Development of a Chemically Reactive Plume Model for Application in the AOSERP Study Area
Development of a Chemically Reactive Plume Model for Application in the AOSERP Study Area

Project AS 3.5.4

April 1981
These research reports describe the results of investigations funded under the Alberta Oil Sands Environmental Research Program. This program was designed to direct and co-ordinate research projects concerned with the environmental effects of development of the Athabasca Oil Sands in Alberta.

A list of research reports published to date is included at the end of this report.

Enquiries pertaining to the reports in the series should be directed to:

Research Management Division
15th Floor, Oxbridge Place
9820 - 106 Street
Edmonton, Alberta
T5K 2J6
(403) 427-3943

Development of a Chemically Reactive Plume Model
for Application in the AOSERP Study Area

Project AS 3.5.4
AOSERP Report 117

This report may be cited as:

The Hon. J.W. (Jack) Cookson  
Minister of the Environment  
222 Legislative Building  
Edmonton, Alberta  

Sir:  

Enclosed is the report "Development of a Chemically Reactive Plume Model for Application in the AOSERP Study Area."

This report was prepared for the Alberta Oil Sands Environmental Research Program, through its Air System, under the Canada-Alberta Agreement of February 1975 (amended September 1977).

Respectfully,

W. Solodzuk, P. Eng.  
Chairman, Steering Committee, AOSERP  
Deputy Minister, Alberta Environment
This report is made available as a public service. The Department of Environment neither approves nor disagrees with the conclusions expressed herein, which are the responsibility of the authors.
DEVELOPMENT OF A CHEMICALLY REACTIVE PLUME MODEL
FOR APPLICATION IN THE AOSERP STUDY AREA

by

J.W. BOTTENHEIM
O.P. STRAUSZ

Department of Chemistry
University of Alberta

for

ALBERTA OIL SANDS
ENVIRONMENTAL RESEARCH PROGRAM

Project AS 3.5.4

April 1981
# TABLE OF CONTENTS

DECLARATION ......................................................... ii
LETTER OF TRANSMITTAL ........................................ iii
LIST OF TABLES ...................................................... ix
LIST OF FIGURES .................................................... x
ABSTRACT .................................................................. xii
ACKNOWLEDGEMENTS .................................................. xiv

1. INTRODUCTION .................................................. 1

2. THE CHEMICAL MODEL ........................................... 3
   2.1 Overview ......................................................... 3
   2.2 The Photostationary State and Reactions of \( \text{O}^{(3p)} \) Atoms ......................................................... 8
   2.3 The Free Radical Oxidation of NO ................................ 8
   2.4 The Hydrocarbon Chemistry ...................................... 8
   2.5 Radical Termination Reactions ................................... 11
   2.6 The Homogeneous Oxidation of \( \text{SO}_2 \) ......................... 12
   2.6.1 Product Channel of Reaction 23 .............................. 12
   2.6.2 Other Homogeneous Oxidation Reactions of \( \text{SO}_2 \) ....... 13

3. SIMULATION OF SMOG CHAMBER DATA ....................... 15
   3.1 Smog Chamber Peculiarities .................................... 15
   3.2 Simulation of \( \text{NO}_x \)-Hydrocarbon Smog Chamber Data .... 21
   3.2.1 Statewide Air Pollution Research Centre Data .......... 21
   3.2.2 Environmental Protection Agency Data ................... 22
   3.2.3 Dodge and Bufalini Data on \( \text{NO}_x \)-1-butene Mixtures .. 22
   3.3 Simulation of \( \text{NO}_x \)-Hydrocarbon-SO \( _2 \) Smog Chamber Data ................................................. 23
   3.3.1 Grobicki and Nebel's Experiments ........................ 23
   3.3.2 Wilson and Levy's Experiments ............................. 23
   3.3.3 Smith and Urone's Experiments ............................ 25
   3.3.4 Miller's Experiments ......................................... 27
   3.4 Conclusions ...................................................... 31

