-31	1.500D-31
52.	H + H + M > H ₂ + M	8.300D-33	8.300D-33	8.300D-33
53.	H + NO ₂ > OH + NO	1.200D-10	1.700D-10	2.200D-10
54.	SO ₂ + OH + H ₂ O > HSO ₃ ·H ₂ O	3.900D-30	3.900D-30	1.950D-30
55.	H + HO ₂ > 2OH	3.200D-11	3.200D-11	3.200D-11
56.	H + O ₃ > OH + O ₂	2.700D-11	3.900D-11	5.100D-11
57.	H + HNO > H ₂ + NO	3.000D-13	3.000D-13	3.000D-13
58.	N + NO ₂ > N ₂ O + O	1.400D-12	1.400D-12	1.400D-12
59.	N + N + M > N ₂ + M	4600D-33	3.200D-33	2.400D-33

TABLE 5. (Continued)

NO.	REACTION	k(298°K)	k(373°K)	k(473°K)
60.	$N + OH \rightarrow NO + H$	5.300D-11	5.300D-11	5.300D-11
61.	$N + O + M \rightarrow NO + M$	1.050D-32	9.300D-33	8.300D-33
62.	$N + O_2 \rightarrow NO + O$	7.500D-17	5.300D-16	5.100D-15
63.	$N + O_3 \rightarrow NO + O_2$	5.000D-16	5.000D-16	5.000D-16
64.	$O + O_2 + M \rightarrow O_3 + M$	6.500D-34	4.400D-34	2.500D-34
65.	$O + HO_2 \rightarrow OH + O_2$	3.500D-11	3.500D-11	3.500D-11
66.	$O + O_3 \rightarrow 2O_2$	7.800D-15	3.900D-14	1.300D-13
67.	$O + NO_2 + M \rightarrow NO_3 + M$	6.500D-32	5.100D-32	6.900D-32
68.	$OH + CO \rightarrow CO_2 + H$	2.700D-13	2.700D-13	2.700D-13
69.	$OH + OH \rightarrow O + H_2O$	2.000D-12	2.600D-12	3.500D-12
70.	$OH + NO_2 + M \rightarrow HNO_3 + M$	5.700D-31	1.100D-30	6.900D-31
71.	$OH + HNO_3 \rightarrow NO_3 + H_2O$	8.500D-14	8.500D-14	8.500D-14
72.	$OH + HO_2 \rightarrow H_2O + O_2$	4.000D-11	4.000D-11	4.000D-11
73.	$OH + HNO_2 \rightarrow NO_2 + H_2O$	6.600D-12	6.600D-12	6.600D-12
74.	$OH + O_3 \rightarrow HO_2 + O_2$	6.300D-14	1.300D-13	2.300D-13
75.	$OH + N_2O \rightarrow HNO + NO$	3.800D-17	3.800D-17	3.800D-17
76.	$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$	1.000D-31	7.100D-32	2.100D-32
77.	$HO_2 + O_3 \rightarrow OH + 2O_2$	1.500D-15	2.300D-15	3.200D-15
78.	$NO_2 + O_3 \rightarrow NO_3 + O_2$	2.800D-17	1.690D-16	6.800D-16
79.	$SO_3 + H_2O + (M) \rightarrow H_2SO_4 + M$	9.100D-13	9.100D-13	9.100D-13
80.	$O + NO_2 \rightarrow NO + O_2$	9.300D-12	9.300D-12	9.300D-12
81.	$O + NO_3 \rightarrow O_2 + NO_2$	1.000D-11	1.000D-11	1.000D-11
82.	$O + OH \rightarrow H + O_2$	4.000D-11	4.000D-11	4.000D-11
70.	$OH + NO_2 + M \rightarrow HNO_3 + M$	5.700D-31	1.100D-30	6.900D-31
71.	$OH + HNO_3 \rightarrow NO_3 + H_2O$	8.500D-14	8.500D-14	8.500D-14

TABLE 5 (Continued)

<u>NO.</u>	<u>REACTION</u>	<u>k(298°K)</u>	<u>k(373°K)</u>	<u>k(473°K)</u>
72.	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	4.000D-11	4.000D-11	4.000D-11
73.	$\text{OH} + \text{HNO}_2 \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	6.600D-12	6.600D-12	6.600D-12
74.	$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	6.300D-14	1.300D-13	2.300D-13
75.	$\text{OH} + \text{N}_2\text{O} \rightarrow \text{HNO} + \text{NO}$	3.800D-17	3.800D-17	3.800D-17
76.	$\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2 + \text{M}$	1.000D-31	7.100D-32	2.100D-32
77.	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	1.500D-15	2.300D-15	3.200D-15
78.	$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	2.800D-17	1.690D-16	6.800D-16
79.	$\text{SO}_3 + \text{H}_2\text{O} + (\text{M}) \rightarrow \text{H}_2\text{SO}_4 + \text{M}$	9.100D-13	9.100D-13	9.100D-13
80.	$\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$	9.300D-12	9.300D-12	9.300D-12
81.	$\text{O} + \text{NO}_3 \rightarrow \text{O}_2 + \text{NO}_2$	1.000D-11	1.000D-11	1.000D-11
82.	$\text{O} + \text{OH} \rightarrow \text{H} + \text{O}_2$	4.000D-11	4.000D-11	4.000D-11
83.	$\text{OH} + \text{OH} + (\text{M}) \rightarrow \text{H}_2\text{O}_2 + \text{M}$	4.700D-12	3.200D-12	2.700D-12
84.	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	7.700D-13	1.300D-12	2.000D-12
85.	$\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$	1.400D-11	1.400D-11	1.400D-11
86.	$\text{HO}_2\text{NO}_2 + (\text{M}) \rightarrow \text{HO}_2 + \text{NO}_2 + \text{M}$	7.400D-02	1.050D+02	3.800D+04
87.	$\text{OH} + \text{HNO} \rightarrow \text{H}_2\text{O} + \text{NO}$	7.000D-11	7.000D-11	7.000D-11

Note: 2000-11 = $2.000 \times 10^{-11} \text{ cm}^3/\text{sec}$

for which only one literature value has been obtained [35].

The set of coupled rate equations that describe the 49 processes in our model were numerically integrated on an IBM computer using the Gear algorithm, a sixth order predictor-corrector method that also allows for variable integration order and variable step size [36]. This method is usually applied to stiff sets of differential equations in which the characteristic time constants (eigenvalues) have widely differing values as is the case in the SO_x/NO_x kinetics codes.

7. Results and Comparison with Experimental Data

Model predictions from the code were generated for both room temperature and two elevated temperatures, 373°K and 473°K. The room temperature runs correspond to the experimental conditions (1% H_2O , 3% O_2 , 13% CO_2 , 83% N_2) for the AERL SO_x removal data in Figure 12 and the elevated temperature runs that correspond to the experimental conditions (1.3% H_2O , 0-20% O_2 , 0-5% CO , bal. N_2) of some published work of the JAERI group in Japan. In general, we found that the code predicted the elevated temperature results reasonably well, but failed to adequately explain the room temperature results. For the purposes of comparison of code and experiment, we limit the discussion in this section to the elevated temperature results and reserve the discussion of the comparison of the room temperature results to Section II.C.2.

A comparison between code and experimental results for an initial concentration of 1400 ppmV SO_x at 373°K is given in Figure 15. The dotted line is our extrapolation of the Japanese data down to zero dose [12]. The code accurately predicts the absolute SO_x removal at low dose, but appears to slightly underpredict the absolute removal at high dose by no more than 15 percent. Over the linear portion of the SO_x removal data, the data yield a $G(-\text{SO}_2)$ value of 5.33 while the code predicts $G(-\text{SO}_2) = 4.5$. It is not clear at this point whether the disagreement at high dose is significant given that the error estimates on both the data and code results are not well known. In any event, the agreement is satisfying given the number of simplifying assumptions that go into the code.

Figure 15 Comparison SO_x Removal Code Results and Experiment at 100°C.
Dose dependence (see Ref. 12).

For the conditions of Figure 15, we list additional information in Table 6 in the form of code predictions for the concentrations of various neutral stable species that are products of the e-beam irradiation of SO_x containing flue gas at the 90% SO_x removal level. The high level of nitric acid formation is due to NO formation via processes such as:

followed by reactions with O and OH to yield HNO_3 . Note that nitrous oxide is predicted to be a fairly significant sink of NO_x . In addition, the ozone level for these conditions is about 100 ppmV.

In order to test the range of validity of the code, a number of input parameters were varied and compared to existing data. Variations in gas temperature, O_2 content and CO content were examined. A variation in H_2O content could not be tested because it is known that the model assumptions break down at very low water content. A variation in NO_x content (with SO_x present) was not attempted because it is known (see Section III.B) that the code cannot accurately predict NO_x removal. Also, variations in SO_2 content and CO_2 content were not made because this high temperature data does not exist.

There is experimental data on the temperature variation of SO_x removal over the temperature range 373 - 523°K [37]. However, in general, the rate constant values input to the code have only been critically evaluated over the range 200 - 400°K. Above 400°K, we are forced to extrapolate the rate constant values. One additional code run was undertaken at 473°K, a temperature which provides us with the minimum extrapolation needed to compare to another high temperature data point. A comparison of the code and experimental G values obtained at this temperature and 373°K are shown in Figure 16. The code is clearly overpredicting the amount of SO_x removal at the higher temperature. This difference appears to be too large to be explained by errors in the extrapolated rate constants. If we also ignore experimental errors, then a more likely possibility is that the code is missing a process which inhibits SO_x removal and has a fairly high activation energy so that it is unimportant at 373°K but is significant at 473°K.

TABLE 6
CODE PREDICTIONS OF SOME STABLE SPECIES

<u>Species</u>	<u>Concentration (ppmV)</u>
NO	~ 0.02
NO ₂	~ 20
NO ₃	~ 1
N ₂ O	~ 400
HNO ₃	~ 600
SO ₃	NONE
H ₂ SO ₄ + HSO ₃	~ 1260
O ₃	~ 100

Figure 16 Comparison of SO_x Removal Code Results and Experiment. Temperature dependence. (see Ref. 37).

The code predictions and data [37] for the O_2 variation are shown in Figure 17. The code does reasonably at predicting the relative shape of the curve. The increase in SO_2 removal at low O_2 addition is due to the additional contribution from

The absolute G values from the code are low by as much as 67% at zero concentration O_2 decreasing to only about 15-25% low at high O_2 content.

The code predictions and data [37] for the CO variation are shown in Figure 18. For these cases the code and experiment are in reasonably good agreement over the entire range of CO content that was investigated. A possible explanation for the good agreement stems from the fact that the only role played by the CO impurity is that of scavenging OH via one reaction:

and this process is adequately accounted for in the model.

B. NO_x REMOVAL MECHANISM

Experiments have shown that there is a fundamental difference between the NO_x and SO_x removal mechanism. NO_x can be efficiently removed in a dry environment whereas SO_x requires the presence of water. Therefore, given the prominent role that water plays in the model assumptions that underlie the SO_x removal mechanism, it was doubtful that the SO_x code could adequately explain NO_x removal even though the NO_x code contains a sufficient number of neutral reactions that can remove NO_x . Indeed, it was found that the SO_x code could not adequately predict the NO_x removal in wet flue gas mixtures. Even in dry mixtures containing only NO and N_2 , the code grossly overestimated the amount of NO removal.

One of the primary NO_x removal mechanisms in simple NO/ N_2 mixtures are the processes:

Figure 17 Comparison of SO_x Removal Code Results and Experiment. O₂ dependence. (see Ref. 37).

Figure 18 Comparison of SO_x Removal Code Results and Experiment. (CO dependence (see Ref. 37)).

The overprediction of the code results in NO/N₂ mixtures suggested that the true N atom yield in NO/N₂ mixtures is much less than the N atom yield input to the code calculation. In this regard, it should be reiterated that the code value is based upon N atom yields in Pure N₂ and, therefore, might be suspect when applied to NO/N₂ mixtures. Code calculations were run for which the primary N atom production via

was reduced until agreement with experiment was obtained. It was found that reasonably good agreement was obtained for NO loss if the primary N atom production yield, G(N), was reduced to 1/4 of its original value for initial NO concentrations in the range 100-500 ppm. (See Figure 19 and Figure 20) [8]. There is also experimental data on NO₂ production in the same mix [8]. Using the reduced G(N) value that best fits the NO loss data, we find that the code overpredicts NO₂ production by about a factor of 2.5 (see Figure 21). A more significant discrepancy was found when we attempted to model NO/O₂/N₂ mixtures (see Figure 22) [8].

We attempted to explain this empirically deduced N atom yield, G*(N), by explicitly adding in ion chemistry to the SO_x neutral chemistry code. The ion chemistry code is listed in Table 7. It was believed that the N atom yield would be smaller in NO/N₂ mixtures than it is in pure N₂ because attachment, ion-ion and ion electron recombination processes such as:

Figure 19 Comparison of NO_x Removal Code Results and Experiment (500 ppm NO). (see Ref. 8).

Figure 20 Comparison of NO_x Removal Code Results and Experiment (250 ppm NO). (see Ref. 8).

Figure 21 Comparison of NO_x Removal Code Results and Experiment. NO₂ production. (see Ref. 8).

Figure 22 Comparison of NO_x Removal Code Results and Experiment.
NO/O₂/N₂ mixtures (see Ref. 8).

TABLE 7
ION CHEMISTRY PROCESSES

<u>NO.</u>	<u>PROCESS</u>	<u>k (cm³/sec)</u>
88	$N_2^+ + 2N_2 \longrightarrow N_4^+ + N_2$	1.230D-09
89	$N^+ + 2N_2 \longrightarrow N_3^+ + N_2$	4.410D-10
90	$N_3^+ + NO \longrightarrow NO^+ + N + N_2$	1.400D-10
91	$N_4^+ + NO \longrightarrow NO^+ + 2N_2$	3.300D-10
92	$N^+ + NO \longrightarrow N + NO^+$	8.000D-10
93	$N_2^+ + NO \longrightarrow NO^+ + N_2$	3.300D-10
94	$NO^+ + NO + N_2 \longrightarrow NONO^+ + N_2$	1.230D-10
95	$NO^+ + N_2 + N_2 \longrightarrow NON_2^+ + N_2$	4.900D-12
96	$N_2^+ + e_s \longrightarrow 2N$	2.000D-07
97	$N_3^+ + e_s \longrightarrow N + N_2$	7.000D-07
98	$N_4^+ + e_s \longrightarrow 2N_2$	2.000D-06
99	$NO^+ + e_s \longrightarrow N + O$	4.000D-07
100	$NONO^+ + e_s \longrightarrow N + O + NO$	1.700D-06
101	$NON_2^+ + e_s \longrightarrow N + O + N_2$	1.500D-06
102	$e_s + NO_2 + N_2 \longrightarrow NO_2^- + N_2$	4.000D-11
103	$e_s + O_2 + N_2 \longrightarrow O_2^- + N_2$	3.700D-12
104	$O_2^- + N_2 + N_2 \longrightarrow N_2O_2 + N_2$	7.350D-13
105	$O_2^- + N \longrightarrow NO_2^- + e_s$	5.000D-10
106	$O_2^- + NO_2 \longrightarrow O_2 + NO_2^-$	1.200D-09
107	$N_2O_2^- + NO_2 \longrightarrow NO_2^- + N_2 + O_2$	5.000D-10
108	$O_2^- + N \longrightarrow O^- + NO$	1.000D-10

TABLE 7 (Continued)

NO.	PROCESS	k (cm ³ /sec)
109	$N_2O_2^- + N \longrightarrow NO + O^- + N_2$	1.000D-10
110	$N_2O_2^- + NO \longrightarrow NO_3^- + O_2$	2.500D-10
111	$NO_3^- + NO \longrightarrow NO_2^- + NO_2$	1.500D-11
112	$NO^+ + NO_2^- + N_2 \longrightarrow NO + NO_2 + N_2$	4.900D-06
113	$NO^+ + NO_2^- \longrightarrow NO + NO_2$	1.000D-07
114	$NON_2^+ + NO_2 \longrightarrow NO + NO_2$	1.000D-07
115	$NON_2^+ + NO_2 + N_2^- \longrightarrow NO + NO_2 + N_2$	4.900D-06
116	$NON_2^+ + N_2O_2 \longrightarrow NO + O_2 + 2N_2$	1.000D-07
117	$NON_2^+ + N_2O_2 + N_2 \longrightarrow NO + O_2 + 3N_2$	4.900D-06
118	$N(^2D) + N_2 \longrightarrow N + N_2$	2.000D-18
119	$N(^2D) + O_2 \longrightarrow NO + O$	2.00D-12
120	$N(^2D) + NO \longrightarrow N_2 + O$	3.000D-11

would reduce the number of free secondary electrons which can generate N atoms via:

However, modelling calculations indicated that the net effect was small, and the ion chemistry code does not explain the NO_x experimental results. For example, although process (99) generates only one N atom per electron as compared with process (121) which generates 2, the O atom is effective in removing NO by three body formation of NO_2 . In addition, attachment to NO_2 and O_2 only becomes significant at high NO removal (high NO_2 and O_2 yields) yet discrepancies between the code and experiment are clearly apparent at low NO removal where attachment and ion-ion recombination processes are small.

We interpret these results as implying that the predominant N atom yield is not due to process (121), but, instead, comes from primary electron impact on N_2 via:

and this yield is reduced in going from N_2 to NO/N_2 mixtures.

The mechanism that explains this yield reduction is not yet understood. One possibility is a cooling of the secondary electron distribution during the transient phase. It is not clear as to how a gas impurity at the 1000 ppmV level would modify the electron energy distribution sufficiently to reduce the dissociation yield by a factor of 4.

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APPENDIX A

LISTING OF SO_x/NO_x COMPUTER CODE

The computer code that was used to calculate the kinetics predictions of SO₂ and NO_x removal is listed below. The code contains a main program and calls four subroutines (DIFFUN, MATINV, PEDERV, DIFSUB). The main program handles all the input and output controls, initialization and calculates certain quantities that are used within the code as well as output quantities. The subroutine DIFSUB integrates a set of N (up to 42 for the cases considered here) ordinary differential equations using the Gear integration method. The subroutine DIFFUN calculates the time derivatives of each of the species (dependent variables) included in the code. The subroutine MATINV is a standard matrix inversion routine needed for the Gear integration routine. The subroutine PEDERV (as used in the listed program below) is a dummy subroutine needed only to link all the subroutines together. In this case, the subroutine DIFSUB numerically calculates the Jacobian matrix needed for the integration routine. In the more general case (not considered here) the user supplies the PEDERV subroutine which contains analytic expression for the Jacobian matrix. The reader should note that the computer listing contains a sufficient number of comment cards to make the detailed operation of the code reasonably self-explanatory.

To run the code, the user simply inputs one data file containing the values of the following integration control parameters:

TSTART	- Start time of integration
TSTOP	- Stop time of integration
TSOUT	- Start time of output routine
NOUT	- Number of output points
MDIST	- Sets distribution of output points
MAXSTP	- Maximum number of steps allowed
EPS	- Maximum estimated error per step
MAXDER	- Maximum order of integration method
METHOD	- Integration method
	0 = Adams Predictor - Converter
	1 = Stiff, User Supplied PEDERV
	2 = Stiff, Dummy PEDERV
H	- Initial step size to be attempted
HMIN	- Minimum allowable step size
HMAX	- Maximum allowable step size
NGRAPH	- Graph every Ngraph'th point
N	- Number of species
NRATE	- Number of chemical reactions
NTIMES	- Number of times source function change

as well as the initial values of all N species and values for all of the NRATE rate constants. A typical input data file is included in the code listing.

SOXLIB.FORT(SOX1)

THIS IS THE ROOT PROGRAM FOR THE SOX KINETICS SIMULATION

VERSION 6.3 3 APR 82 S.F.FULGHUM

THIS VERSION OF THE SOX KINETICS PROGRAM CONTAINS
28 SPECIES AND 48 RATES.

A VECTOR OF SOURCE FUNCTIONS SOURCE(I) COMBINED WITH A CORRESPONDING
VECTOR OF TIMES TIME(I) ALLOWS THE SOURCE FUNCTION TO BE VARIED
STEPWISE THROUGH THE INTEGRATION INTERVAL.
AT EACH TIME(I) POINT DIFSUB IS RESTARTED AT ORDER 1 AND A SMALL
TIME STEP.

THIS PROGRAM CALLS THE GEAR INTEGRATION PROGRAM DIFSUB
DIFSUB CALLS 3 OTHER SUBROUTINES

DIFFUN(T,Y,DY) CALCULATES THE DERIVATIVES DY OF THE
DEPENDENT VARIABLES Y AT TIME T
PEDERV(T,Y,PW,NMAX) CALCULATES THE PARTIALS OF THE
ABOVE DERIVATIVES WITH RESPECT TO
ALL OF THE OTHER VARIABLES TO
GIVE THE JACOBIAN MATRIX PW
MATINV(A,N,NMAX,JFLAG) INVERTS THE GENERAL MATRIX PW

THE SUBROUTINE PEDERV(T,Y,PW,NMAX) WILL NOT BE CALLED IF
A FLAG IN THE CALL TO DIFSUB IS PROPERLY SET.
IN THIS CASE DIFSUB WILL ESTIMATE THE JACOBIAN MATRIX
NUMERICALLY (SAVING A GREAT DEAL OF EFFORT FOR THE USER)
AT A SMALL COST IN EXECUTION TIME.
HOWEVER, A DUMMY SUBROUTINE PEDERV MUST THEN BE SUPPLIED
TO SATISFY THE COMPUTER WHEN IT LINKS ALL THE SUBROUTINES
TOGETHER TO FORM THE COMPLETE PROGRAM.

SEE THE LISTING OF DIFSUB FOR A FULL DESCRIPTION OF THE
METHOD AND REQUIRED SUBROUTINES SPECIFIC TO THE PARTICULAR
SET OF EQUATIONS TO BE INTEGRATED

AN INPUT FILE IS READ FOR THE FOLLOWING INITIALIZATION
PARAMETERS IN THE ORDER DESCRIBED

TSTART - START TIME OF INTEGRATION

00000010
00000020
00000030
00000040
00000050
00000060
00000070
00000080
00000090
00000100
00000110
00000120
00000130
00000140
00000150
00000160
00000170
00000180
00000190
00000200
00000210
00000220
00000230
00000240
00000250
00000260
00000270
00000280
00000290
00000300
00000310
00000320
00000330
00000340
00000350
00000360
00000370
00000380
00000390
00000400
00000410
00000420
00000430
00000440
00000450
00000460
00000470
00000480