4. THE DISPERSION MODEL .......................................... 32

5. CALCULATIONS USING THE COMPLETE MODEL .............. 36
   5.1 'Standard' Plume Calculations ................................ 36
   5.2 Modelling of the GCOS Power Plant Plume, dd. 19 June 1977 ................................. 46
   5.3 Modelling of a Power Plant Plume from Milwaukee, Wisconsin, dd. 20 July 1977 ............ 53
   5.4 Conclusions ...................................................... 62
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6. SUMMARY AND RECOMMENDATIONS</td>
<td>64</td>
</tr>
<tr>
<td>6.1 Oxidation Mechanism of SO₂</td>
<td>64</td>
</tr>
<tr>
<td>6.2 Experimental Plume Data for HNO₃ and PAN</td>
<td>65</td>
</tr>
<tr>
<td>6.3 Experimental Plume Data for Hydrocarbons</td>
<td>65</td>
</tr>
<tr>
<td>6.4 Experimental Plume Data Immediately after Emission</td>
<td>65</td>
</tr>
<tr>
<td>6.5 Comparison with other Reactive Plume Models</td>
<td>66</td>
</tr>
<tr>
<td>6.6 Use of the Model for Pollution Control</td>
<td>66</td>
</tr>
<tr>
<td>7. REFERENCES CITED</td>
<td>68</td>
</tr>
<tr>
<td>8. APPENDICES</td>
<td>74</td>
</tr>
<tr>
<td>8.1 Determination of the Fate of RCHO</td>
<td>74</td>
</tr>
<tr>
<td>8.2 Figures of Smog Chamber Simulation Studies</td>
<td>77</td>
</tr>
<tr>
<td>8.3 Computer Code RPLM</td>
<td>107</td>
</tr>
<tr>
<td>8.3.1 Main</td>
<td>107</td>
</tr>
<tr>
<td>8.3.2 Subroutine INPUTS</td>
<td>107</td>
</tr>
<tr>
<td>8.3.3 Subroutine RMECH</td>
<td>107</td>
</tr>
<tr>
<td>8.3.4 Subroutine PRATE 1</td>
<td>108</td>
</tr>
<tr>
<td>8.3.5 Subroutine LOADA</td>
<td>108</td>
</tr>
<tr>
<td>8.3.6 Subroutine DIFFUN and DJAC</td>
<td>108</td>
</tr>
<tr>
<td>8.3.7 Subroutine REPORT</td>
<td>108</td>
</tr>
<tr>
<td>8.3.8 Listing of Code RPLM</td>
<td>109</td>
</tr>
<tr>
<td>8.3.9 Listing of Sample Input to Code RPLM</td>
<td>132</td>
</tr>
<tr>
<td>8.3.10 Output Generated by RPLM with Sample Input</td>
<td>136</td>
</tr>
<tr>
<td>9. LIST OF AOSERP RESEARCH REPORTS</td>
<td>143</td>
</tr>
</tbody>
</table>
**LIST OF TABLES**