C	TSTOP	- STOP TIME OF INTEGRATION	00000490
C	TSDUT	- START TIME OF OUTPUT ROUTINE	00000500
C		(OUTPUT STOPS AT TSTOP)	00000510
C	NOUT	- NUMBER OF OUTPUT POINTS	00000520
C		(DIVISIONS BETWEEN TSTART AND TSTOP)	00000530
C	MDIST	- SETS DISTRIBUTION OF OUTPUT POINTS	00000540
C		0=LINEAR 1=LOGARITHMIC	00000550
C	MAXSTP	- MAXIMUM NUMBER OF STEPS ALLOWED	00000560
C	EPS	- MAXIMUM ESTIMATED ERROR PER STEP	00000570
C	MAXDER	- MAXIMUM ORDER OF INTEGRATION METHOD	00000580
C	METHOD	- INTEGRATION METHOD	00000590
C		0- ADAMS PREDICTOR-CORRECTOR FOR NON-STIFF	00000600
C		PROBLEMS	00000610
C		1- STIFF METHOD, REQUIRES USER TO SUPPLY	00000620
C		JACOBIAN SUBROUTINE PEDERV	00000630
C		2- STIFF METHOD, CALCULATES JACOBIAN NUMERICALLY	00000640
C	H	- INITIAL STEP SIZE TO BE ATTEMPTED	00000650
C	HMIN	- MINIMUM ALLOWABLE STEP SIZE	00000660
C	HMAX	- MAXIMUM ALLOWABLE STEP SIZE	00000670
C	NGRAPH	- GRAPH OUTPUT. EVERY NGRAPH TH POINT. 0=NONE	00000680
C	N	- NUMBER OF DEPENDENT VARIABLES	00000690
C	NRATE	- NUMBER OF RATE CONSTANTS (REACTIONS)	00000700
C	NTIMES	- NUMBER OF TIMES SOURCE CHANGES	00000710
C			00000720
C	Y(1,1)	- INITIAL VALUE OF FIRST DEPENDENT VARIABLE	00000730
C	Y(1,N)	- INITIAL VALUE OF FINAL DEPENDENT VARIABLE	00000740
C			00000750
C	RK(1)	- FIRST RATE CONSTANT	00000760
C			00000770
C	RK(NRATE)	- FINAL RATE CONSTANT	00000780
C			00000790
C	OFERAC	- FRACTION OF SOURCE INTO H-OH PAIRS	00000800
C			00000810
C	TIME(1),SRCE(1)	- START TIME AND INITIAL SOURCE RATE	00000820
C	TIME(1),SRCE(1)	- CHANGES IN SOURCE AND TIME OF CHANGE	00000830
C			00000840
C			00000850
C			00000860
C			00000870
C			00000880
C	LIMIT	- LOGICAL, SET TO TRUE TO SIGNAL THAT THE PROGRAM	00000890
C		SHOULD REINITIALIZE DIFSUB.	00000900
C	LCUT	- LOGICAL, SET TO TRUE TO ENTER OUTPUT ROUTINE AT TIMES	00000910
C		OTHER THAN THE USUAL DISTRIBUTION BETWEEN TSTART	00000920
C		AND TSTOP	00000930
C	NSTEP	- STEP COUNTER FOR EVERY SUCCESSFUL CALL TO DIFSUB	00000940
C	NPOINT	- OUTPUT POINT COUNTER FOR THE USUAL DISTRIBUTION OF	00000950
C		TIMES BETWEEN TSTART AND TSTOP. DOES NOT INCREMENT	00000960

```

C      AT OTHER OUTPUT TIMES (LOUT, STEPS 1 AND 2)
C      NTIME - STEP COUNTER FOR CHANGING THE SOURCE FUNCTION DURING
C              THE INTEGRATION
C
C      SOX SIMULATION SPECIFIC VARIABLES
C      Y(1,1) - DENSITY OF MOLECULAR SPECIES, CM-3
C
C              1- N2      11- HO2      21- HSO3      31- (NO+)
C              2- CO2     12- NO2      22- H2SO4     32- (NO+H2O)
C              3- H2O     13- NO3      23- C
C              4- O2      14- HNO      24- H2
C              5- SO2     15- HO2NO2   25- CO
C              6- NO      16- N2O      26- H2O2
C              7- H       17- HNO2     27- HSO3.H2O
C              8- N       18- HNO3     28- HE
C              9- OH      19- SO3 29- (E-)
C              10- OH     20- O3 30- (N2+)
C
C      RHO - DENSITY OF GAS, GM CM-3
C      SOURCE - IONIZATION PAIRS CREATED CM-3 SEC-1 BY E-BEAM
C      EVAVG - EV/ION PAIR AVERAGED OVER PRIMARY SPECIES AND
C              WEIGHTED BY THEIR INITIAL MOLE FRACTIONS
C      EVRATE - ENERGY DEPOSITION RATE, EV CM-3 SEC-1
C      EVTOTL - TOTAL ENERGY DEPOSITED TO DATE, EV CM-3
C      EVEFF - EV REQUIRED TO REMOVE EACH SO2 OR NO MOLECULE TO DATE
C      DCSRAT - DOSE RATE MEGARADS SEC-1 (1 MRAD = 10 JOULES GM-1)
C      DGSE - DOSE MEGARADS
C
C      DENSITY - TOTAL DENSITY OF MOLECULES, CM-3
C      DISO2 - INITIAL DENSITY OF SO2 MOLECULES
C      DINO - INITIAL DENSITY OF NO MOLECULES
C      DREMOV - SO2 AND NO MOLECULES REMOVED TO DATE, CM-3
C      RSO2 - % SO2 REMOVED TO DATE
C      RNO - NO REMOVED TO DATE IN PPM
C      PPMNO - INITIAL PPM OF NO
C      DINITN - INITIAL DENSITY OF NITROGEN ATOMS
C              (CONTAINED IN ALL SPECIES- FOR NUMBER
C              CONSERVATION TESTS DURING INTEGRATION)
C      DINITO - INITIAL DENSITY OF OXYGEN ATOMS
C      DINITC - INITIAL DENSITY OF CARBON ATOMS
C      DINITH - INITIAL DENSITY OF HYDROGEN ATOMS
C      DINITS - INITIAL DENSITY OF SULFUR ATOMS
C
C      DFRACN - CURRENT N ATOM DENSITY DIVIDED BY INITIAL
C              N ATOM DENSITY. SHOULD REMAIN AT 1.0000

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C	IN THE ABSENCE OF ROUND OFF ERRORS	00001450
C	DFRACO, DFRACC, DFRACH, DFRACS	00001460
C		00001470
C	SWN2 - WEIGHTED SOURCE TERMS FOR ELECTRON IMPACT	00001480
C	DISSOCIATION OF PRIMARY SPECIES (N2, CO2,	00001490
C	H2O, O2). BASED ON MCLE FRACTION, RELATIVE	00001500
C	CROSS SECTION AND CURRENT SOURCE RATE OF	00001510
C	IONIZATIONS. NORMALIZED TO 1. CM-3 SEC-1	00001520
C	SWCO2, SWH2O, SWO2	00001530
C		00001540
C	SCRN2 - SOURCE TERM BASED ON THE EXCITATION PROBABILITIES	00001550
C	FOUND IN WILLIS AND BOYD EXCITATION IN THE	00001560
C	RADIATION CHEMISTRY OF INORGANIC GASES INT.	00001570
C	J. RADIAT. PHYS. CHEM. VOL.8 PP.71-111 1976	00001580
C	CM-3 SEC-1	00001590
C	SCRCO2, SCRH2O, SCRN, SCRO, SCRH, SCRCO, SCRH2	00001600
C	SCROH, SCROH (EXCITED OXYGEN, 1D STATE)	00001610
C		00001620
C	DQUEN - FRACTION OF O(1D) QUENCHED TO O(3P)	00001630
C	SSO1D - STEADY STATE O(1D) POPULATION	00001640
C		00001650
C	SINIT - INITIAL SOURCE RATE	00001660
C	SFRAC - FRACTION OF INITIAL SOURCE RATE	00001670
C	OHFRAC - FRACTION OF INITIAL SOURCE INTO H-OH PAIRS	00001680
C		00001690
C		00001700
C	RANDOM SCRATCH VARIABLES USED FOR SUMS, ETC.	00001710
C		00001720
C	DSUM	00001730
C		00001740
C	REVISION HISTORY	00001750
C	VERSION 1.4 24 MAR 81 - ORIGINAL CVR/SFF PROGRAM REWRITTEN	00001760
C	REMOVED CO2 = C+ + 2O + E-	00001770
C	DIF1 1.0 20 FEB 81	00001780
C	VERSION 2.1 1 APR 81 - REPLACES ABOVE SOURCE REACTION	00001790
C	DELETES N2O5, ADDS C, ADDS R42,43,44	00001800
C	DIF1 2.0 1 APR 81	00001810
C	VERSION 3.4 8 APR 81 - CORRECTS H,OH SOURCE RATE	00001820
C	ADDs H2O2, R45,46,47	00001830
C	DIF1 3.2 8 APR 81	00001840
C	PEO1 2.0 6 APR 81	00001850
C	VERSION 4.0 9 APR 81 - INCLUDES QUENCHING OF O(1D)	00001860
C	VERSION 5.2 27 APR 81 - INCLUDES DISSOC. OF HO2NC2	00001870
C	SO2-OH+H2O - HS03.H2O	00001880
C	DIF1 4.0 23 APR 81	00001890
C	PEO1 3.0 23 APR 81	00001900
C	VERSION 6.1 13 MAY 81 - ALLOWS MODIFICATION OF SOURCE TO	00001910
C	H-OH PAIR PRODUCTION	00001920

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C  VERSION 6.3   3 APR 82 - INCLUDES HE AS BUFFER SPECIES
C                      WITH 40 EV G-VALUE
C                      DIF1  4.1  29 MAR 82
C                      PED1  3.1  29 MAR 82
C
C  VERSION 6.4   19 JUL 83 - NEW SUBROUTINE DIFFUN
C                      * ION KINETICS *
C
C-----
C  DIMENSION VARIABLES AND WORK SPACES FOR DIFSUB
C
0001  REAL*8  Y(8,50),SAVE(10,60),YMAX(50),ERROR(50)
0002  REAL*8  H,HMIN,HMAX,EPS,T
0003  REAL*4  PW(2500)
0004  INTEGER N,METHOD,KFLAG,JSTART,MAXDER,NPW,NSAVE
C
C-----
C  DECLARE VARIABLE TYPES FOR OUTPUT ROUTINE
C
0005  REAL*8  TSTART,TSTOP,HLAST
0006  REAL*8  TSCUT,TLOG8,TLOGE,DFNPT,DFNOUT,TEST
0007  REAL*8  TIME(10),SORCE(10)
0008  REAL*4  STEST
0009  INTEGER NTIMES,NTIME
0010  LOGICAL*1 PLABEL(60,16),VLABEL(60,50),RLABEL(60,90),LABEL(60,8)
0011  LOGICAL*1 CLABEL(60,1)
0012  LOGICAL LINIT,LOUT
C
C-----
C  DECLARE VARIABLE TYPES FOR SOX ROOT PROGRAM CALCULATIONS
C
0013  REAL*8  RHO,EVAVG,DOSRAT,EVRATE,EVTUTL,DISO2,DINO,DREMGV,
1          EVEFF,DENSITY,DINITN,DINITO,DINITC,DINITH,DINITs,
2          DFRACN,DFRACU,DFRACC,DFRACH,DFRACS,SWN2,SWCQ2,
3          SWH2O,SWO2,SORN2,SORCO2,SORO2,SORH2O,SORN,SORO,SORH,
4          SORCC,SOROIC,SORH2,SOROH,SORC,DSUM,DQUEN,SINIT,SFRAC,
5          QHFRAC,SSO1D
0014  REAL*4  PPMsO2,PPMNO,RSO2,RNO
C
C-----
C  DIMENSION VARIABLES REQUIRED BY SUBROUTINES DIFFUN AND PEDERV
C  WHICH ARE NOT PASSED THROUGH THE CALL FROM DIFSUB
C  PASSED INSTEAD VIA A NAMED COMMON BLOCK
C
0015  REAL*8  RK(90),R(90),SOURCE

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0016      INTEGER IEM(12),NTIMES,NTIME          00002340
C*****                                     00002350
0017      COMMON IWH                           00002350
C*****                                     00002350
0018      COMMON /RATES/ RK,R,SOURCE          00002360
0019      COMMON /SORXXX/ SORN2,SORCO2,SORH2G,SORO2,SORH,SURN,SORO, 00002370
1          SOROF,SURH2,SORCO,SORC,SORCE      00002380
0020      COMMON ZGN2P,ZGNP,ZGA4S,ZGN2D
C
C DATA FILE OF THREE BODY RATE CONSTANTS TO BE CONVERTED
C TO TWO BODY RATE CONSTANTS BY MULTIPLYING BY DENSITY
C
0021      DATA IEM /2,6,8,12,13,14,21,23,26,29,32,38/
C
C -----
C SET SYSTEM ERROR HANDLING FACILITY SO THAT IT WILL SUPPRESS
C MESSAGES FOR ERROR 208 (UNDERFLOW) WHICH OFTEN OCCURS IN SUBROUTINE
C MATINV. THIS IS NOT A FATAL ERROR AND IS PROPERLY HANDLED BY THE
C SYSTEM WHICH MERELY SETS THE RESULT TO ZERO.
C THIS IS AN IBM-SUPPLIED SUBROUTINE IN THE FORTRAN LIBRARY
C
0022      CALL ERRSET(208,0,-1,1,0,0)
C
C -----
C READ INPUT DATA FROM INPUT FILE (10)
C EACH LINE OF THE FILE CONTAINS A VARIABLE AND ITS LABEL
C
0023      2 FORMAT (D10.3,60A1)
0024      3 FORMAT (I10,60A1)
0025      4 FORMAT (D14.7,D10.3)
C
C      5 FORMAT (60A1)
C
C DO 6 J = 1,8
C      6 READ (10,5) (LABEL(I,J),I=1,60)
C
0026      READ (10,2) TSTART, (PLABEL(I,1),I=1,60)
0027      READ (10,2) TSTOP, (PLABEL(I,2),I=1,60)
0028      READ (10,2) TSOUT, (PLABEL(I,3),I=1,60)
0029      READ (10,3) NGUT, (PLABEL(I,4),I=1,60)
0030      READ (10,3) MDIST, (PLABEL(I,5),I=1,60)
0031      READ (10,3) MAXSTP, (PLABEL(I,6),I=1,60)
0032      READ (10,2) EPS, (PLABEL(I,7),I=1,60)
0033      READ (10,3) MAXDER, (PLABEL(I,8),I=1,60)
0034      READ (10,3) METHOD, (PLABEL(I,9),I=1,60)
0035      READ (10,2) H, (PLABEL(I,10),I=1,60)
0036      READ (10,2) HMIN, (PLABEL(I,11),I=1,60)
0037      READ (10,2) HMAX, (PLABEL(I,12),I=1,60)
0038      READ (10,3) NGRAPH, (PLABEL(I,13),I=1,60)

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0039      READ (10,3) N,      (PLABEL(I,14),I=1,60)      00002790
0040      READ (10,3) NRATE,   (PLABEL(I,15),I=1,60)      00002800
0041      READ (10,3) NTIMES,  (PLABEL(I,16),I=1,60)      00002810
0042      READ (10,99) IMPRTR   00002810
0043      READ (10,299) ZGN2P, ZGNP, ZGN4S, ZGN2D          00002810
0044      99      FORMAT (F10.0)
0045      299      FORMAT (4F10.0)
C
C*****
0046      READ (15,*) IWH      00002820
C*****      00002820
C      00002820
C      DO 7 J = 1,N          00002830
0047      7      READ (10,2) Y(1,J), (VLABEL(I,J),I=1,60) 00002840
0048      C      00002850
C      DO 8 J = 1,NRATE      00002850
0049      8      READ (10,2) RK(J), (RLABEL(I,J),I=1,60) 00002860
0050      C      00002870
C      READ (10,2) OHFRAC, (CLABEL(I,1),I=1,60)          00002880
0051      C      00002890
C      DO 10 J = 1,NTIMES  00002900
0052      10      READ(10,4) TIME(J), SOURCE(J)            00002910
0053      C      00002920
C      -----      00002930
C      CALCULATE QUANTITIES WHICH DEPEND ONLY ON INITIAL DATA 00002940
C      00002950
C      SOURCE = SOURCE(1)  00002960
0054      SINIT = SOURCE    00002970
0055      C      00002980
C      CALCULATE TOTAL MOLECULAR DENSITY 00002990
C      00003000
C      DENSITY = 0.000     00003010
0056      DO 12 I = 1,N     00003020
0057      12      DENSITY = DENSITY + Y(1,I) 00003030
0058      C      00003040
C      CALCULATE DOSE RATE FOR THIS SOURCE AND GAS COMPOSITION 00003050
C      00003060
C      RHO = (Y(1,1)*28 + Y(1,2)*44 + Y(1,3)*18 + Y(1,4)*32 + Y(1,5)*64 00003070
0059      1      + Y(1,6)*30 + Y(1,28)*2 ) / 6.023E+23 00003080
0060      1      EVAVG = (Y(1,1)*34.5 + Y(1,2)*32.9 + Y(1,3)*30.0 + Y(1,4)*30.8 00003090
0061      1      + Y(1,28)*40.0 ) / DENSITY 00003100
C      DOSRAT = SOURCE*EVAVG*1.6E-19/(10.0*RHO) 00003110
C      00003120
C      CALCULATE QUANTITIES FOR EFFICIENCY CALCULATIONS 00003130
C      00003140
C      DISJ2 = Y(1,5) + 1.0E0 00003150
0062      DIN2 = Y(1,6) + 1.0E0 00003160
0063      EVRATE = EVAVG * SOURCE 00003170
0064      00003180

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0065      PPMO2 = SNGLDISO2/ENSITY) * 1.0E+6      00003190
0066      PPMO2 = SNGLDISO2/ENSITY) * 1.0E+6      00003200
C      CALCULATE INITIAL DENSITY OF ATOMIC SPECIES      00003210
C      00003220
C      00003230
0067      DINITN = Y(1,1)+Y(1,1)+Y(1,6)+Y(1,8)+Y(1,12)+Y(1,13)      00003240
1      +Y(1,14)+Y(1,15)+2.000*Y(1,16)+Y(1,17)+Y(1,18)      00003250
2      +2.000*Y(1,30)+Y(1,31)+Y(1,32)      00003250
0068      IF (DINITN.LT. 1.000) DINITN = 1.000      00003260
C      00003270
0069      DINITO = Y(1,3)+Y(1,6)+Y(1,9)+Y(1,10)+Y(1,14)+Y(1,16)+Y(1,25)      00003280
1      + 2.000*(Y(1,2)+Y(1,4)+Y(1,5)+Y(1,11)+Y(1,12)      00003290
2      +Y(1,26)+Y(1,17)) + 3.000*(Y(1,13)+Y(1,18)+Y(1,19)      00003300
3      +Y(1,20)+Y(1,21)) + 4.000*(Y(1,15)+Y(1,22)+Y(1,27))      00003310
4      +Y(1,31)+2.000*Y(1,32)      00003310
0070      IF (DINITO.LT. 1.000) DINITO = 1.000      00003320
C      00003330
0071      DINITC = Y(1,2)+Y(1,25)+Y(1,23)      00003340
0072      IF (DINITC.LT. 1.000) DINITC = 1.000      00003350
C      00003360
0073      DINITH = Y(1,7)+Y(1,10)+Y(1,11)+Y(1,14)+Y(1,15)+Y(1,17)      00003370
1      +Y(1,18)+Y(1,21) + 2.000*(Y(1,3)+Y(1,22)+Y(1,24)      00003380
2      +Y(1,26)) + 3.000*Y(1,27)+2.000*Y(1,22)      00003390
0074      IF (DINITH.LT. 1.000) DINITH = 1.000      00003400
C      00003410
0075      DINIT5 = Y(1,5)+Y(1,19)+Y(1,21)+Y(1,22)+Y(1,27)      00003420
0076      IF (DINIT5.LT. 1.000) DINIT5 = 1.000      00003430
C      00003440
C      00003450
C      00003460
C      00003470
C      00003480
C      00003490
C      00003500
C      00003510
C      00003520
C      00003530
C      00003540
C      00003550
C      00003560
C      00003570
C      00003580
C      00003590
C      00003600
C      00003610
C      00003620
C      00003630
C      00003640
0077      SWN2 = Y(1,1) * 0.22700
0078      SWCO2 = Y(1,2) * 0.3200
0079      SWH2O = Y(1,3) * 0.1700
0080      SWO2 = Y(1,4) * 0.2800
0081      DSUM = SWN2 + SWCO2 + SWH2O + SWO2
0082      SWN2 = (SWN2/DSUM) * SOURCE
0083      SWCO2 = (SWCO2/DSUM) * SOURCE
0084      SWH2O = (SWH2O/DSUM) * SOURCE
0085      SWO2 = (SWO2/DSUM) * SOURCE
C      CALCULATE ACTUAL SOURCE TERMS FOR PRIMARY SPECIES DISSOCIATED

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C BY THE ELECTRON BEAM (LCSS) AND THE PRODUCT SPECIES OF THOSE
C DISSOCIATIONS (GAINS).
C
C N2 DISSOCIATION
0086      SORN2 = -1.05225D0 * SWN2
0087      SORN = +2.0D0 * (-SORN2)
C
C O2 DISSOCIATION
0088      SORO2 = -0.43428D0 * SWO2
0089      SORO = +2.0D0 * (-SORO2)
C
C CO2 DISSOCIATION
0090      SORCO2 = -1.7066D0 * SWCO2
0091      SORO = SORO + 0.27692D0 * SWCO2
0092      SORCO = +1.68406 * SWCO2
0093      SORO1D = +1.45222D0 * SWCO2
0094      SORC = +0.02254 * SWCO2
C
C H2O DISSOCIATION
0095      SORH2O = -1.602D0 * SWH2O
0096      SORH = +1.446D0 * SWH2O
0097      SORH2 = +0.156D0 * SWH2O
0098      SORO = SORO + SORH2
0099      SOROH = SORH
C
C THE EXCITED OXYGEN (1D) PRODUCED FROM CO2 REACTS WITH WATER
C VAPOR TO GIVE 2(OH). IT IS ALSO QUENCHED TO O(3P) BY
C THE PRIMARY SPECIES. DQUEN IS THE FRACTION QUENCHED
C BASED ON 100 DEG C RATES. (NOT VERY TEMP SENSITIVE)
0100      DQUEN = Y(1,1)*2.7D-11 + Y(1,2)*9.3D-11 +
1          Y(1,4)*3.5D-11 + Y(1,6)*4.2D-11
0101      SSU1D = SORO1D / (Y(1,3)*2.3D-10 + DQUEN)
0102      DQUEN = DQUEN / (Y(1,3)*2.3D-10 + DQUEN)
C
0103      SORH2O = SORH2O - SORO1D * (1.0D0-DQUEN)
0104      SOROH = SOROH + SORO1D * 2.0D0 * (1.0D0-DQUEN)
0105      SORO = SORO + SORO1D * DQUEN
C
C CHARGE EXCHANGE RESULTS IN AN H,OH PAIR BEING FORMED FOR EVERY
C SOURCE EVENT BEYOND THE ABOVE SOURCE TERMS.
C FOR BALANCE, 1 SOURCE RATE IS SUBTRACTED FROM
C THE SOURCE RATE OF H2O.
C THIS HAS BEEN MODIFIED TO ALLOW ONLY PARTIAL PRODUCTION

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00003990
00004000
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00004090
00004100
00004110
00004120

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0108

C

SORH	=	SORH	+	SOLRCE	*	OHFRAC
SOROH	=	SOROH	+	SOLRCE	*	OHFRAC
SORH2O	=	SORH2O	-	SOLRCE	*	OHFRAC

00004130
00004140
00004150
00004160

C
C
C WRITE INPUT DATA TO OUTPUT FILE (20)

00004170
00004180
00004190
00004200

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0110
0111

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13 FORMAT (' ',6CA1)
14 FORMAT (' ',1FE10.3,2X,60A1)
15 FORMAT (' ',1F0,2X,6CA1)

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00004210
00004220
00004230

0112
0113

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WRITE (06,16)
16 FORMAT (/////'SOX KINETICS SIMULATION'/////
1      'SOX1 VERSION 6.3   3 APR 82   S.F.FULGHUM',
2      '-----',
3      'COMMENTS'//)

```

00004240
00004250
00004260
00004270
00004280
00004290

0114
0115
0116
0117

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17 WRITE (06,13) (LABEL(I,J),I=1,60)
18 FORMAT (06,18)

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0123
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0125
0126
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0136

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1          INTEGRATION CONTROL PARAMETERS' /
WRITE      (06,14) TSTART, (PLABEL(1,1),I=1,60)
WRITE      (06,14) TSTOP,  (PLABEL(1,2),I=1,60)
WRITE      (06,14) TSCUT,  (PLABEL(1,3),I=1,60)
WRITE      (06,15) NCUT,   (PLABEL(1,4),I=1,60)
WRITE      (06,15) NCIST,  (PLABEL(1,5),I=1,60)
WRITE      (06,15) MAXSTP, (PLABEL(1,6),I=1,60)
WRITE      (06,14) EPS,    (PLABEL(1,7),I=1,60)
WRITE      (06,15) MAXDER, (PLABEL(1,8),I=1,60)
WRITE      (06,15) METHODC, (PLABEL(1,9),I=1,60)
WRITE      (06,14) H,      (PLABEL(1,10),I=1,60)
WRITE      (06,14) HMIN,   (PLABEL(1,11),I=1,60)
WRITE      (06,14) HMAX,   (PLABEL(1,12),I=1,60)
WRITE      (06,15) NGRAPH, (PLABEL(1,13),I=1,60)
WRITE      (06,15) N,      (PLABEL(1,14),I=1,60)
WRITE      (06,15) NRATE,  (PLABEL(1,15),I=1,60)
WRITE      (06,15) NTIMES, (PLABEL(1,16),I=1,60)
WRITE      (06,14) TMRPTR,
WRITE      (06,19) ZGN2P,ZGNP,ZGN4S,ZGN2D
19  FORMAT (4E10.3)

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00004500
00004500
00004500

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0138

```

36 WRITE (C5,36)
   FORMAT (1'-----'