1. The Chemical Mechanism ........................................ 5
2. Distribution of Products of Reactions 13 and 14 at Different Initial $\pi$-butane/propylene Ratios ................. 10
3. Photochemical Rate Constants Used for Smog Chamber Modelling .......................................................... 17
4. Overview of Studies Modelled and Initial Values that Were Used ................................................................. 18
5. Results of Modelling of Wilson-Levy Experiments .......... 24
6. Results of Modelling of Smith and Urone's Experiments ..... 26
7. Results of Modelling Miller's Experiments .................. 29
8. Input Data for Modelling GCOS Power Plant Plume, dd. 19 June 1977 ......................................................... 48
9. Input Data for Modelling a Power Plant Plume over Lake Michigan, dd. 20 July 1977 ........................... 54
10. Estimated Air Composition, Entrained by a Power Plant Plume over Lake Michigan, dd. 20 July 1977 ........... 55
11. Experimental and Estimated Maximum Levels of SO$_2$ and NO$_X$, and Derived Dispersion Parameters for a Power Plant Plume over Lake Michigan, dd. 20 July 1977 ............ 57
12. Calculated and Experimental Oxidation Rate of SO$_2$ and the O$_3$ Level at Plume Centre for a Power Plant Plume over Lake Michigan, dd. 20 July 1977 .......................... 58
13. Experimental and Calculated Data on Average Pollutant Levels in a Power Plant Plume over Lake Michigan, dd. 20 July 1977 .......................................................... 59
14. Calculated Data on Average Levels of NO$_X$ Species in a Power Plant Plume over Lake Michigan, dd. 20 July 1977 ... 60
15. Reactions Determining the Reactivity of RCHO .............. 75
16. Product Distribution for Reactions 13 and 14 ............... 76
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Division of Plume Cross-Section Downwind from the Stack</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>Calculated Oxidation Rate of $\text{SO}_2$ in Different Rings as Function of Plume Age for &quot;Standard&quot; Plume Conditions</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>Calculated Ozone Mixing Ratio in Different Rings as a Function of Plume Age for &quot;Standard&quot; Plume Conditions</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>Time Required to Reach an Average Oxidation Rate of $\text{SO}_2$ of 1% h$^{-1}$ as a Function of the Ratio Between the Assumed Initial Mixing Ratio of $\text{HNO}_2$ and Its Equilibrium Value from Reactions 37 and 38 of Table 1</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>Calculated Average Oxidation Rate of $\text{SO}_2$ as a Function of the Initial Mixing Ratio of $\text{HNO}_2$ for &quot;Standard&quot; Plume Conditions</td>
<td>43</td>
</tr>
<tr>
<td>6</td>
<td>Time Required to Reach an Average Oxidation Rate of $\text{SO}_2$ of 1% h$^{-1}$ as a Function of the $\text{HC}/\text{NO}_x$ Ratio in Ambient Air</td>
<td>44</td>
</tr>
<tr>
<td>7</td>
<td>Time Required to Reach an Average Oxidation Rate of $\text{SO}_2$ of 1% h$^{-1}$ as a Function of the $\text{NO}_x/\text{SO}_2$ Ratio in the Plume</td>
<td>45</td>
</tr>
<tr>
<td>8</td>
<td>Time Required to Reach an Average Oxidation Rate of $\text{SO}_2$ of 1% h$^{-1}$ as a Function of the Dispersion Parameter Product $\sigma_y\sigma_z$</td>
<td>47</td>
</tr>
<tr>
<td>9</td>
<td>Crosswind $\text{SO}_2$ and $\text{O}_3$ Profiles near the Stack and Downwind 19 June 1977, 1300 to 1515 h (LST), 1978</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>Comparison between Experimental and Computed Plume Profiles for $\text{O}_3$ on 19 June 1977 in the GCOS Plume</td>
<td>52</td>
</tr>
<tr>
<td>11</td>
<td>Simulation of Run EC-11</td>
<td>78</td>
</tr>
<tr>
<td>12</td>
<td>Simulation of Run EC-17</td>
<td>79</td>
</tr>
<tr>
<td>13</td>
<td>Simulation of Run EC-18</td>
<td>80</td>
</tr>
<tr>
<td>14</td>
<td>Simulation of Run EC-39</td>
<td>81</td>
</tr>
<tr>
<td>15</td>
<td>Simulation of Run EC-41</td>
<td>82</td>
</tr>
<tr>
<td>16</td>
<td>Simulation of Run EC-42</td>
<td>83</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>17.</td>
<td>Simulation of Run EC-178</td>
<td>85</td>
</tr>
<tr>
<td>18.</td>
<td>Simulation of Run EC-106</td>
<td>87</td>
</tr>
<tr>
<td>19.</td>
<td>Simulation of Run EC-115</td>
<td>89</td>
</tr>
<tr>
<td>20.</td>
<td>Simulation of Run EC-122</td>
<td>91</td>
</tr>
<tr>
<td>21.</td>
<td>Simulation of Run EPA-306</td>
<td>92</td>
</tr>
<tr>
<td>22.</td>
<td>Simulation of Run EPA-325</td>
<td>93</td>
</tr>
<tr>
<td>23.</td>
<td>Simulation of Run EPA-459</td>
<td>94</td>
</tr>
<tr>
<td>24.</td>
<td>Simulation of Run EPA-348</td>
<td>95</td>
</tr>
<tr>
<td>25.</td>
<td>Simulation of Run EPA-352</td>
<td>96</td>
</tr>
<tr>
<td>26.</td>
<td>Simulation of Run DB-2</td>
<td>97</td>
</tr>
<tr>
<td>27.</td>
<td>Simulation of Run DB-2000</td>
<td>98</td>
</tr>
<tr>
<td>28.</td>
<td>Simulation of Run GN</td>
<td>99</td>
</tr>
<tr>
<td>29.</td>
<td>Simulation of Run WL-33</td>
<td>100</td>
</tr>
<tr>
<td>30.</td>
<td>Profiles of SO$_2$, Experimental and Calculated, with Different Mechanistic Assumptions of Run WL-33</td>
<td>101</td>
</tr>
<tr>
<td>31.</td>
<td>Profiles of SO$_2$, Experimental and Calculated, with Different Mechanistic Assumptions of Run SU-1</td>
<td>102</td>
</tr>
<tr>
<td>32.</td>
<td>Simulation of Run AP-30</td>
<td>103</td>
</tr>
<tr>
<td>33.</td>
<td>Simulation of Run AP-37</td>
<td>104</td>
</tr>
<tr>
<td>34.</td>
<td>Profiles of Sulphate Formation, Experimental and Calculated, with Different Mechanistic Assumptions of Run AP-30.</td>
<td>105</td>
</tr>
<tr>
<td>35.</td>
<td>Profiles of Sulphate Formation, Experimental and Calculated, with Different Mechanistic Assumptions of Run AP-37.</td>
<td>106</td>
</tr>
</tbody>
</table>
A chemically reactive plume model was developed, describing the homogeneous gas phase chemistry of an SO$_2$-NO$_x$ containing power plant plume dispersing in a Gaussian fashion in ambient air containing reactive hydrocarbons. A condensed chemical mechanism was designed based on recent compact models for smog chemistry but tuned specifically for plume chemistry. The model was validated with various smog chamber data and shown to predict the NO$_x$-O$_3$-HC chemistry quite accurately. The SO$_2$ chemistry is not well-understood and, as a result, modelling results were somewhat less satisfactory.

The discrete Gaussian dispersion model of Freiberg (1976), expanded by Lusis (1976), was employed to describe plume dispersion. Using the complete chemistry-dispersion model, calculations with a set of assumed plume conditions were performed to explore whether in theory the model conformed to known plume behaviour, and the sensitivity of modelling results as a function of (uncertain) input parameters was determined.

It was shown that the model reproduced the effect of entrainment of ambient air in the creation of different reactive "zones", while, initially, the outer part of the plume was more progressed in terms of ozone formation and SO$_2$ oxidation. It was suggested that, in a plume containing high levels of SO$_2$ and NO$_x$, substantial oxidation of SO$_2$ can be expected from homogeneous gas phase reactions involving HO radicals produced by photolysis of heterogeneously formed HN0$_2$.

The model was then applied to recent field observations from the 1977 summer field study in the AOSERP study area and the data collected in 1977 by a Battelle research team concerning a power plant plume dispersing over Lake Michigan. The model predicted the observed occurrence of an ozone bulge downwind from the stack and the rate of oxidation of SO$_2$ within a factor of 3. The calculations suggested that, at the time of appearance of excess ozone formation, almost 90% of initially emitted NO$_x$ (= NO + NO$_2$) was converted to PAN and HNO$_3$. 
ACKNOWLEDGEMENTS

The authors would like to express their thanks to Dr. M.A. Lusis (Ontario Ministry of the Environment) for suggesting this study. Thanks are due also to Dr. A.J. Alkezweeny (Battelle Northwest), Dr. J.G. Calvert (Ohio State University), Dr. M.C. Dodge (Environmental Protection Agency), Mr. D.F. Miller (Battelle Columbus), and Dr. A.M. Winer (University of California at Riverside) for their assistance and stimulating discussions during parts of this project.

The authors gratefully acknowledge the interest in this work by the members of the Hydrocarbon Research Centre and the Photochemistry Group at the Department of Chemistry of the University of Alberta, in particular, Dr. F.C. James and Dr. E.M. Lawn; and the staff of the Research Management Division of Alberta Environment, particularly Mr. W.B. Hume, Mr. A. Mann, and Dr. H.S. Sandhu.

Finally, we wish to thank Mrs. C. Elbrink for transforming our scribbling into a perfectly typewritten report.

This research project AS 3.5.4 was funded by the Alberta Oil Sands Environmental Research Program, a program established to fund, direct, and co-ordinate environmental research in the Athabasca Oil Sands area of northeastern Alberta.
1. **INTRODUCTION**

Interest in the dispersion characteristics and chemical reactions of pollutants emitted by power plants has been extensive in recent years, and there is now an abundance of field measurements reported in the literature (see for example, Levy et al. 1976; Bottenheim and Strausz 1977; Husar et al. 1978; Hegg et al. 1977; Hegg and Hobbs 1980). Plume chemistry has been largely confined to the rate and mechanism of oxidation of $\text{SO}_2$ and particulate analysis. Recently, the scope has been broadened by the observation of an ozone bulge within the plume boundaries at some distance downwind (Davis et al. 1974; Miller et al. 1978; Miller and Alkezweeny 1979; Lusis et al. 1978; Gillani and Wilson 1979). Since ozone formation is intimately related to the chemistry of oxides of nitrogen, this has prompted renewed attention to the determination of their plume behaviour, in particular the $\text{NO}_2$/NO ratio (e.g., Hegg et al. 1977).

Mathematical modelling of the results of field measurements has focussed mainly on either the physical aspects of dispersion or the chemical question of the oxidation mechanism of $\text{SO}_2$. Attempts to develop models which include both these plume phenomena have been made but have been hampered by the complexity of the mathematics involved in a description of chemical reactions in a turbulent fluid. As a result, these models normally include only the most basic essentials of pollution chemistry [e.g., the photostationary state between NO, $\text{NO}_2$, and $\text{O}_3$ (e.g., Shu et al. 1978 and references therein)], which in itself is inadequate to provide an understanding of how plume dispersion and chemistry together can lead to the creation of an ozone bulge downwind in an $\text{SO}_2$-$\text{NO}_x$ containing plume.

Freiberg (1976) has recently proposed a more simplified approach to modelling plume dispersion and chemistry, in which dispersion is described by an ideal, discrete Gaussian formulation, and the chemistry is partly decoupled from dispersion. This model has been extended by Lusis (1976) to include diffusion within the plume and entrainment of ambient air. Overall, the model is simple enough to allow consideration of a reasonably extensive chemical mechanism.
Interest in plume chemistry modelling, in the context of the Alberta Oil Sands Environmental Research Program (AOSERP), was raised by the results of the 1977 summer and winter field studies, organized to obtain data concerning the meteorology and air quality in the AOSERP study area (Fanaki 1979a, 1979b). During these studies, it was observed that notable oxidation of SO₂ only occurred during summer day time. Often such oxidation would be accompanied by the formation of ozone bulges downwind from the emitting source (Lusis et al. 1978). It was therefore considered important to initiate a plume chemistry modelling project to obtain insight into the mechanisms causing these observations.