```

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00004530

0139
0140

```

1      ' INITIAL VALUES OF VARIABLES' )
DO 40 J = 1, N
40    WRITE (6, 14) Y(1, J), (VLABEL(I, J), I=1, 60)

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00004540
00004550
00004560
00004570

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0141      WRITE (06,44)
0142      44 FORMAT (' RATE CONSTANTS')
0143      DO 46 J = 1,NRATE
0144      46 WRITE (06,14) RK(J),(RLABEL(I,J),I=1,60)
C
0145      WRITE (06,14) DHFRAC,(CLABEL(I,1),I=1,60)
C
0146      WRITE (06,50)
0147      50 FORMAT (' TIME, SOURCE')
0148      DO 52 J = 1,NTIMES
0149      52 WRITE (06,54) TIME(J),SORCE(J)
0150      54 FORMAT (1PE14.7,2X,E10.3)
C
C-----
C WRITE QUANTITIES CALCULATED FROM INPUT DATA TO OUTPUT FILE
C
0151      WRITE (06,600)
0152      600 FORMAT ('-----')
C
0153      1 WRITE (06,605) DENSITY
0154      605 FORMAT (' GAS DENSITY, CM-3 =',1PE10.3)
0155      WRITE (06,610) RHO
0156      610 FORMAT (' GAS DENSITY, GM CM-3 =',1PE10.3)
0157      WRITE (06,601) IMPHTR
0158      601 FORMAT (5X,'TEMPERATURE, K =',F6.0)
0159      WRITE (06,615) EVAVG
0160      615 FORMAT (' AVG. IONIZATION ENERGY, EV =',F7.3)
0161      WRITE (06,620) DOSRAT
0162      620 FORMAT (' DOSE RATE, MEGARAD SEC-1 =',F7.3)
0163      WRITE (06,625) PPMSO2,PPMNO
0164      625 FORMAT (' INITIAL PPM SO2 =',F6.0,' INITIAL PPM NO =',F6.0)
0165      WRITE (06,630) SORN2,SCRCO2,SORH2C,SORC2,SORH,SORN,SORC,SGROH,
C      SORC,SORH2,SORCO,SORC1D
0166      630 FORMAT (' SOURCE RATES'/' SORN2 =',1PE14.7,' SORCO2 =',E14.7,'
1      SORH2O =',E14.7,' SORC2 =',E14.7,' SORH =',E14.7,'
2      SORN =',E14.7,' SORO =',E14.7,' SORCH =',E14.7,'
3      SORC =',E14.7,' SORH2 =',E14.7,' SORCO =',E14.7,'
4      SORC1D =',E14.7)
0167      WRITE (06,635) DQUEN
0168      635 FORMAT (' FRACTION C(1D) QUENCHED =',F6.3)
0169      WRITE (06,640) SSOL1D
0170      640 FORMAT (' STEADY STATE O(1D) =',1PD10.3)
C
C-----
C WRITE HEADING TO OUTPUT FILE
C
0171      WRITE (06,700)
0172      700 FORMAT ('-----')

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1      ' INTEGRATION OUTPUT'//)
0173  WRITE (05,705)
0174  705  FORMAT (/10X,'N2',9X,'CO2',9X,'H2O',10X,'O2',9X,'SO2',10X,'NU',
1      11X,'H',11X,'N',11X,'O',10X,'OH',9X,'HO2',9X,'H2O2',9X,
2      'NO3',9X,
3      'HNO',6X,'HO2NO2',9X,'N2O',8X,'HNO2',8X,'HNO3',9X,'SO3',
4      10X,'O3',7X,'HSO3',7X,'H2SO4',11X,'C',10X,'H2',10X,
5      'CO',8X,'H2O2',4X,'HSO3.H2O')
C
C -----
C  CALCULATIONS REQUIRED BY DIFFUN AND PEDERV BEFORE INTEGRATION
C  CONVERT THREE BODY RATE CONSTANTS TO TWO BODY
C
0175  DO 800 I = 1,12
0176  JEM = IEM(I)
0177  RK(JEM) = RK(JEM) * DENSITY
0178  800  CONTINUE
C
C -----
C  INITIALIZATION FOR OUTPUT CHECK
C  INITIALIZE TIME AND THE STEP AND OUTPUT POINT COUNTERS
C  AND CALCULATE CONSTANTS FOR OUTPUT ROUTINE
C
0179  T = TSTART
0180  NSTEP = 0
0181  NPOINT = 0
0182  NTIME = 2
0183  LINIT = .FALSE.
0184  LOUT = .FALSE.
0185  TLOGB = DLOG10(TSOUT)
0186  TLOGE = DLOG10(TSTGP)
0187  DFOUT = DBLE(FLOAT(NOUT))
0188  FGRAPH = FLOAT(NGRAPH)
C
C -----
C  INITIALIZE INTERNAL VARIABLES FOR DIFSUB
C  YMAX(J) IS THE MAXIMUM VALUE OF Y(I,J) TO CURRENT TIME
C  JSTART MUST BE 0 ON FIRST CALL TO INITIALIZE DIFSUB
C  LATER JSTART IS SET TO CURRENT ORDER
C  CALCULATE DIMENSION INFORMATION FOR DIFSUB WORK SPACE
C
0189  DO 900 J = 1,N
0190  YMAX(J) = 1.000
0191  900  CONTINUE
0192  JSTART = 0
0193  NPW = M*N
0194  NSAVE = N + INT((2.0*N)/10.0 + 0.9)
C

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-79-

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0195 C -----
0196 C BEGINNING POINT FOR A TIME STEP
0197 C
0198 C SET TOLD TO CURRENT TIME FOR STEP SIZE CALCULATION.
0199 C CHECK TO SEE IF OUTPUT POINT SECTION HAS SET THE LIMIT FLAG
0200 C TO TRUE, MEANING THAT A SOURCE CHANGE POINT HAS BEEN REACHED.
0201 C IF TRUE THEN CHANGE TO NEW SOURCE RATE AND REINITIALIZE DIFSUB.
0202 C
0203 C
0204 C
0205 C
0206 C
0207 C
0208 C
0209 C
0210 C
0211 C
0212 C
0213 C
0214 C
0215 C
0216 C
0217 C
0218 C
0219 C
0220 C
0221 C

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```

1000 TOLD = T
IF (.NOT. LIMIT) GO TO 1004
SOURCE = SOURCE(NTIME)
SFRAC = SOURCE / SINIT
SORN2 = SORN2 * SFRAC
SORCO2 = SORCO2 * SFRAC
SORH2O = SORH2O * SFRAC
SORO2 = SORO2 * SFRAC
SORH = SORH * SFRAC
SORN = SORN * SFRAC
SORO = SORO * SFRAC
SOROH = SOROH * SFRAC
SORC = SORC * SFRAC
SORH2 = SORH2 * SFRAC
SORCO = SORCO * SFRAC
SORO10 = SORO10 * SFRAC
NTIME = NTIME + 1
JSTART = 0
H = 10.000 * HMIN
DO 1002 J = 1, N
YMAX(J) = 1.000
1002 CONTINUE
LIMIT = .FALSE.
LCUT = .TRUE.
C
1004 IF (H .GT. HMAX) H = HMAX
C
C *****
CALL DIFSUB (N,T,Y,SAVE,H,HMIN,HMAX,EPS,METHOD,YMAX,
1 ERROR,KFLAG,JSTART,MAXDER,PW,NPH,NSAVE)
C *****
C -----
DIFSUB ERROR FLAG CHECKING
C THE OUTPUT VARIABLE KFLAG INDICATES ERRORS OR WARNS OF
C IMPENDING DOOM. THE SITUATION MAY OR MAY NOT BE FATAL AND
C MAY BE AUTOMATICALLY CORRECTABLE. IN THIS PROGRAM THE
C RESULT IS AN ERROR MESSAGE FOLLOWED BY A PROGRAM HALT
C
IF (KFLAG .GT. -4) GO TO 1220

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0222      WRITE (06,1212) NSTEP
0223      FORMAT (' NSTEP=',I4,' REQUESTED ERROR TOO SMALL')
0224      GO TO 1280
0225      1220 IF (KFLAG.GT.-3) GO TO 1230
0226      WRITE (06,1222) NSTEP
0227      1222 FORMAT (' NSTEP=',I4,' CORRECTOR CONVERGENCE COULD NOT
      1      BE ACHIEVED FOR H.GT.HMIN')
0228      GO TO 1280
0229      1230 IF (KFLAG.GT.-2) GO TO 1240
0230      WRITE (06,1232) NSTEP
0231      1232 FORMAT (' NSTEP=',I4,' MAXIMUM ORDER TOO LARGE')
0232      GO TO 1280
0233      1240 IF (KFLAG.GT.-1) GO TO 1290
0234      WRITE (06,1242) NSTEP
0235      1242 FORMAT (' NSTEP=',I4,' STEP TAKEN WITH HMIN BUT NOT
      1      REQUESTED ERROR NOT ACHIEVED')
C
C      ERROR DETECTED, EXIT PROGRAM BY JUMPING TO FINAL LINE
C
0236      1280 GO TO 9999
C
C      NO ERRORS DETECTED, CONTINUE ON
C
0237      1290 CONTINUE
C
C      -----
C      THE STEP WAS SUCCESSFUL, INCREMENT STEP COUNTER
C      IF PAST THE MAXIMUM STEP COUNT, EXIT
C      IF PAST MAXIMUM TIME (ERROR IN OUTPUT ROUTINE), EXIT
C      TO EXIT, JUMP TO FINAL LINE OF PROGRAM
C
0238      NSTEP = NSTEP + 1
0239      IF (NSTEP.GT.MAXSTP) GO TO 9999
0240      IF (T.GT.(1.2D+00*TSTOP)) GO TO 9999
C
C      -----
C      GRAPHICS OUTPUT SECTION. EVERY NGRAPH-TH POINT IS OUTPUT.
C      IF NGRAPH=0, THEN THIS SECTION IS SKIPPED.
C
0241      2000 IF (NGRAPH.EQ.0) GO TO 3000
0242      STEST = FLOAT(NSTEP) / FGRAPH
0243      IF ((STEST - INT(STEST)).GT.0.01) GO TO 3000
C
0244      IF (SOURCE.GT.0.000) EVTOTL = EVRATE * T
0245      IF (SOURCE.GT.0.000) DUSE = DOSRAT * T
0246      DREMOV = (DISO2+DINO) - (Y(1,5)+Y(1,6))
0247      IF (DREMOV.EQ.0.000) GO TO 2002
0248      EVEFF = EVTOTL / DREMOV

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0249      2002      CONTINUE                                00006480
0250      RSO2 = (1.0 - SNGL(Y(1,5)/DISO2)) * 100.0          00006490
0251      RNU = SNGL((DINO-Y(1,6))/DNSITY) * 1.0E+6          00006500
C
0252      WRITE (06,2010) T,Y(1, 8),Y(1, 6),Y(1,12),Y(1,13),Y(1,16), 00006510
C      1      Y(1,14),Y(1,17),Y(1,18),Y(1,15),Y(1, 1), 00006520
0253      WRITE (06,2010) T,Y(1, 9),Y(1,20),Y(1, 7),Y(1,24),Y(1,10), 00006530
C      1      Y(1,11),Y(1,26),Y(1, 4),Y(1, 3),Y(1, 2), 00006540
0254      WRITE (06,2010) T,Y(1, 5),Y(1,19),Y(1,21),Y(1,27),Y(1,22), 00006550
C      1      Y(1, 6),Y(1,23),Y(1,25),Y(1,10),Y(1, 9) 00006560
0255      WRITE (06,2012) T,EVEFF,DOSE,RSC2,RNO 00006570
0256      2010      FORMAT (1PE10.3,7(E10.3)) 00006580
0257      2012      FORMAT (1PE10.3,4(E10.3),'/') 00006590
C
C-----
C      OUTPUT POINT CHECK                                00006600
C      AT OR PAST AN OUTPUT POINT YET IF NOT THEN STEP AGAIN. 00006610
C      IF PAST A SOURCE RATE CHANGE POINT TIME(NTIME) 00006620
C      THEN MAKE THE STEP EXACT BY CALCULATING THE PROPER STEP SIZE 00006630
C      TO TAKE STARTING FROM THE PREVIOUS POINT AND TAKING THE LAST 00006640
C      STEP OVER. THIS REQUIRES SETTING JSTART TO -1. 00006650
C
C      IF MDIST=0, USE LINEAR DISTRIBUTION, =1 LOGARITHMIC 00006660
C
0258      3000 IF (NSTEP.LE.3 .OR. LOUT .OR. T.GE.TSTOP) GO TO 3090 00006670
0259      IF (MDIST.EQ. 1) GO TO 3060 00006680
C
C      LINEAR DISTRIBUTION OUTPUT SECTION 00006690
C
C      IF (NTIME .GT. NTIMES) GO TO 3052 00006700
C      IF (T .LT. 0.999D0*TIME(NTIME)) GO TO 3052 00006710
C      JSTART = -1 00006720
C      H = HMIN + DABS(TIME(NTIME)-TOLD) 00006730
C      LIMIT = .TRUE. 00006740
C      LOUT = .TRUE. 00006750
C      GO TO 3065 00006760
C
0260      3052      DFNPT = DBLE(FLOAT(NPOINT)) 00006770
0261      TEST = TSOUT+DFNPT*(TSTOP-TSOUT)/DFNOUT 00006780
0262      IF (T .LT. TEST) GO TO 3070 00006790
0263      GO TO 3080 00006800
0264      00006810
0265      00006820
0266      00006830
C
0267      00006840
0268      00006850
0269      00006860
0270      00006870
C
C      LOGARITHMIC DISTRIBUTION OUTPUT SECTION 00006880
C
0271      3060 IF (NTIME .GT. NTIMES) GO TO 3062 00006890
0272      IF (T .LT. 0.999D0*TIME(NTIME)) GO TO 3062 00006900
0273      JSTART = -1 00006910
0274      H = HMIN + DABS(TIME(NTIME)-TOLD) 00006920

```

0275
0276
0277

LIMIT = .TRUE.
LOUT = .TRUE.
GO TO 3065

00006960
00006970
00006980

0278
0279
0280
0281

C
3062 DFNPT = DBLE(FLOAT(NPOINT))
TEST = TLOG8-DFNPT*(TLOG8-TLOGE)/DFNOUT
IF (DLOG10(T) .LT. TEST) GO TO 3070
GO TO 3080

00006990
00007000
00007010
00007020
00007030
00007040

0282

C
C PAST A SOURCE CHANGE TIME
C GO BACK AND RETAKE LAST STEP WITH NEW H TO MAKE STEP EXACT
C
3065 GO TO 1004

00007050
00007060
00007070
00007080
00007090

0283

C
C BETWEEN OUTPUT POINTS
C RETURN TO DIFSUB TO TAKE ANOTHER STEP
C
3070 GO TO 1000

00007100
00007110
00007120
00007130
00007140

0284

C
C AT AN OUTPUT POINT, INCREMENT OUTPUT POINT COUNTER
C AND CONTINUE ON TO OUTPUT ROUTINE
C
3080 NPOINT = NPOINT + 1

00007150
00007160
00007170
00007180
00007190

0285
0286

C
C OUTPUT WITHOUT INCREMENTING OUTPUT POINT COUNTER
C
3090 HLAST = T - TOLD
LOUT = .FALSE.

00007200
00007210
00007220
00007230
00007240

0287
0288
0289
0290
0291
0292
0293
0294

C
C -----
C CALCULATE QUANTITIES FOR OUTPUT BASED ON CURRENT VALUES
C OF VARIABLES AND TIME
C
4000 IF (SOURCE .GT. 0.000) EVTOTL = EVRATE * T
IF (SOURCE .GT. 0.000) DOSE = DOSRAT * T
DREMOV = (DISO2+DINO) - (Y(1,5)+Y(1,6))
IF (DREMOV .LE. 0.000) GO TO 4020
EVEFF = EVTOTL / DREMOV
4020 CONTINUE
RSO2 = (1.0 - SMGL(Y(1,5)/DISO2)) * 100.0
RNO = SMGL((DINO-Y(1,5))/DNSITY) * 1.0E+6

00007250
00007260
00007270
00007280
00007290
00007300
00007310
00007320
00007330
00007340
00007350
00007360
00007370

0295

C
DFRACN = (Y(1,1)+Y(1,1)+Y(1,6)+Y(1,8)+Y(1,12)+Y(1,13)
1 +Y(1,14)+Y(1,15)+2.000*Y(1,16)+Y(1,17)+Y(1,18)
2 + Y(1,30)+Y(1,31)+Y(1,32)+Y(1,30))/ DLIMITN

00007380
00007390
00007400
00007410

0296

C
DFRACD = (Y(1,3)+Y(1,6)+Y(1,9)+Y(1,10)+Y(1,14)+Y(1,16)+Y(1,25)
1 + 2.000*(Y(1,2)+Y(1,4)+Y(1,5)+Y(1,11)+Y(1,12)

00007420
00007430

```

      2      +Y(1,17)+Y(1,26)) + 3.000*(Y(1,13)+Y(1,18)+Y(1,19) 00007440
      3      +Y(1,20)+Y(1,21)) + 4.000*(Y(1,15)+Y(1,22)+Y(1,27)) 00007450
      4      +Y(1,31)+2.000*Y(1,32))/ DINITO 00007460
C      DFRACC = ( Y(1,2)+Y(1,25)+Y(1,23) ) / DINITC 00007470
C      DFRACH = ( Y(1,7)+Y(1,10)+Y(1,11)+Y(1,14)+Y(1,15)+Y(1,17) 00007480
      1      +Y(1,18)+Y(1,21) + 2.000*(Y(1,3)+Y(1,22) 00007490
      2      +Y(1,24)+Y(1,26)) + 3.000*Y(1,27) 00007500
      3      +2.000*Y(1,32))/ DINITH 00007510
C      DFRACS = ( Y(1,5)+Y(1,19)+Y(1,21)+Y(1,22)+Y(1,27) ) / DINITS 00007520
C      ----- 00007530
C      OUTPUT ROUTINE 00007540
C      5000 WRITE (06,5002) T,HLAST,H,JSTART,NSTEP 00007550
      5002 FORMAT (// ' TIME=',1PE14.7, ' HLAST=',E10.3, ' H=',E10.3, 00007560
      1      ' ORDER=',I2, ' NSTEP=',I4) 00007570
C      5010 WRITE (06,5010) 00007580
      5010 FORMAT (// ' VARIABLES ' ) 00007590
      5020 WRITE (06,5020) (Y(1,I),I=1,10) 00007600
      5020 WRITE (06,5020) (Y(1,I),I=11,20) 00007610
      5020 WRITE (06,5020) (Y(1,I),I=21,30) 00007620
      5020 WRITE (06,5020) (Y(1,I),I=31,40) 00007630
      5020 WRITE (06,5020) (Y(1,I),I=41,50) 00007640
      5020 FORMAT (10(2X,1PE10.3)) 00007650
      5022 FORMAT (10(2X,1PE10.3)) 00007660
C      5030 WRITE (06,5030) 00007670
      5030 FORMAT ( ' RATES ' ) 00007680
      5020 WRITE (06,5020) (R(I),I=1,10) 00007690
      5020 WRITE (06,5020) (R(I),I=11,20) 00007700
      5020 WRITE (06,5020) (R(I),I=21,30) 00007710
      5020 WRITE (06,5020) (R(I),I=31,40) 00007720
      5020 WRITE (06,5020) (R(I),I=41,50) 00007730
      5020 WRITE (06,5020) (R(I),I=51,60) 00007740
      5020 WRITE (06,5020) (R(I),I=61,70) 00007750
      5020 WRITE (06,5020) (R(I),I=71,80) 00007760
      5020 WRITE (06,5020) (R(I),I=81,90) 00007770
C      5036 WRITE (06,5036) SCURCE,DOSE,EVEFF,RSQ2,RNO 00007780
      5036 FORMAT ( ' SOURCE=',1PE10.3, ' DOSE=',E10.3, 00007790
      1      ' EV/(SO2+NO REMOVED)=' ,E10.3, ' % SO2 REMOVED=' , 00007800
      2      ' 0PF7.1, ' PPM NO REMOVED=' ,F6.0) 00007810
C      5040 WRITE (06,5040) DFRACN,DFRACO,DFRACH,DFRACC,DFRACS 00007820
      5040 00007830
      5040 00007840

```


0325	5040 FORMAT (1 CONSERVATION	N=',F17.14,' O=',F17.14,' H=',F17.14,	00007850
	1 C=',F17.14,' S=',F17.14)		00007860
	C -----		00007870
	C EXIT ROUTINE		00007880
	C IF NOT COMPLETELY FINISHED, TAKE ANOTHER STEP		00007890
	C		00007900
0326	IF (T.LT.TSTOP) GO TO 1000		00007910
	C		00007920
	C FINAL STATEMENT FOR ERRCR EXITS		00007930
	C		00007940
0327	9999 CONTINUE		00007950
	C		00007960
0328	END		00007970
			00007980

0001

0002
0003
0004
0005
0006
0007

```

C-----
C      SUBROUTINE DIFFUN (T,Y,DY)
C
C*****
C      COMMON IWH
C      IF (IWH.GT.15) GOTO 456
C      WRITE(6,455)
C      FORMAT (45H CALL TO CORRECT DIFFUN SUBROUTINE SUCCESSFUL)
C      CCNTINUE
C      IWH=IWH+1
C*****

```

19 JUL 83

THIS SUBROUTINE CALCULATES THE TIME DERIVATIVES OF THE
DEPENDENT VARIABLES Y AND STORES THEM IN THE VECTOR DY...