In the latter stages of this work, it became apparent that, for a good understanding of the chemical processes at play, additional air quality data were necessary that had not been collected during the 1977 field trips. Consequently, additional field trips were organized in 1980 to obtain chemistry specific data. The results of these studies will be published in an upcoming report in the AOSERP monograph series. Most of the model development in this report was finished by early 1979 but completion was delayed pending some pertinent data from the 1980 field trips necessary for model evaluation with the 1977 data.

In this report, first, the development of a simple yet reasonably accurate chemical mechanism is outlined and then its validation with smog chamber data is presented. Next, the Freiburg/Lusis plume dispersion model is described. The dispersion model is then combined with the chemical mechanism and the sensitivity towards variation in several plume parameters is investigated. Finally, the model is applied to the results from one particular day of the 1977 summer field study and, as an independent test, to data collected in 1977 over Lake Michigan by a Battelle research team (Miller et al. 1978).
2. THE CHEMICAL MODEL

2.1 OVERVIEW

In modelling plume chemistry, a balance has to be struck between the requirements of a minimum number of chemical species and a mechanism which includes the basic features of pollution chemistry. Thus, the following features of pollution chemistry should be represented:

1. The photostationary state between NO\textsubscript{x} and O\textsubscript{3};
2. The free radical oxidation of NO to NO\textsubscript{2};
3. Hydrocarbon chemistry in terms of source and maintenance of free radicals;
4. Radical termination reactions; and
5. The homogeneous oxidation of S\textsubscript{O}\textsubscript{2}.

Several compact models have been proposed in recent years, such as the C-bond mechanism (CBM) (Whitten and Hogo 1977; Whitten et al. 1980), SCHEME (Levine and Schwartz 1978), and the mechanism developed for LIRAQ (Gelinas and Skewes-Cox 1977). With the possible exception of SCHEME, all these models were developed for urban-type pollution, whereas the purpose here is to model plume chemistry. The rather specific application intended here suggested the following simplifications of more complete chemical models:

1. (Pseudo-) stable species were deleted where possible. This applied to species at a high mixing ratio whose concentration does not vary due to chemical reactions (O\textsubscript{2}, H\textsubscript{2}O), and product species of little interest that are marginally involved in the overall chemistry. In the former case, their atmospheric mixing ratio was incorporated in the rate constants of reactions in which they participate.
2. Where possible, only rate determining steps were included. The species R•, O(3P), and RO were omitted.
3. Hydrocarbon chemistry was represented in a lumped version. Only reactions with HO radicals and the O\textsubscript{3} + olefin reaction are included. Aromatics were initially not
considered but were later included during this study following the procedure of Whitten et al. (1980).

4. The NO₂ + O₃ → NO₃ → N₂O₅ → HNO₃ cycle was omitted, unless data on nitrate formation was to be obtained.

5. Radical control is initially by NOₓ and SO₂ (present at high levels). Hence, radical-radical interactions were deleted for short time runs, but formation of peroxy nitrates (PAN, PA1N, PNA) was included.

The final chemical model is shown in Table 1. In this table, rate coefficients shown are the most recent values (as of August 1980). Rate coefficients were continually updated, and the values shown between square brackets were used for smog chamber validation calculations, which were performed during the latter part of 1978. No major differences from using the updated rate coefficient data are to be expected, however.

The model can be subdivided in order of decreasing importance:

1. Reactions 1 to 25 constitute the main body of the model.
2. Reactions 26 to 29 are included when information on HNO₃ formation is sought.
3. Reactions 30 to 36 are radical-radical reactions. They become important when \((\text{NO}_2)/(\text{NO}) > 1\) and noticeable \(O_3\) formation is observed; hence, they are included in smog chamber calculations and plume calculations where an ozone bulge formation is expected.
4. Reactions 37 to 42 are only important under special conditions: (a) all are important at the very early stages of plume dilution (first minute) when the NOₓ and SO₂ mixing ratios are very high; (b) Reactions 37 and 38 should be included in most smog chamber simulations with much higher rate constants to take heterogeneous wall effects into account; and (c) Reactions 39 to 42 play a role in smog chamber simulations where the initial NO₂ mixing ratio is higher than the initial NO mixing ratio. These reactions constitute a surrogation of \(O(^3P)\) atoms, as suggested by Levine and Schwartz (1978).
Table 1. The chemical mechanism.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant (^a)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.</strong> (\text{NO}_2 + \text{hv} \xrightarrow{0.2} \text{NO} + \text{O}_3)</td>
<td>(k_{hv1})</td>
<td>b</td>
</tr>
<tr>
<td><strong>2.</strong> (\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2)</td>
<td>(3.4 \times 10^3 \exp(-1450/T))</td>
<td>c</td>
</tr>
<tr>
<td><strong>3.</strong> (\text{O}_3 + \text{hv} + \text{2HO})</td>
<td>(k_{hv2} \times a)</td>
<td>b,c,d</td>
</tr>
<tr>
<td><strong>4.</strong> (\text{NO}_2 + \text{HO} \rightarrow \text{HNO}_2)</td>
<td>(1.0 \times 10^4 [1.7 \times 10^4])</td>
<td>e,f</td>
</tr>
<tr>
<td><strong>5.</strong> (\text{HNO}_2 + \text{hv} \rightarrow \text{NO} + \text{HO})</td>
<td>(k_{hv3})</td>
<td>b</td>
</tr>
<tr>
<td><strong>6.</strong> (\text{CO} + \text{HO} \xrightarrow{0.2} \text{HO}_2 + \text{CO}_2)</td>
<td>(4.1 \times 10^2 [4.4 \times 10^2])</td>
<td>c</td>
</tr>
<tr>
<td><strong>7.</strong> (\text{NO}_2 + \text{HO} \rightarrow \text{HNO}_3)</td>
<td>(1.6 \times 10^4)</td>
<td>g,f</td>
</tr>
<tr>
<td><strong>8.</strong> (\text{NO} + \text{HO}_2 + \text{NO}_2 + \text{HO})</td>
<td>(1.2 \times 10^4)</td>
<td>c</td>
</tr>
<tr>
<td><strong>9.</strong> (\text{olefin} + \text{HO} \rightarrow \text{RCHO} + \text{RO}_2)</td>
<td>(3.8 \times 10^4)</td>
<td>c</td>
</tr>
<tr>
<td><strong>10.</strong> (\text{olefin} + \text{O}_3 + 0.2 \text{RCHO} + 0.2 \text{HO} + 0.1 \text{HO}_2 + 0.1 \text{RCO}_3)</td>
<td>(9.0 \exp(-1900/T))</td>
<td>c,h</td>
</tr>
<tr>
<td><strong>11.</strong> (\text{paraffin} + \text{HO} \rightarrow \text{RO}_2)</td>
<td>(4.0 \times 10^3 [4.4 \times 10^3])</td>
<td>c</td>
</tr>
<tr>
<td><strong>12.</strong> (\text{aromatic} + \text{HO} \rightarrow 3\text{RO}_2 + 3\text{RCHO})</td>
<td>(9.4 \times 10^3)</td>
<td>c,i</td>
</tr>
<tr>
<td><strong>13.</strong> (\text{RCHO} + \text{hv} \rightarrow 0.6 \text{HO}_2 + 0.1 \text{RO}_2 + 0.05 \text{RCO}_3 + \text{CO})</td>
<td>(k_{hv4})</td>
<td>b,j</td>
</tr>
<tr>
<td><strong>14.</strong> (\text{RCHO} + \text{HO} + 0.3 \text{HO}_2 + 0.3 \text{RO}_2 + 0.7 \text{RCO}_3 + 0.3 \text{CO})</td>
<td>(2.1 \times 10^4)</td>
<td>j</td>
</tr>
<tr>
<td><strong>15.</strong> (\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RCHO} + \text{HO}_2)</td>
<td>(1.1 \times 10^4 [1.0 \times 10^4])</td>
<td>c</td>
</tr>
<tr>
<td><strong>16.</strong> (\text{NO} + \text{RCO}_3 \rightarrow \text{NO}_2 + \text{RO}_2 (\text{+ CO}_2))</td>
<td>(5.0 \times 10^3)</td>
<td>k</td>
</tr>
<tr>
<td><strong>17.</strong> (\text{NO}_2 + \text{HO}_2 \rightarrow \text{NO}_2\text{HO}_2)</td>
<td>(1.7 \times 10^3 [2 \times 10^3])</td>
<td>f,l</td>
</tr>
<tr>
<td><strong>18.</strong> (\text{NO}_2 + \text{RO}_2 \rightarrow \text{RO}_2\text{NO}_2)</td>
<td>(2.4 \times 10^3 [4 \times 10^3])</td>
<td>c</td>
</tr>
<tr>
<td><strong>19.</strong> (\text{NO}_2 + \text{RCO}_3 \rightarrow \text{RCO}_3\text{NO}_2)</td>
<td>(1.5 \times 10^3)</td>
<td>k</td>
</tr>
<tr>
<td><strong>20.</strong> (\text{HO}_2\text{NO}_2 \rightarrow \text{NO}_2 + \text{HO}_2)</td>
<td>(1.7 \times 10^{15} \exp(-10000/T))</td>
<td>l</td>
</tr>
<tr>
<td></td>
<td>([1.7 \times 10^{16} \exp(-10500/T)])</td>
<td></td>
</tr>
<tr>
<td><strong>21.</strong> (\text{RO}_2\text{NO}_2 \rightarrow \text{NO}_2 + \text{RO}_2)</td>
<td>(1.4 \times k_{19} [2 \times k_{19}])</td>
<td>m</td>
</tr>
<tr>
<td><strong>22.</strong> (\text{RCO}_3\text{NO}_2 \rightarrow \text{NO}_2 + \text{RCO}_3)</td>
<td>(1.2 \times 10^{18} \exp(-13600/T))</td>
<td>k</td>
</tr>
<tr>
<td><strong>23.</strong> (\text{SO}_2 + \text{HO} \rightarrow \text{ sulphate} + \text{HO}_2)</td>
<td>(1.6 \times 10^3)</td>
<td>h</td>
</tr>
<tr>
<td><strong>24.</strong> (\text{SO}_2 + \text{HO}_2 \rightarrow \text{ sulphate} + \text{HO})</td>
<td>(1.3)</td>
<td>h</td>
</tr>
<tr>
<td><strong>25.</strong> (\text{SO}_2 + \text{RO}_2 \rightarrow \text{ sulphate} + \text{RCHO} + \text{HO}_2)</td>
<td>(1.0 \times 10^1 [4.7])</td>
<td>n</td>
</tr>
</tbody>
</table>