THESE ARE THE SOX SIMULATION RATE EQUATIONS

1- N2	11- H2O2	21- HSO3	31- (N4+)	
2- CO2	12- NO2	22- H2SO4	32- (N3+)	41- (NO3-)
3- H2O	13- NO3	23- C	33- (NO+)	42- (N2O)
4- O2	14- HNO	24- H2	34- (NONO+)	
5- SO2	15- HC2NO2	25- CO	35- (NON2+)	
6- NO	16- N2O	26- H2O2	36- (E-)	
7- H	17- HNO2	27- HSC3.H2O	37- (O2-)	
8- N	18- HNO3	28- H	38- (NO2-)	
9- O	19- SO3	29- (N2+)	39- (N2O2-)	
10- OH	20- O3	30- (N+)	40- (O-)	

RK(I) - RATE CONSTANTS (TWO AND THREE BODY)

1 -	SO2 + OH	-	M	HSO3
2 -	SO2 + O	-	M	SO3
3 -	SO2 + HO2	-		SO3 + OH
4 -	SO2 + NO2	-		SO3 + NO
5 -	NO + HO2	-		NO2 + OH
6 -	NO + O	-	M	NO2
7 -	NO + OH	-	M	HNO2
8 -	NO + H	-	M	HNO
9 -	NO + NO3	-		2NO2
10 -	NO + O3	-		NO2 + O2
11 -	NO + N	-		N2 + O
12 -	H + O2	-	M	HO2
13 -	H + OH	-	M	H2O
14 -	H + H	-	M	H2

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00000330
00000340
00000350
00000360
00000370

C	15-	H + NO2	-	OH + NO	00000380
C	16-	SO2+GH+H2O	-	HSC3.H2O	00000380
C	17-	H + HO2	-	2OH	00000380
C	18-	H + U3	-	OH + O2	00000380
C	19-	H + HNO	-	H2 + NO	00000380
C	20-	N + NO2	-	N2O + O	00000380
C	21-	N + N	- M	N2	00000380
C	22-	N + OH	-	NO + H	00000380
C	23-	N + O	- M	NO	00000380
C	24-	N + O2	-	NO + J	00000380
C	25-	N + O3	-	NO + O2	00000380
C	26-	G + U2	- M	O3	00000380
C	27-	U + HO2	-	OH + O2	00000380
C	28-	O + O3	-	2O2	00000380
C	29-	O + NO2	- M	NO3	00000380
C	30-	OH + CO	-	CO2 + H	00000380
C	31-	OH + OH	-	O + H2O	00000380
C	32-	OH + NO2	- M	HNO3	00000380
C	33-	OH + HNO3	-	NO3 + H2O	00000380
C	34-	OH + HO2	-	H2O + O2	00000380
C	35-	OH + HNO2	-	NO2 + H2O	00000380
C	36-	OH + O3	-	HO2 + O2	00000380
C	37-	OH + N2O	-	PRODUCTS HNO + NO	00000380
C	38-	HO2 + NO2	- M	HO2NO2	00000380
C	39-	HO2 + O3	-	OH + 2O2	00000380
C	40-	NO2 + O3	-	NO3 + O2	00000380
C	41-	SO3 + H2O	- M	PRODUCTS (ASSUME H2SO4 CALVERT)	00000380
C	42-	U + NO2	-	NO + O2	00000380
C	43-	O + NO3	-	O2 + HO2	00000380
C	44-	J + OH	-	H + O2	00000380
C	45-	OH + OH	- M	H2O2	00000380
C	46-	OH + H2O2	-	H2O + HO2	00000380
C	47-	H + HO2	-	H2 - O2	00000380
C	48-	HC2WO2	- M	HO2 + NO2	00000380
C	49-	OH - HNO	-	H2O + NO	00000380
C	50-	(N2+)+2N2	-	(N4+)+N2	00000250
C	51-	(N+)+2N2	-	(N3+)+N2	00000260
C	52-	(N3-)+NO	-	(NO+)+N+N2	00000270
C	53-	(N4-)+NO	-	(NO+)+2N2	00000280
C	54-	(N+)+NO	-	N + (NO+)	00000290
C	55-	(N2-)+NO	-	(NO+)+N2	00000300
C	56-	(NO+)+NO-N2	-	(NO+)+N2	00000310
C	57-	(NO+)+N2+N2	-	(NO+)+N2	00000320
C	58-	(N2+)+E	-	2N	00000330
C	59-	(N3+)+E	-	N+N2	00000340
C	60-	(N4+)+E	-	2N2	00000350
C	61-	(NO+)+E	-	N+G	00000360
C	62-	(NO+)+E	-	N+O+NO	00000370

```

C      63- (NON2+)+E - N+Q+N2 00000380
C      64- (E-)+NO2+N2 - (NO2-) + N2 00000380
C      65- (E-)+O2+N2 - (O2-) + N2 00000380
C      66- (O2-)+N2+N2 - (N2O2-) + N2 00000380
C      67- (C2-) + N - NO2 + (E-) 00000380
C      68- (O2-)+NO2 - O2 + (NO2-) 00000380
C      69- (N2O2-)+NO2 - (NO2-) + N2 + O2 00000380
C      70- (O2-) + N - (O-) + NO 00000380
C      71- (N2O2-)+N - NO + (C-) + N2 00000380
C      72- (N2O2-)+NO - (NO3-) + O2 00000380
C      73- (NO3-)+NO - (NO2-) + NO2 00000380
C      74- (NO+)+(NO2-)+N2 - NO + NO2 + N2 00000380
C      75- (NO+)+(NO2-) - NO + NO2 00000380
C      76- (NON2+)+(NO2-) - NO + NO2 00000380
C      77- (NON2+)+(NO2-)+N2 - NO + NO2 + N2 00000380
C      78- (NON2+)+(N2O2-) - NO + O2 + 2N2 00000380
C      79- (NON2+)+(N2O2-)+N2 - NO + O2 + 3N2 00000380
C      80- N(2D) + N2 - N + N2 00000380
C *****
C      81- N(2D) + O2 - NO + O 00000380
C      82- N(2D) + NO - N2 + O 00000380

```

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C      -----
C      REAL*8 Y(8,50),DY(50),T 00000750
C      REAL*8 RK(90),R(90),SOURCE 00000760
C      REAL*8 SCR2,SORC2,SRH2G,SOR2,SORH,SORN,SORO,SORH, 00000770
C      1 SCR2,SORCO,SORC,SORCE(1) 00000780
C      COMMON /RATES/ RK,R,SOURCE 00000790
C      COMMON /SORXXX/ SORN2,SORC2,SRH2G,SOR2,SORH,SORN,SORO, 00000800
C      1 SORH,SORH2,SORCC,SORC,SORCE(1) 00000810
C      5 00000820
C      00000830

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***** 01) IG10371 PREDIMENSIONED WRN.
0013 COMMON ZGN2P,ZGNP,ZGN4S,ZGN2D

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C      NEGATIVE POPULATIONS ARE UNPHYSICAL. SET TO 0.0 00000840
C      DO 10 I = 1,42 00000850
C      IF (Y(1,I) .LT. 0.000) Y(1,I) = 0.000 00000860
C      10 CONTINUE 00000870
C      DEFINE RATES FROM RATE CONSTANTS AND DENSITIES 00000880
C      00000890
C      00000900
C      00000910
C      00000920
C      00000930
C      00000940
C      00000950
C      00000960

```

```

0017 R(1) = RK(1) * Y(1,5) * Y(1,10)
0018 R(2) = RK(2) * Y(1,5) * Y(1,9)
0019 R(3) = RK(3) * Y(1,5) * Y(1,11)
0020 R(4) = RK(4) * Y(1,5) * Y(1,12)

```

0021	R(5) = RK(5) * Y(1,11) * Y(1,6)	00000970
0022	R(6) = RK(6) * Y(1,9) * Y(1,6)	00000980
0023	R(7) = RK(7) * Y(1,10) * Y(1,6)	00000990
0024	R(8) = RK(8) * Y(1,6) * Y(1,7)	00001000
0025	R(9) = RK(9) * Y(1,6) * Y(1,13)	00001010
0026	R(10) = RK(10) * Y(1,6) * Y(1,20)	00001020
0027	R(11) = RK(11) * Y(1,6) * Y(1,8)	00001030
0028	R(12) = RK(12) * Y(1,4) * Y(1,7)	00001040
0029	R(13) = RK(13) * Y(1,10) * Y(1,7)	00001050
0030	R(14) = RK(14) * Y(1,7) * Y(1,7)	00001060
0031	R(15) = RK(15) * Y(1,7) * Y(1,12)	00001060
0032	R(16) = RK(16) * Y(1,5) * Y(1,10) * Y(1,3)	00001060
0033	R(17) = RK(17) * Y(1,7) * Y(1,11)	00001060
0034	R(18) = RK(18) * Y(1,7) * Y(1,20)	00001060
0035	R(19) = RK(19) * Y(1,7) * Y(1,14)	00001060
0036	R(20) = RK(20) * Y(1,8) * Y(1,12)	00001060
0037	R(21) = RK(21) * Y(1,8) * Y(1,8)	00001060
0038	R(22) = RK(22) * Y(1,8) * Y(1,10)	00001060
0039	R(23) = RK(23) * Y(1,9) * Y(1,9)	00001060
0040	R(24) = RK(24) * Y(1,9) * Y(1,4)	00001060
0041	R(25) = RK(25) * Y(1,3) * Y(1,20)	00001060
0042	R(26) = RK(26) * Y(1,9) * Y(1,4)	00001060
0043	R(27) = RK(27) * Y(1,9) * Y(1,11)	00001060
0044	R(28) = RK(28) * Y(1,9) * Y(1,20)	00001060
0045	R(29) = RK(29) * Y(1,9) * Y(1,12)	00001060
0046	R(30) = RK(30) * Y(1,10) * Y(1,25)	00001060
0047	R(31) = RK(31) * Y(1,10) * Y(1,10)	00001060
0048	R(32) = RK(32) * Y(1,10) * Y(1,12)	00001060
0049	R(33) = RK(33) * Y(1,10) * Y(1,18)	00001060
0050	R(34) = RK(34) * Y(1,10) * Y(1,11)	00001060
0051	R(35) = RK(35) * Y(1,10) * Y(1,17)	00001060
0052	R(36) = RK(36) * Y(1,10) * Y(1,20)	00001060
0053	R(37) = RK(37) * Y(1,10) * Y(1,16)	00001060
0054	R(38) = RK(38) * Y(1,11) * Y(1,12)	00001060
0055	R(39) = RK(39) * Y(1,11) * Y(1,20)	00001060
0056	R(40) = RK(40) * Y(1,12) * Y(1,20)	00001060
0057	R(41) = RK(41) * Y(1,9) * Y(1,3)	00001060
0058	R(42) = RK(42) * Y(1,9) * Y(1,12)	00001060
0059	R(43) = RK(43) * Y(1,9) * Y(1,13)	00001060
0060	R(44) = RK(44) * Y(1,9) * Y(1,10)	00001060
0061	R(45) = RK(45) * Y(1,10) * Y(1,10)	00001060
0062	R(46) = RK(46) * Y(1,10) * Y(1,26)	00001060
0063	R(47) = RK(47) * Y(1,7) * Y(1,11)	00001060
0064	R(48) = RK(48) * Y(1,15)	00001060
0065	R(49) = RK(49) * Y(1,10) * Y(1,14)	00001060
0066	R(50) = RK(50) * Y(1,29) * Y(1,1)	00001060
0067	R(51) = RK(51) * Y(1,30) * Y(1,1)	00001060
0068	R(52) = RK(52) * Y(1,32) * Y(1,6)	00001060

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0069      R(53) = RK(53) * Y(1,31) * Y(1,6)      00001060
0070      R(54) = RK(54) * Y(1,30) * Y(1,6)      00001060
0071      R(55) = RK(55) * Y(1,29) * Y(1,6)      00001060
0072      R(56) = RK(56) * Y(1,33) * Y(1,6)      00001060
0073      R(57) = RK(57) * Y(1,33) * Y(1,1)      00001060
0074      R(58) = RK(58) * Y(1,36) * Y(1,29)      00001060
0075      R(59) = RK(59) * Y(1,36) * Y(1,32)      00001060
0076      R(60) = RK(60) * Y(1,36) * Y(1,31)      00001060
0077      R(61) = RK(61) * Y(1,36) * Y(1,33)      00001060
0078      R(62) = RK(62) * Y(1,36) * Y(1,34)      00001060
0079      R(63) = RK(63) * Y(1,36) * Y(1,35)      00001060
0080      R(64) = RK(64) * Y(1,36) * Y(1,12)      00001060
0081      R(65) = RK(65) * Y(1,36) * Y(1,4)      00001060
0082      R(66) = RK(66) * Y(1,37) * Y(1,1)      00001060
0083      R(67) = RK(67) * Y(1,37) * Y(1,8)      00001060
0084      R(68) = RK(68) * Y(1,37) * Y(1,12)      00001060
0085      R(69) = RK(69) * Y(1,39) * Y(1,12)      00001060
0086      R(70) = RK(70) * Y(1,37) * Y(1,8)      00001060
0087      R(71) = RK(71) * Y(1,39) * Y(1,8)      00001060
0088      R(72) = RK(72) * Y(1,39) * Y(1,6)      00001060
0089      R(73) = RK(73) * Y(1,41) * Y(1,6)      00001060
0090      R(74) = RK(74) * Y(1,33) * Y(1,38)      00001060
0091      R(75) = RK(75) * Y(1,33) * Y(1,38)      00001060
0092      R(76) = RK(76) * Y(1,35) * Y(1,38)      00001060
0093      R(77) = RK(77) * Y(1,35) * Y(1,38)      00001060
0094      R(78) = RK(78) * Y(1,35) * Y(1,39)      00001060
0095      R(79) = RK(79) * Y(1,35) * Y(1,39)      00001060
0096      R(80) = RK(80) * Y(1,42) * Y(1,1)      00001060
0097      R(81) = RK(81) * Y(1,42) * Y(1,4)      00001060
0098      R(82) = RK(82) * Y(1,42) * Y(1,6)      00001060

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C
C
C

SUM RATES TO GET TIME DERIVATIVES OF VARIABLES

```

0099      DY(1) = R(11)+R(21)-R(50)-R(51)+R(52)+2.0*R(53)+R(55)-R(57)      00001430
1          +R(59)+2.0*R(60)+R(63)+R(69)+R(71)      00001430
2          +2.0*(R(78)+R(79))-SORCE(1)*(ZGN2P+ZGNP+ZGN4S      00001430
3          +ZGN2D)+R(80)-R(80)+R(82)      00001430
0100      DY(2) = SURCQ2 + R(30)      00001440
0101      DY(3) = SORH20 + R(13)+R(31)+R(33)+R(34)+R(35)+R(46)      00001450
1          -(R(41)+R(16))+R(49)      00001460
0102      DY(4) = SORU2 + R(10)+R(18)+R(25)+R(27)+R(28)+R(28)+R(34)      00001470
1          + R(36)+R(39)+R(39)+R(40)+R(42)+R(43)+R(44)      00001480
2          + R(47) - (R(12)+R(24)+R(26))-R(65)+R(68)+R(69)      00001490
3          +R(72)+R(78)+R(79)-R(81)      00001490
0103      DY(5) = -(R(1)+R(2)+R(3)+R(4)+R(16))      00001500
0104      DY(6) = R(4)+R(15)+R(19)+R(22)+R(23)+R(24)+R(25)+R(37)+R(42)      00001510
1          - (R(5)+R(6)+R(7)+R(8)+R(9)+R(10)+R(11))+R(49)      00001520
2          -R(52)-R(53)-R(54)-R(55)-R(56) +R(62)      00001520

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3      +R(70)+R(71)-R(72)-R(73)+R(74)+R(75)+R(76)+R(77)      00001520
4      +R(78)+R(79)+R(81)-R(82)      00001520
0105  DY(7) = SORH + R(22)+R(30)+R(44) - (R(8)+R(12)+R(13)+R(14)+R(14) 00001530
1      +R(15)+R(17)+R(18)+R(19)+R(47))      00001540
0106  DY(8) = - (R(11)+R(20)+R(21)+R(21)+R(22)+R(23)+R(24)      00001550
1      +R(25)) +(SORCE(1)*ZGN45)+R(52)+R(54)      00001560
2      +2.0*R(58)+R(59)+R(61)+R(62)+R(63)-R(67)-R(70)-R(71)      00001560
3      +R(80)      00001560
0107  DY(9) = SORC + R(11)+R(20)+R(24)+R(31) - (R(2)+R(6)+R(23)      00001570
1      +R(26)+R(27)+R(28)+R(29)+R(42)+R(43)+R(44))      00001580
2      +R(61)+R(62)+R(63)+R(81)+R(82)      00001580
0108  DY(10) = SOROH + R(3)+R(5)+R(15)+R(17)+R(17)+R(18)+R(27)      00001590
1      +R(39) - (R(1)+R(7)+R(13)+R(22)+R(30)+R(31)+R(31)+R(32)      00001600
2      +R(33)+R(34)+R(35)+R(36)+R(37)+R(44)+R(45)      00001610
3      +R(45)+R(46)+R(46))-R(49)      00001620
0109  DY(11) =      R(12)+R(36)+R(46)+R(48)      00001630
1      -R(3)-R(5)-R(17)-R(27)-R(34)-R(38)-R(39)-R(47)      00001640
0110  DY(12) =      R(5)+R(6)+R(9)+R(9)+R(10)+R(35)+R(43)+R(48)      00001650
1      -R(4)-R(15)-R(20)-R(29)-R(32)-R(38)-R(40)-R(42)      00001660
2      -R(64)+R(67)-R(68)-R(69)+R(73)+R(74)+R(75)+R(76)      00001660
3      +R(77)      00001660
0111  DY(13) =      R(29)+R(33)+R(40)      -R(51)-R(43)      00001670
0112  DY(14) =      R(8)+R(37)      -R(19)-R(49)      00001680
0113  DY(15) =      R(38)      -R(48)      00001690
0114  DY(16) =      R(20)      00001700
0115  DY(17) =      R(7)      -R(35)      00001710
0116  DY(18) =      R(32)      -R(33)      00001720
0117  DY(19) =      R(2)+R(3)+R(4)      -R(41)      00001730
0118  DY(20) =      R(26)      00001740
1      -R(10)-R(18)-R(25)-R(28)-R(36)-R(39)-R(40)      00001750
0119  DY(21) =      R(1)      00001760
0120  DY(22) =      R(41)      00001770
0121  DY(23) = SORC      00001780
0122  DY(24) = SORH2 + R(14)+R(19)+R(47)      00001790
0123  DY(25) = SORCO - R(30)      00001800
0124  DY(26) =      R(45) -R(46)      00001810
0125  DY(27) =      R(16)      00001820
0126  DY(28) = G.0      00001821
0127  DY(29) = SORCE(1)*ZGN2P - R(50)-R(55)-R(58)      00001821
0128  DY(30) = (SORCE(1)*ZGNP)- R(51)-R(54)      00001821
0129  DY(31) = R(50)-R(53)-R(60)      00001821
0130  DY(32) = R(51)-R(52)-R(59)      00001821
0131  DY(33) = R(52)+R(53)+R(54)+R(55)-R(56)-R(57)-R(61)-R(74)-R(75)      00001821
0132  DY(34) = R(56)-R(62)      00001821
0133  DY(35) = R(57)-R(63)-R(76)-R(77)-R(78)-R(79)      00001821
0134  DY(36) = SORCE(1)*(ZGN2P+ZGNP)-R(58)-R(59)-R(60)-R(61)      00001821
1      -R(62)-R(63)-R(64)-R(65)+R(67)      00001821
0135  DY(37) = R(65)-R(66)-R(67)-R(68)-R(70)      00001821

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0136	DY(38) = R(64)+R(68)+R(69)+R(73)-R(74)-R(75)-R(76)-R(77)	00001821
0137	DY(39) = R(66)-R(69)-R(71)-R(72)-R(78)-R(79)	00001821
0138	DY(40) = R(70)+R(71)	00001821
0139	DY(41) = R(72)-R(73)	00001821
0140	DY(42) = SCRC(1)*ZGN2D-R(80)-R(81)-R(82)	00001821
		00001830
0141	C 777 CONTINUE	
0142	RETURN	00001840
0143	END	00001850


```

0007      DO 80 K=1,N      00000000
0008      NK=NK+N          00000000
0009      L(K)=K           00000000
0010      M(K)=K           00000000
0011      KK=NK+K          00000000
0012      BIGA=A(KK)       00000000
0013      DO 20 J=K,N      00000000
0014      IZ=N*(J-1)        00000000
0015      DO 20 I=K,N       00000000
0016      IJ=IZ+I           00000000
0017      10 IF(ABS(BIGA)-ABS(A(IJ))) 15,20,20 00000000
0018      15 BIGA=A(IJ)      00000000
0019      L(K)=I             00000000
0020      M(K)=J             00000000
0021      20 CONTINUE      00000000
C      INTERCHANGE ROWS  00000000
C      J=L(K)             00000000
C      IF(J-K) 35,35,25   00000000
0022      25 K1=K-N          00000000
0023      DO 30 I=1,N        00000000
0024      K1=K1+N            00000000
0025      HOLD=-A(K1)        00000000
0026      J1=K1-K+J          00000000
0027      A(K1)=A(J1)        00000000
0028      30 A(J1)=HOLD      00000000
C      INTERCHANGE COLUMNS 00000000
C      I=M(K)             00000000
C      IF(I-K) 45,45,38   00000000
0031      38 JP=N*(I-1)      00000000
0032      DO 40 J=1,N        00000000
0033      JK=NK+J             00000000
0034      JI=JP+J            00000000
0035      HGLD=-A(JK)        00000000
0036      A(JK)=A(JI)        00000000
0037      40 A(JI)=HGLD      00000000
C      DIVIDE COLUMN BY MINUS PIVOT (VALUE OF PIVOT ELEMENT IS 00000000
C      CONTAINED IN BIGA) 00000000
C      45 IF(BIGA) 48,46,48 00000000
0040      46 D=0.0           00000000
0041      JFLAG = -1         00000000
0042      RETURN              00000000
0043      C                  00000000

```

0072 K=14

[illegible]

```

0073      100 K=(K-1)                                00000000
0074      IF(K) 150,150,105                          00000000
0075      105 I=L(K)                                00000000
0076      IF(I-K) 120,120,108                        00000000
0077      108 JQ=N*(K-1)                             00000000
0078      JR=N*(I-1)                                00000000
0079      DO 110 J=1,N                               00000000
0080      JK=JQ+J                                     00000000
0081      HOLD=A(JK)                                00000000
0082      JI=JR+J                                     00000000
0083      A(JK)=-A(JI)                               00000000
0084      110 A(JI)=HOLD                             00000000
0085      120 J=M(K)                                 00000000
0086      IF(J-K) 100,100,125                       00000000
0087      125 KI=K-N                                 00000000
0088      DO 130 I=1,N                               00000000
0089      KI=KI+N                                     00000000
0090      HOLD=A(KI)                                00000000
0091      JI=KI-K+J                                  00000000
0092      A(KI)=-A(JI)                              00000000
0093      130 A(JI)=HOLD                             00000000
0094      GO TO 100                                  00000000
0095      150 IF (D.EQ. 0.0) JFLAG = -1             00000000
0096      RETURN                                     00000000
0097      END                                         00000000

```

```
0001      C -----
      C      SUBROUTINE PEDERV (T,Y,PW,NMAX)
      C      VERSION 3.1  29 MAR 82  S.F.FULGHUM
      C      SCXLIB.FORT(PED1)
      C      THIS IS A DUMMY SUBROUTINE TO SATISFY THE COMPILER
      C      USE ONLY WITH DIFSUB SET FOR METHCD=2
      C      THIS SUBROUTINE CALCULATES THE ELEMENTS OF THE ARRAY PW
      C      WHERE PW(I,J) IS DEFINED AS THE PARTIAL OF THE I TH
      C      EQUATION WITH RESPECT TO THE J TH VARIABLE
      C      THIS SUBROUTINE IS FOR THE SOX KINETICS SIMULATION
      C      -----
0002      REAL*8  T,Y(8,34)
0003      REAL*4  PW(34,34)
0004      INTEGER NMAX
      C
0005      RETURN
0006      END
```

```
00000010
00000020
00000030
00000040
00000050
00000051
00000052
00000053
00000054
00000060
00000070
00000080
00000090
00000100
00000110
00000120
00000130
00000140
00000150
00000160
00000180
00000190
00000200
00000210
```

0001

```

C -----
C
C      SUBROUTINE DIFSUB (N,T,Y,SAVE,H,HMIN,HMAX,EPS,MF,YMAX,
C      1      ERROR,KFLAG,JSTART,MAXDER,PW,NPW,NSAVE)
C
C      REVISION DATE 15-AUG-80
C
C      THIS SUBROUTINE IS TAKEN FROM C.W.GEAR NUMERICAL INITIAL
C      VALUE PROBLEMS IN ORDINARY DIFFERENTIAL EQUATIONS
C      PRENTICE-HALL 1971, PP. 158-166
C
C      THIS SUBROUTINE INTEGRATES A SET OF N ORDINARY DIFFERENTIAL
C      FIRST ORDER EQUATIONS OVER 1 STEP OF LENGTH H AT EACH CALL.
C      H CAN BE SPECIFIED BY THE USER AT EACH STEP, BUT IT MAY BE
C      INCREASED OR DECREASED BY THE PRESENT SUBROUTINE WITHIN THE
C      RANGE HMIN TO HMAX IN ORDER TO ACHIEVE AS LARGE A STEP AS
C      POSSIBLE WHILE NOT COMMITTING A SINGLE STEP ERROR WHICH IS
C      LARGER THAN EPS IN THE L-2 NORM, WHERE EACH COMPONENT OF
C      THE ERROR IS DIVIDED BY THE COMPONENTS OF YMAX.
C
C      THE PROGRAM REQUIRES THREE SUBROUTINES NAMED
C      DIFFUN (T,Y,DY)
C      MATINV (PW,N,M,J)
C      PEDERV (T,Y,PW,M)
C
C      DIFFUN EVALUATES THE DERIVATIVES OF THE DEPENDENT VARIABLES
C      STORED IN Y(I,I) FOR I = 1 TO N AND STORES THE
C      DERIVATIVE IN THE ARRAY DY.
C      MATINV IS CALLED ONLY IF THE METHOD FLAG MF IS SET TO
C      1 OR 2 FOR STIFF METHODS. IT MUST INVERT THE
C      THE N BY N MATRIX STORED IN THE ARRAY PW(M,M).
C      IF THE INVERSION IS SUCCESSFUL, J SHOULD BE
C      SET TO 1, OTHERWISE IT SHOULD BE SET TO -1.
C      PEDERV IS USED ONLY IF MF IS 1, AND COMPUTES THE
C      PARTIAL DERIVATIVES OF THE EQUATIONS AS
C      DESCRIBED UNDER THE MF PARAMETER.
C
C      THE PROGRAM USES DOUBLE PRECISION ARITHMETIC FOR ALL
C      FLOATING POINT VARIABLES EXCEPT THOSE STARTING WITH P.
C      THESE ARE SINGLE PRECISION TO SAVE TIME AND SPACE.
C
C      TEMPORARY STORAGE SPACE IS PROVIDED BY THE CALLER IN THE
C      HOLD THE MATRIX OF THE SAME NAME, BUT SAVE IS USED TO
C      HOLD SEVERAL ARRAYS. THE REGIONS USED ARE
C
C      SAVE(J,I) 1 .LE. J .LE. 8 AND 1 .LE. 1 .LE. N IS USED TO
C      SAVE THE VALUES OF Y IN CASE A STEP HAS TO BE
C      REPEATED
C

```

C SAVE(9,1) IS USED MAINLY TO HOLD THE CORRECTION TERMS IN
 C THE CORRECTOR LCOP
 C SAVE(10,1) IS USED TO SAVE THE VALUES OF THE SUMS OF ALL
 C OF THE CORRECTION TERMS IN THE PREVIOUS STEP
 C AFTER THEY HAVE BEEN ACCUMULATED IN THE ARRAY
 C ERROR IN THE CURRENT STEP. THIS ENABLES THE
 C BACKWARDS DIFFERENCE OF ERROR TO BE FORMED.
 C IT IS USED TO ESTIMATE THE STEP SIZE FOR ONE
 C ORDER HIGHER THAN CURRENT.
 C SAVE(N1+1,1) IS USED TO STORE THE DERIVATIVES WHEN THEY ARE
 C COMPUTED BY DIFFUN. IT IS ALSO ACCESSED AS
 C SAVE(N2,1) AS A COMPLETE ARRAY
 C SAVE(NS+1,1) HOLDS THE DERIVATIVES DURING JACOBIAN
 C EVALUATIONS. IT IS REFERENCED AS SAVE(NS,1)
 C AS A COMPLETE ARRAY.
 C
 C INPUT AND OUTPUT PARAMETERS
 C
 C N THE NUMBER OF FIRST ORDER DIFFERENTIAL EQUATIONS
 C N MAY BE DECREASED ON LATER CALLS IF THE NUMBER
 C OF ACTIVE EQUATIONS REDUCES, BUT IT MUST NOT BE
 C INCREASED WITHOUT CALLING JSTART = 0
 C
 C M THE VALUE OF N ON THE FIRST CALL TO DIFSUB
 C
 C NPW THE VALUE N*N USED TO DIMENSION PW AS A VECTOR
 C
 C NSAVE THE VALUE N+INT(2.0*N/10.0+0.9) USED TO DIMENSION
 C THE WORKSPACE SAVE(10,NSAVE)
 C
 C T THE INDEPENDENT VARIABLE
 C
 C Y AN N X 8 ARRAY CONTAINING THE DEPENDENT VARIABLES
 C AND THEIR SCALED DERIVATIVES. Y(J+1,1) CONTAINS THE
 C JTH DERIVATIVE OF Y(1) SCALED BY H**J/FACTORIAL J,
 C WHERE H IS THE CURRENT STEP SIZE. ONLY Y(1,1) NEED
 C BE PROVIDED BY THE CALLING PROGRAM ON THE FIRST
 C ENTRY. IF IT IS DESIRED TO INTERPOLATE BETWEEN
 C MESH POINTS, THESE VALUES CAN BE USED. IF THE
 C CURRENT STEP SIZE IS H AND THE VALUE AT T+E IS
 C NEEDED, FORM S=E/H AND COMPUTE
 C $Y(1)(T+E) = \sum_{J=0}^{NQ} Y(J+1,1) * S^{J+1}$
 C
 C SAVE A BLOCK OF AT LEAST 12*N SCRATCH LOCATIONS USED BY
 C THE SUBROUTINES. DIMENSIONED AS A MATRIX WITH 10 ROWS
 C AND NSAVE COLUMNS
 C
 C H THE STEP SIZE TO BE ATTEMPTED ON THE NEXT STEP.

C H MAY BE ADJUSTED UP OR DOWN BY THE PROGRAM IN ORDER
C TO ACHIEVE AN ECONCMICAL INTEGRATION. HOWEVER, IF THE
C H PROVIDED BY THE USER DOES NOT CAUSE AN ERROR LARGER
C THAN REQUESTED, IT WILL BE USED. TO SAVE COMPUTER
C TIME, THE USER IS ADVISED TO USE A FAIRLY SMALL STEP
C FOR THE FIRST CALL. IT WILL BE AUTOMATICALLY
C INCREASED LATER.
C
C HMIN THE MINIMUM STEP SIZE THAT WILL BE USED FOR THE
C INTEGRATION. NOTE THAT ON STARTING THIS MUST BE MUCH
C SMALLER THAN THE AVERAGE H EXPECTED SINCE A FIRST
C ORDER METHOD IS USED INITIALLY.
C
C HMAX THE MAXIMUM SIZE TO WHICH THE STEP SIZE WILL BE
C INCREASED
C
C EPS THE ERROR TEST CONSTANT. SINGLE STEP ERROR ESTIMATES
C DIVIDED BY YMAX(I) MUST BE LESS THAN THIS IN
C THE EUCLIDEAN NORM. THE STEP AND/OR ORDER IS
C ADJUSTED TO ACHIEVE THIS.
C
C MF THE METHOD INDICATOR. THE FOLLOWING ARE AVAILABLE
C 0 AN ADAMS PREDICTOR-CORRECTOR IS USED.
C 1 A MULTISTEP METHOD SUITABLE FOR STIFF SYSTEMS
C IS USED. IT WILL ALSO WORK FOR NON-STIFF
C SYSTEMS. HOWEVER, THE USER MUST PROVIDE A
C SUBROUTINE PEDERV WHICH EVALUATES THE PARTIAL
C DERIVATIVES OF THE DIFFERENTIAL EQUATIONS
C WITH RESPECT TO THE Y'S. THIS IS DONE BY
C CALL PEDERV(I,Y,PW,M). PW IS AN N BY N ARRAY
C WHICH MUST BE SET TO THE PARTIAL OF THE I-TH
C EQUATION WITH RESPECT TO THE J DEPENDENT
C VARIABLE IN PW(I,J). PW IS ACTUALLY STORED
C IN AN M BY M ARRAY WHERE M IS THE
C N USED ON THE FIRST CALL TO THIS PROGRAM.
C
C 2 THE SAME AS CASE 1, EXCEPT THAT THIS
C SUBROUTINE COMPUTES THE PARTIAL DERIVATIVES
C BY NUMERICAL DIFFERENCING OF THE DERIVATIVES.
C HENCE, PEDERV IS NOT CALLED.
C
C YMAX AN ARRAY OF N LOCATIONS WHICH CONTAINS THE MAXIMUM
C OF EACH Y SEEN SO FAR, AUTOMATICALLY UPDATED AFTER
C EACH COMPLETED STEP (UNLESS THE USER OVERRIDES IT
C BY CHANGING YMAX BEFORE A SUBSEQUENT CALL).
C ALL OF THE COMPONENTS OF YMAX SHOULD BE INITIALIZED
C TO 1.0 BEFORE THE FIRST ENTRY. (CF. ALSO THE
C DESCRIPTION FOR EPS, GIVEN ABOVE.)