continued...
Table 1. Continued.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant(^a)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ppm(^{-1}) min(^{-1}) or min(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>26. (\text{NO}_3 + h\nu \rightarrow 0.33 \text{NO} + 0.67 \text{NO}_2) + 0.67 (\text{O}_3)</td>
<td>(k_{h\nu5})</td>
<td>b</td>
</tr>
<tr>
<td>27. (\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3)</td>
<td>(1.8 \times 10^2 \exp(-2450/T))</td>
<td>c</td>
</tr>
<tr>
<td>28. (\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2)</td>
<td>(1.3 \times 10^4)</td>
<td>c</td>
</tr>
<tr>
<td>29. (\text{NO}_3 + \text{NO}_2 \rightarrow \text{HNO}_3)</td>
<td>(1.1 \times 10^{-2} [\text{H}_2\text{O}])</td>
<td>c</td>
</tr>
<tr>
<td>30. (\text{HO}_2 + \text{HO}_2 \rightarrow )</td>
<td>(3.4 \times 10^3 [3.7 \times 10^3])</td>
<td>c</td>
</tr>
<tr>
<td>31. (\text{HO}_2 + \text{RO}_2 \rightarrow )</td>
<td>(9.6 \times 10^3 [2 \times 10^3])</td>
<td>c</td>
</tr>
<tr>
<td>32. (\text{HO}_2 + \text{RCO}_3 \rightarrow )</td>
<td>(9.6 \times 10^3 [2 \times 10^3])</td>
<td>c</td>
</tr>
<tr>
<td>33. (\text{HO}_2 + \text{HO} \rightarrow )</td>
<td>(5.1 \times 10^4)</td>
<td>c</td>
</tr>
<tr>
<td>34. (\text{RO}_2 + \text{RO}_2 \rightarrow 2\text{HO}_2 + 2 \text{RCO}_3)</td>
<td>(5 \times 10^2)</td>
<td>o</td>
</tr>
<tr>
<td>35. (\text{RO}_2 + \text{RCO}_3 \rightarrow \text{RO}_2 + \text{HO}_2 + \text{RCO}_3)</td>
<td>(5 \times 10^2)</td>
<td>o</td>
</tr>
<tr>
<td>36. (\text{RCO}_3 + \text{RCO}_3 \rightarrow 2\text{RO}_2)</td>
<td>(5 \times 10^2)</td>
<td>o</td>
</tr>
<tr>
<td>37. (\text{NO} + \text{NO}_2 \rightarrow 2\text{HNO}_2)</td>
<td>(2.2 \times 10^{-9} [\text{H}_2\text{O}])</td>
<td>p</td>
</tr>
<tr>
<td>38. (2\text{HNO}_2 \rightarrow \text{NO} + \text{NO}_2)</td>
<td>(3.5 \times 10^3 \exp(-4365/T))</td>
<td>p</td>
</tr>
<tr>
<td>39. (\text{NO}_2 + \text{SO}_2 \rightarrow \text{NO} + \text{sulphate})</td>
<td>(k_{h\nu1} \times 1.1 \times 10^{-4} \exp(-530/T))</td>
<td>h,q</td>
</tr>
<tr>
<td>40. (\text{NO}_2 + \text{NO} \rightarrow 2\text{NO}_2)</td>
<td>(k_{h\nu1} \times 1.4 \times 10^{-4} \exp(-430/T))</td>
<td>c,q</td>
</tr>
<tr>
<td>41. (\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_3)</td>
<td>(k_{h\nu1} \times 3.7 \times 10^{-2} \exp(-530/T))</td>
<td>c,q</td>
</tr>
<tr>
<td>42. (\text{NO}_2 + \text{NO}_2 \rightarrow 2\text{NO})</td>
<td>(k_{h\nu1} \times 3.2 \times 10^{-2} \exp(-810/T))</td>
<td>c,q</td>
</tr>
</tbody>
</table>

\(^a\) Rate constants shown in this table are the most recently updated values. Some of these differ from those used in the calculations of Section 4 which utilized the data recommended by Hampson and Garvin (1978) and Hendry et al. (1978).