ERROR AN ARRAY OF N ELEMENTS WHICH CONTAIN THE ESTIMATED ONE STEP ERROR IN EACH COMPONENT.

KFLAG A COMPLETION CODE WITH THE FOLLOWING MEANING..

- +1 THE STEP WAS SUCCESSFUL. T IS ADVANCED TO (T+H) AND RESULTS OF THE INTEGRATION ARE RETURNED TO THE CALLING PROGRAM
- 1 THE STEP WAS TAKEN WITH $H = H_{MIN}$, BUT THE REQUESTED ERROR WAS NOT ACHIEVED. T IS ADVANCED TO (T+DT). CALLING PROGRAM MUST APPROVE FAILURE OF ACCURACY.
- 2 THE MAXIMUM ORDER SPECIFIED WAS FOUND TO BE TOO LARGE
- 3 CORRECTOR CONVERGENCE COULD NOT BE ACHIEVED FOR $H = H_{MIN}$. T IS NOT ADVANCED. CALLING PROGRAM MUST DECREASE H AND H_{MIN} AND TRY AGAIN.
- 4 THE REQUESTED ERROR IS SMALLER THAN CAN BE HANDLED FOR THIS PROBLEM. T IS NOT ADVANCED. ETA MUST BE INCREASED.

JSTART INPUT INDICATOR WITH THE FOLLOWING MEANINGS..

- 1 REPEAT LAST STEP WITH A NEW H
- 0 PERFORM THE FIRST STEP. THE FIRST STEP MUST BE DONE WITH THIS VALUE OF JSTART SO THAT THE SUBROUTINE CAN INITIALIZE ITSELF.
- +1 TAKE A NEW STEP CONTINUING FROM THE LAST.

JSTART IS SET TO NO, THE CURRENT ORDER OF THE METHOD AT EXIT. NO IS ALSO THE ORDER OF THE MAXIMUM DERIVATIVE AVAILABLE.

MAXDER THE MAXIMUM DERIVATIVE THAT SHOULD BE USED IN THE METHOD. SINCE THE ORDER IS EQUAL TO THE HIGHEST DERIVATIVE USED, THIS RESTRICTS THE ORDER. IT MUST BE LESS THAN 8 FOR ADAMS AND 7 FOR THE STIFF METHODS.

PN A BLOCK OF AT LEAST $N*2$ SCRATCH LOCATIONS. DIMENSIONED AS A VECTOR.

C ADDED COMMENTS S.F. FULGHUM 4-APR-80

C RECENT REPORTS SUGGEST THAT THE SIXTH ORDER EQUATIONS
C HAVE A RELATIVELY POOR STABILITY REGION AND MAY NOT ALLOW
C THE ORDER TO BE LOWERED PROPERLY. THUS MAXDER MIGHT BE
C SET TO 5 TO AVOID THIS PROBLEM. SEE L.F. SHAMPINE
C STABILITY PROPERTIES OF ADAMS CODES ACM TRANS. ON MATH.
C SOFTWARE VOL.4, NO.4, DEC 1978, PP 323-329
C REDUCING THE ORDER MAY REDUCE EFFICIENCY, PARTICULARLY
C WITH TIGHT ERROR TOLERANCES.
C IMPROVED VERSIONS OF THIS PROGRAM HAVE BEEN WRITTEN
C WHICH ARE SOMEWHAT FASTER. SEE ABOVE

C NOTE THE FOLLOWING METHODS OF VARIABLE STORAGE
C IN THE SUBROUTINE DIFSUB WHICH MUST BE OBSERVED IN
C BOTH THE MAIN PROGRAM AND THE SUBROUTINES CALLED BY DIFSUB.

- C 1. THE CURRENT VALUES OF THE DEPENDENT VARIABLES
C ARE STORED AS PART OF A DOUBLE PRECISION ARRAY
C Y(8,N). IN PARTICULAR THEY ARE IN THE COLUMN Y(1,I)
C WHERE I VARIES FROM 1 TO N AND N IS THE TOTAL
C NUMBER OF DEPENDENT VARIABLES.
- C 2. THE SINGLE PRECISION ARRAY PW IS EXPLICITLY VECTORED
C IN DIFSUB FOR FASTER EXECUTION AND IS STORED AS A
C VECTOR WITH DIMENSION PW(N*2). IT CAN BE TREATED AS
C AN ARRAY IN MATINV AND PEDERV AND DIMENSIONED THERE AS
C PW(N,N) SINCE ONLY THE ADDRESS OF THE FIRST ARRAY
C ELEMENT IS PASSED IN THE SUBROUTINE CALL. THUS THE
C VECTOR AND ARRAY ARE AUTOMATICALLY EQUIVALENT.
- C 3. THE DERIVATIVES DY(I) IN DIFFUN ARE FIRST READ INTO
C SCRATCH LOCATIONS BY DIFSUB AND LATER TRANSFERRED TO
C Y(2,I) AFTER SOME MODIFICATIONS. THUS DY IS PROPERLY
C DIMENSIONED AS DY(N) IN DIFFUN.

C IMPLICIT REAL*8 (A-H,Q-Z)
C REAL*8 Y(8,N),YMAX(N),SAVE(10,NSAVE),ERROR(N),A(8)
C REAL*4 PERTST(7,2,3),PW(NPW)

C THE COEFFICIENTS IN PERTST ARE USED IN SELECTING THE STEP
C AND ORDER. THEREFORE, ONLY ABOUT ONE PERCENT ACCURACY
C IS NEEDED

C DATA PERTST /2.0, 4.5, 7.333, 10.42, 13.7, 17.15, 1.0,
1 2.0, 12.0, 24.0, 37.89, 53.33, 70.08, 87.97,
2 3.0, 6.0, 9.167, 12.5, 15.98, 1.0, 1.0,
3 12.0, 24.0, 37.89, 53.33, 70.08, 87.97, 1.0,
4 1.0, 1.0, 0.5, 0.1667, 0.04133, 0.008267, 1.0,

-101-

0002
0003
0004

0005

```

      5      1.0, 1.0, 2.0, 1.0, 0.3157, 0.07407, 0.0139 /
C
0006      DATA A(2) / -1.0D+00 /
0007      IRET = 1
0008      KFLAG = 1
0009      IF (JSTART .LE. 0) GO TO 140
C
C      BEGIN BY SAVING INFORMATION FOR POSSIBLE RESTARTS
C      AND CHANGING H BY THE FACTOR 2 IF THE CALLER HAS CHANGED H.
C      ALL VARIABLES DEPENDENT ON H MUST ALSO BE CHANGED.
C      E IS A COMPARISON FOR ERRORS OF THE CURRENT ORDER, NQ.
C      EUP IS TO TEST FOR INCREASING THE ORDER
C      EDWN FOR DECREASING THE ORDER. HNEW IS THE STEP
C      SIZE THAT WAS USED ON THE LAST CALL.
C
0010      100 DC 110 I = 1, N
0011          DO 110 J = 1, K
0012              SAVE(J, I) = Y(J, I)
0013      110 CONTINUE
C
0014      HCLD = HNEW
0015      IF (H .EQ. FOLD) GO TO 130
0016      120 RACUM = H/HCLD
0017      IRET1 = 1
0018      GO TO 750
C
0019      130 NGOLD = NQ
0020      TOLD = T
0021      RACUM = 1.0
0022      IF (JSTART .GT. 0) GO TO 250
0023      GO TO 170
C
0024      140 IF (JSTART .EQ. -1) GO TO 160
C
C      ON THE FIRST CALL, THE ORDER IS SET TO 1 AND THE INITIAL
C      DERIVATIVES ARE CALCULATED.
C
0025      N1 = 1
0026      N3 = N
0027      N1 = N*10
0028      N2 = N1 + 1
0029      N4 = N*2
0030      N5 = N1 + N
0031      N5 = N5 + 1
C
C      -----
0032      CALL DIFFUN (T, Y, SAVE(N2, 1))
C      -----

```

0033
0034C DO 150 I = 1,N
150 Y(2,I) = SAVE(N1+I,1) * H0035
0036
0037C HNEW = H
K = 2
GO TO 100

C REPEAT LAST STEP BY RESTORING SAVED INFORMATION

0038
0039
0040
0041
0042C 160 IF (NQ.EQ. NQOLD) JSTART = 1
J = TOLD
NQ = NQOLD
K = NQ+1
GO TO 120C SET COEFFICIENTS THAT DETERMINE THE ORDER AND METHOD TYPE.
CHECK FOR EXCESSIVE ORDER. THE LAST TWO STATEMENTS OF THIS
SECTION SET IWEVAL 0 IF PW IS TO BE REEVALUATED BECAUSE OF
THE ORDER CHANGE, THEN REPEAT THE INTEGRATION STEP IF IT
HAS NOT YET BEEN DONE (IRET=1) OR SKIP TO A FINAL SCALING
BEFORE EXIT IF IT HAS BEEN COMPLETED (IRET=2).0043
0044
0045C 170 IF (MF.EQ. 0) GO TO 180
IF (NQ.GT. 6) GO TO 190
GO TO (221,222,223,224,225,226), NQ0046
0047
0048
0049C 180 IF (NQ.GT. 7) GO TO 190
GO TO (211,212,213,214,215,216,217), NQ
190 KFLAG = -2
RETURNC THE FOLLOWING COEFFICIENTS SHOULD BE DEFINED TO THE MAXIMUM
ACCURACY PERMITTED BY THE MACHINE. THEY ARE, IN THE ORDER
USED...C -1
C -1/2,-1/2
C -5/12,-3/4,-1/6
C -3/8,-11/12,-1/3,-1/24
C -251/720,-25/24,-35/72,-5/48,-1/120
C -95/288,-137/120,-5/8,-17/96,-1/40,-1/720
C -19087/60480,-49/40,-203/270,-49/192,-7/144,-7/1440,-1/5040C -1
C -2/3,-1/3
C -6/11,-6/11,-1/11

C -12/25,-7/10,-1/5,-1/50
C -120/274,-255/274,-85/274,-15/274,-1/274
C -180/441,-58/63,-15/36,-25/252,-3/252,-1/1764
C

0050
0051

211 A(1) = -1.0
GO TO 230

0052
0053
0054

C 212 A(1) = -0.5
A(3) = -0.5
GO TO 230

0055
0056
0057
0058

C 213 A(1) = -0.4166666666666667
A(3) = -0.75
A(4) = -0.1666666666666667
GO TO 230

0059
0060
0061
0062
0063

C 214 A(1) = -0.375
A(3) = -0.9166666666666667
A(4) = -0.3333333333333333
A(5) = -0.4166666666666667E-01
GO TO 230

0064
0065
0066
0067
0068
0069

C 215 A(1) = -0.3486111111111111
A(3) = -1.0416666666666667
A(4) = -0.4861111111111111
A(5) = -0.1041666666666667
A(6) = -0.8333333333333333E-02
GO TO 230

0070
0071
0072
0073
0074
0075
0076

C 216 A(1) = -0.3298611111111111
A(3) = -1.1416666666666667
A(4) = -0.625
A(5) = -0.1770833333333333
A(6) = -0.025
A(7) = -0.1338888888888889E-02
GO TO 230

0077
0078
0079
0080
0081
0082
0083
0084

C 217 A(1) = -0.3155919312169312
A(3) = -1.225
A(4) = -0.7518518518518519
A(5) = -0.2552083333333333
A(6) = -0.0436111111111111
A(7) = -0.0048611111111111
A(8) = -0.0001984126584126984
GO TO 230

0085
0086

C 221 A(1) = -1.0
GO TO 230

```

0087      C
0088      222 A(1) = -0.6666666666666667
0089      A(3) = -0.3333333333333333
          GO TO 230

0090      C
0091      223 A(1) = -C.5454545454545454
0092      A(3) = -C.5454545454545454
0093      A(4) = -C.0909090909090909
          GO TO 230

0094      C
0095      224 A(1) = -C.48
0096      A(3) = -C.70
0097      A(4) = -C.20
0098      A(5) = -C.02
          GO TO 230

0099      C
0100      225 A(1) = -C.437956204379562
0101      A(3) = -C.8211678832116788
0102      A(4) = -C.3102189781021898
0103      A(5) = -C.05474452554744526
0104      A(6) = -C.0036496350364963504
          GO TO 230

0105      C
0106      226 A(1) = -C.4081632653061225
0107      A(3) = -C.9206349206349206
0108      A(4) = -C.4186666666666667
0109      A(5) = -C.0992063492063492
0110      A(6) = -C.0119047619047619
0111      A(7) = -C.000566893424036282

0111      C
0112      230 K = NQ + 1
0113      IDOUB = K
          MTYP = (4-MF)/2

          C
          C MTYP = 1 FOR STIFF (MF = 1 OR 2)
          C MTYP = 2 FOR ADAMS-MOULTON (MF = 0)
          C

0114      ENQ2 = 0.500/DBLE( FLOAT(NQ+1) )
0115      ENQ3 = 0.500/DBLE( FLOAT(NQ+2) )
0116      ENQ1 = 0.500/DBLE( FLOAT(NQ) )
0117      PEP SH = EPS
0118      EUP = (PERTST(NQ,MTYP,2) * PEP SH)**2
0119      E = (PERTST(NQ,MTYP,1) * PEP SH)**2
0120      EDWN = (PERTST(NQ,MTYP,3) * PEP SH)**2
0121      IF (EDWN.EQ. 0.0) GO TO 780
0122      BND = EPS * ENQ3 / DBLE(FLCAT(N))
0123      240 IWEVAL = MF
0124      GO TO (250,680), IRET

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C      THIS SECTION COMPUTES THE PREDICTED VALUES BY EFFECTIVELY
C      MULTIPLYING THE SAVED INFORMATION BY THE PASCAL
C      TRIANGLE MATRIX
C
0125      250 T = T+H
0126          DO 260 J = 2,K
0127              DO 260 J1 = J,K
0128                  J2 = K-J1+J-1
0129                  DO 260 I = 1,M
0130                      Y(J2,I) = Y(J2,I) + Y(J2+1,I)
0131      260 CONTINUE
C
C      UP TO 3 CORRECTOR ITERATIONS ARE TAKEN. CONVERGENCE IS
C      TESTED BY REQUIRING CHANGES TO BE LESS THAN BND WHICH
C      IS DEPENDENT ON THE ERROR TEST CONSTANT. THE SUM OF THE
C      CORRECTIONS IS ACCUMULATED IN THE ARRAY ERROR(I). IT IS
C      EQUAL TO THE KTH DERIVATIVE OF Y MULTIPLIED BY
C      H**K/(FACTORIAL(K-1)*A(K)), AND IS THEREFORE PROPORTIONAL
C      TO THE ACTUAL ERRORS TO THE LOWEST POWER OF H PRESENT.
C      (H**K)
C
0132          DO 270 I = 1,N
0133      270 ERROR(I) = 0.0
C
C      ***** BEGIN LONG DO LOOP FOR CORRECTOR ITERATIONS *****
C
0134          DO 430 L = 1,3
C
C      -----
0135          CALL DIFFUN (T,Y,SAVE(N2,1))
C      -----
C
C      IF THERE HAS BEEN A CHANGE OF ORDER OR THERE HAS BEEN
C      TROUBLE WITH CONVERGENCE, PW IS RE-EVALUATED PRIOR TO
C      STARTING THE CORRECTOR ITERATION IN THE CASE OF THE
C      STIFF METHODS. INEVAL IS THEN SET TO -1 AS AN
C      INDICATOR THAT IT HAS BEEN DONE
C
0136          IF (INEVAL .LT. 1) GO TO 350
0137          IF (MF .EQ. 2) GO TO 310
C
C      -----
0138          CALL PEDERV (T,Y,PW,N3)
C      -----
C
0139          R = A(1) * H

```

```

0140      DO 280 I = 1,N4
0141      PW(I) = PW(I) * R
0142      280 CONTINUE

C      ADD THE IDENTITY MATRIX TO THE JACOBIAN AND INVERT
C      TO GET PW
C
0143      DO 290 I = 1,N
0144      PW(I*(N3+1)-N3) = 1.0 + PW(I*(N3+1)-N3)
0145      290 CONTINUE
0146      IWEVAL = -1

C      -----
C      CALL MATINV (PW,N,NPW,J1)
C      -----

0148      IF (J1 .GT. 0) GO TO 350
0149      GO TO 440

C      EVALUATE THE JACOBIAN BY NUMERICAL DIFFERENCING.
C      R IS THE CHANGE MADE TO THE ELEMENT OF Y. IT IS EPS
C      RELATIVE TO Y WITH A MINIMUM OF EPS**2.
C
0150      DO 310 I = 1,N
0151      SAVE(9,I) = Y(1,I)
0152      310 CONTINUE
0153      DO 340 J = 1,N
0154      R = EPS*DMAX1(EPS,DABS(SAVE(9,J)))
0155      Y(1,J) = Y(1,J) + R
0156      D = A(1) * H / R

C      -----
C      CALL DIFFUN (T,Y,SAVE(N6,1))
C      -----

0158      DO 330 I = 1,N
0159      PW(I+(J-1)*N3) = (SAVE(N5+I,1) - SAVE(N1+I,1))*C
0160      330 CONTINUE
0161      Y(1,J) = SAVE(9,J)
0162      340 CONTINUE
0163      GO TO 290

C
0164      350 IF (MF .NE. 0) GO TO 370
0165      DO 360 I = 1,N
0166      SAVE(9,I) = Y(2,I) - SAVE(N1+I,1)*H
0167      360 CONTINUE
0168      GO TO 410

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0169      370 CONTINUE
0170          DO 380 I = 1,N
0171              SAVE(N5+I,1) = Y(2,I) - SAVE(N1+1,1)*H
0172      380 CONTINUE
0173          DO 400 I = 1,N
0174              D = 0.000
0175              DO 390 J = 1,N
0176                  D = D + PW(I+(J-1)*N3)*SAVE(N5+J,1)
0177      390 CONTINUE
0178              SAVE(9,I) = D
0179      400 CONTINUE
0180      410 NT = N

C
C      CORRECT AND SEE IF ALL OF THE CHANGES ARE LESS THAN BND
C      RELATIVE TO YMAX. IF SG, THE CORRECTOR IS SAID TO HAVE
C      CONVERGED
C
0181          DO 420 I = 1,N
0182              Y(1,I) = Y(1,I) + A(1)*SAVE(9,I)
0183              Y(2,I) = Y(2,I) - SAVE(9,I)
0184              ERROR(I) = ERROR(I) + SAVE(9,I)
0185              IF (DABS(SAVE(9,I)) .LE. (BND*YMAX(I))) NT = NT-1
0186      420 CONTINUE
C
0187          IF (NT .LE. 0) GO TO 490
C
C      ***** END OF LONG DO LOOP FOR CORRECTOR ITERATION *****
C
0188      430 CONTINUE
C
C      CONTROL PASSES TO THIS SECTION IF THE CORRECTOR ITERATION
C      FAILS TO CONVERGE IN THREE TRIES. VARIOUS POSSIBILITIES
C      ARE CHECKED FOR. IF H IS ALREADY HMIN AND THIS IS EITHER
C      ADAMS-MOULTON OR THE STIFF METHOD IN WHICH THE MATRIX PW
C      HAS ALREADY BEEN REEVALUATED, A NO-CONVERGENCE EXIT IS
C      TAKEN. OTHERWISE, THE MATRIX PW IS REEVALUATED AND/OR THE
C      STEP IS REDUCED TO TRY AND GET CONVERGENCE.
C
0189      440 I = TOLD
0190          IF ((H.LE.(HMIN*1.00001)).AND.((IWEVAL-MTYP).LT.-1))
C
C              1 GO TO 460
C              IF ((MF.EQ.0).OR.(IWEVAL.NE.0)) RACUM = RACUM*0.2500
C              IWEVAL = MF
C              IRETI = 2
C              GO TO 750
C
0191      460 KFLAG = -3
0192      470 DO 430 I = 1,N

```

0197
0198
0199

DO 480 J = 1,K
Y(J,I) = SAVE(J,I)
48C CONTINUE

0200
0201
0202
0203

H = HOLD
NQ = NQJLO
JSTART = NQ
RETURN

C

C
C
C CONTROL IS PASSED TO THE FOLLOWING SECTION IF THE CORRECTOR
C CONVERGED. IF THE ERROR TEST IS OK CONTROL PASSES TO 520
C (OR TO 540 OTHERWISE). IF THE STEP IS OK IT IS ACCEPTED.
C IF IDOUB HAS BEEN REDUCED TO ONE, A TEST IS MADE TO SEE IF
C THE STEP CAN BE INCREASED AT THE CURRENT ORDER OR BY GOING
C TO ONE HIGHER OR ONE LOWER. SUCH A CHANGE IS ONLY MADE IF
C THE STEP CAN BE INCREASED BY AT LEAST 1.1. IF NO CHANGE IS
C POSSIBLE, IDOUB IS SET TO 10 TO PREVENT FURTHER TESTING FOR
C 10 STEPS. IF A CHANGE IS POSSIBLE, IT IS MADE, AND IDOUB IS
C SET TO NQ+1 TO PREVENT FURTHER TESTING FOR THAT NUMBER OF
C STEPS. IF THE ERROR WAS TOO LARGE, THE OPTIMUM STEP SIZE
C FOR THIS OR LOWER ORDER IS COMPUTED, AND THE STEP RETRIED.
C IF IT SHOULD FAIL TWICE MORE IT IS AN INDICATION THAT THE
C DERIVATIVES THAT HAVE ACCUMULATED IN THE Y ARRAY HAVE ERRORS
C OF THE WRONG ORDER SO THE FIRST DERIVATIVES ARE RECOMPUTED
C AND THE ORDER IS SET TO 1.

0204

49C D = 0.0C0

0205
0206

DO 500 I = 1,N
500 D = D + (ERROR(I)/YMAX(I))**2

0207
0208
0209

IWEVAL = 0.
IF (D .GT. E) GO TO 540
IF (K .LT. 3) GO TO 520

C

C
C COMPLETE THE CORRECTION OF THE HIGHER ORDER DERIVATIVES AFTER
C A SUCCESSFUL STEP

0210
0211
0212
0213

DO 510 J = 3,K
DO 510 I = 1,N
Y(J,I) = Y(J,I) + A(J) * ERROR(I)
510 CONTINUE

C

0214
0215
0216
0217

520 KFLAG = 1
HNEW = H
IF (IDOUB .LE. 1) GO TO 550
IDOUB = IDOUB - 1

-110-

```

0218      IF (IDCUB .GT. 1) GO TO 700
C
0219      DO 530 I = 1,N
0220          SAVE(10,I) = ERROR(I)
0221      530 CONTINUE
C
0222      GO TO 700
C
C      REDUCE FAILURE FLAG COUNT TO CHECK FOR MULTIPLE FAILURES.
C      RESTORE T TO ITS ORIGINAL VALUE AND TRY AGAIN UNLESS THERE
C      HAVE BEEN THREE FAILURES. IN THAT CASE, DERIVATIVES ARE
C      ASSUMED TO HAVE ACCUMULATED ERRORS SO A RESTART FROM THE
C      CURRENT VALUE OF Y IS TRIED.
C
0223      540 KFLAG = KFLAG - 2
0224          IF (H .LE. (HMIN*1.00001)) GO TO 740
0225          T = TOLD
0226          IF (KFLAG .LE. -5) GO TO 720
C
C      PR1, PR2, AND PR3 WILL CONTAIN THE AMOUNTS BY WHICH THE
C      STEP SIZE SHOULD BE DIVIDED AT ORDER ONE LOWER, AT THIS
C      ORDER, AND AT ORDER ONE HIGHER, RESPECTIVELY.
C
0227      550 PR2 = (D/E)**ENQ2 * 1.2
0228          PR3 = 1.0E+20
0229          IF ((NQ .GE. MAXDER) .OR. (KFLAG .LE. -1)) GO TO 570
C
0230          D = 0.000
0231          DO 560 I = 1,N
0232              D = D + (ERROR(I) - SAVE(10,I))/YMAX(I)**2
0233      560 CONTINUE
0234          PR3 = (D/EUP)**ENQ3 * 1.4
C
0235      570 PR1 = 1.0E+20
0236          IF (NQ .LE. 1) GO TO 590
C
0237          D = 0.000
0238          DO 580 I = 1,N
0239              D = D + (Y(K,I)/YMAX(I))**2
0240      580 CONTINUE
0241          PR1 = (D/EDWN)**ENQ1 * 1.3
C
0242      590 CONTINUE
C
0243          IF (PR2 .LE. PR3) GO TO 650
0244          IF (PR3 .LT. PR1) GO TO 660
C
C      DECREASE ORDER

```

```

0245      C 600 R = 1.0/AMAX1(PR1,1.0E-04)
0246      NEWQ = NQ - 1
      C
      C DO NOT CHANGE ORDER AGAIN FOR TEN STEPS.
      C
0247      610 IDOUB = 10
0248      IF ((KFLAG.EQ. 1) .AND. (R .LT. (1.1))) GO TO 700
0249      IF (NEWQ .LE. NQ) GO TO 630
      C
      C COMPUTE ONE ADDITIONAL SCALED DERIVATIVE IF ORDER INCREASED
      C
0250      DO 620 I = 1,N
0251      Y(NEWQ+1,I) = ERROR(I) * A(K) / DBLE(FLOAT(K))
0252      620 CONTINUE
      C
0253      630 K = NEWQ + 1
0254      IF (KFLAG.EQ. 1) GO TO 670
0255      RACUM = RACUM * R
0256      IRET1 = 3
0257      GO TO 750
      C
0258      640 IF (NEWQ .EQ. NQ) GO TO 250
0259      NQ = NEWQ
0260      GU TO 170
      C
0261      650 IF (PR2 .GT. PR1) GO TO 600
      C
      C STAY AT SAME ORDER
      C
0262      NEWQ = NQ
0263      R = 1.0/AMAX1(PR2,1.0E-04)
0264      GU TO 610
      C
      C INCREASE ORDER
      C
0265      660 R = 1.0/AMAX1(PR3,1.0E-04)
0266      NEWQ = NQ + 1
0267      GO TO 610
      C
0268      670 IRET = 2
0269      H = H * R
0270      HNEW = H
0271      IF (NQ .EQ. NEWQ) GO TO 680
0272      NQ = NEWQ
0273      GO TO 170
      C
0274      680 R1 = 1.000

```

```

0275      DO 690 J = 2,K
0276          R1 = R1 * R
0277      DO 690 I = 1,N
0278          Y(J,I) = Y(J,I) * R1
0279      690 CONTINUE
C
0280      IDOUB = K
0281      700 DO 710 I = 1,N
0282          YMAX(I) = DMAX1(YMAX(I),DABS(Y(1,I)))
0283      710 CONTINUE
0284      JSTART = NQ
0285      RETURN
C
C
0286      720 IF (NQ .EQ. 1) GO TO 780
C
C
0287      CALL DIFFUN (T,Y,SAVE(N2,1))
C
C
0288      R = H / HOLD
0289      DO 730 I = 1,N
0290          Y(1,I) = SAVE(1,I)
0291          SAVE(2,I) = HOLD*SAVE(N1+1,I)
0292          Y(2,I) = SAVE(2,I) * R
0293      730 CONTINUE
C
0294      NQ = 1
0295      KFLAG = 1
0296      GO TO 170
C
0297      740 KFLAG = -1
0298      HNEW = H
0299      JSTART = NQ
0300      RETURN
C
C      THIS SECTION SCALES ALL VARIABLE CONNECTED WITH H AND
C      RETURNS TO THE ENTERING SECTION
C
0301      750 RACUM = DMAX1(DABS(HMIN/HOLD),RACUM)
0302          RACUM = DMIN1(RACUM,DABS(HMAX/HOLD))
0303          R1 = 1.000
0304      DO 760 J = 2,K
0305          R1 = R1 * RACUM
0306      DO 760 I = 1,N
0307          Y(J,I) = SAVE(J,I) * R1
0308      760 CONTINUE
0309      H = HOLD * RACUM

```

```

0310      DO 770 I = 1,N
0311          Y(1,I) = SAVE(1,I)
0312      770 CONTINUE
0313          IDOUB = K
0314      GO TO (130,250,640), IRET1
      C
0315      780 KFLAG = -4
0316      GO TO 470
      C
0317      END
    
```

SOX KINETICS SIMULATION

SOX1 VERSION 6.3 3 APR 82 S.F.FULGHUM

COMMENTS

INTEGRATION CONTROL PARAMETERS

0.0
6.0000+01
1.0000-02
24
1
1000
1.0000-05
5
2
1.0000-13
1.0000-20
5.0000+00
0
42
82
2
3.980E+02
0.220E-01 0.700E-02 0.150E-01 0.100E-01

INITIAL VALUES OF VARIABLES

2.4490+19
0.0
0.0
0.0
0.0
0.0
1.2300+16
0.0
0.0

0.0	*	FK(1)
0.0	*	2
0.0	*	3
0.0	*	4
0.0	*	5
7.2000-32	*	6
0.0	*	7
0.0	*	8
1.9000-11	*	9
4.7000-14	*	10
3.4000-11	*	11
0.0	*	12
0.0	*	13
0.0	*	14
0.0	*	15
0.0	*	16
0.0	*	17
0.0	*	18
0.0	*	19
1.4000-12	*	20
3.2000-33	*	21
0.0	*	22
9.3000-33	*	23

```

FK(1)      SO2 + GH - (M) HS03
2          SO2 + G - M SO3
3          SO2 + H02 - SO3 + OH
4          SO2 + NO2 - SO3 + NO
5          NO + H02 - NO2 + GH
6          NO + G - M NO2
7          NO + OH - (M) HNC2
8          NO + H - M HNC
9          NO + NO3 - 2NO2
10         NO + O3 - NO2 + O2
11         NO + N - N2 + G
12         H + O2 - M HO2
13         H + GH - M H2G
14         H + H - M H2
15         H + NO2 - OH + NO
16         SO2 + GH + H2O - HS03.H2O
17         H + H02 - 2OH
18         H + O3 - OH + O2
19         H + HNC - H2 + NO
20         N + NO2 - N2O + O
21         N + N - M N2
22         N + GH - NO + H
23         N + G - M NO

```


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5.3000-16	*	24
5.0000-16	*	25
4.4000-34	*	26
0.0	*	27
3.9000-14	*	28
5.1000-32	*	29
0.0	*	30
0.0	*	31
0.0	*	32
0.0	*	33
0.0	*	34
0.0	*	35
0.0	*	36
0.0	*	37
0.0	*	38
0.0	*	39
1.6900-16	*	40
0.0	*	41
9.3000-12	*	42
1.0000-11	*	43
0.0	*	44
0.0	*	45
0.0	*	46
0.0	*	47
0.0	*	48
0.0	*	49
1.2300-09	*	50
4.4100-10	*	51
1.4000-10	*	52
3.3000-10	*	53
8.0000-10	*	54
3.3000-10	*	55
1.2300-10	*	56
4.9000-12	*	57
2.0000-07	*	58
7.0000-07	*	59
2.0000-06	*	60
4.0000-07	*	61
1.7000-06	*	62
1.5000-06	*	63
4.0000-11	*	64
3.7000-12	*	65
7.3500-13	*	66
5.0000-10	*	67
1.2000-09	*	68
5.0000-10	*	69
1.0000-10	*	70
1.0000-10	*	71
2.5000-10	*	72
1.5000-11	*	73
4.9000-06	*	74
1.0000-07	*	75
1.0000-07	*	76
4.9000-06	*	77
1.0000-07	*	78
4.9000-06	*	79
1.8000-14	*	80
6.5000-12	*	81
9.3000-11	*	82
0.0		

N	+	O2	-	NO	+	O	
N	+	O3	-	NO	+	O3	
O	+	O2	-	M	O3		
O	+	HO2	-	OH	+	O2	
O	+	O3	-	2O2			
O	+	NO2	-	M	NO3		
OH	+	CO	-	CO2	+	H	
OH	+	OH	-	O	+	H2O	
OH	+	NO2	-	M	HNO3		
OH	+	HNO3	-	NO3	+	H2O	
OH	+	HO2	-	H2O	+	C2	
OH	+	HNO2	-	NO2	+	H2O	
OH	+	O3	-	HO2	+	O2	
OH	+	N2O	-	PRODUCTS	HNO	+	NO
HO2	+	NO2	-	M	HO2NC2		
HO2	+	O3	-	OH	+	2C2	
NO2	+	O3	-	NO3	+	C2	
SO3	+	H2O	-	(M)	PRODUCTS	(ASSUME H2SO4 CALVER	
O	+	NO2	-	NO	+	C2	
O	+	NO3	-	O2	+	NC2	
O	+	OH	-	H	+	O2	
OH	+	CH	-	(M)	H2O2		
OH	+	H2O2	-	H2O	+	HO2	
H	+	HO2	-	H2	+	C2	
H2NO2	-	(M)	HO2	+	NO2		
OH	+	HNO	-	H2O	+	NO	