\(^b\) Photochemical rate constant.

\(^c\) Hampson (1980).

\(^d\) \(\alpha = (1 + 1.3 \times 10^5/[\text{H}_2\text{O}])^{-1}\).

\(^e\) Anastasi and Smith 1978.

\(^f\) Hampson (1980) recommends a higher value, which appears inappropriate for 1 atmosphere of air.

\(^g\) Anastasi and Smith 1976.

\(^h\) Calvert et al. 1978.

continued...
Table I. Concluded.

This equation is equivalent to that used in the CBM of Whitten et al. (1980). In the CBM, it is prescribed to multiply the aromatic mixing ratio by 3. The rate constant value used here is that for the HO + toluene reaction.

See Appendix 8.1


Graham et al. 1978.

Assuming $k_{20} = (k_{17}/k_{16}) \times k_{19}$. See Hendry et al. 1978.

Kan et al. 1979; Sanhueza et al. 1979.

Hendry et al. 1978.

Chan et al. 1976.

Using $0(3p) = k_{hv1}/3.9 \exp(530/T) \times [O_2]$. 
2.2 THE PHOTOSTATIONARY STATE AND REACTIONS OF O(3P) ATOMS

The photostationary state between NOx and O₃ is represented by Reactions 1 and 2. O(3P) atoms were deleted as separate entities since under most atmospheric conditions reaction with O₂ molecules is the only reaction of importance. Therefore, Reaction 1, in fact, represents the scheme:

\[
\begin{align*}
\text{NO}_2 + \text{hv} &\rightarrow \text{NO} + \text{O}(3P) \\
\text{O}(3P) + \text{O}_2 + \text{M} &\rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

with Reaction 1a being rate determining. The other reaction that would lead to O(3P) formation (Reaction 26) has been treated similarly. Under conditions where Reactions 38 to 42 play a role (vide supra), O(3P) formation from Reaction 1 is much more important than from Reaction 26.

2.3 THE FREE RADICAL OXIDATION OF NO

The free radical oxidation of NO is represented in Reactions 8, 15, and 16. In the initial stage of this study, \( k_{15} \) and \( k_{16} \) were re-evaluated in view of the then known experimental determination by Howard and Evenson (1977). Those re-evaluations were higher than quoted in the NBS tabulation (Hampson and Garvin 1978), but the numbers have now been consolidated by more recent experimental data (Hampson 1980).

2.4 THE HYDROCARBON CHEMISTRY

The hydrocarbon chemistry is most important since it is the source and maintains the chain length of free radicals. Unfortunately, a good representation of the hydrocarbon chemistry would require a complex treatment involving a large number of species. As a result, the number of species in the mechanism would mushroom well beyond the target maximum of 20. Therefore, a lumped scheme was adopted, originally proposed by Hecht et al. (1974) and used in later models since that time (Whitten and Hogo 1977; Gelinas and Skewes-Cox 1977; Levine and Schwartz 1978). In this scheme, propylene is taken as the representative for the olefin fraction and n-butane for the paraffin fraction, while the aldehyde is usually thought to be a 50-50 mixture of CH₂O and CH₃CHO. Toluene represents the aromatic fraction.
There are some obvious drawbacks to this scheme, although simulations of smog chamber data, involving only propylene and/or n-butane, show a surprisingly good agreement between model and experiment (see Section 3). The basic problems with this scheme are:

1. It will underestimate the HO$_2$ and RO$_2$ mixing ratios initially, while over-estimating these radicals late in the calculations.

2. The use of n-butane as surrogate for all paraffins is acceptable but the reactivity of olefins is so disparate that using propylene as representative of all olefins cannot be correct (see discussion by Whitten and Hogo 1977).

3. The lumping procedure does not take into effect the time-dependent change in the reactivity of paraffins and olefins; more reactive components will be more rapidly consumed. This problem will arise when attempting to model actual atmospheric data in which the hydrocarbon distribution is known (see discussion by Gelinas and Skewes-Cox 1977).

4. The model initially did not include reactions involving aromatic hydrocarbons. Attempts to simulate smog chamber data with aromatics (Miller 1978) by using the CBM of Whitten and Hogo (1977) were made, but the results were found not to be very satisfactory (vide infra). Hence, aromatic hydrocarbons were deleted from consideration in the mechanism. In later calculations concerning experimental plume data, aromatics were again included, according to the CBM.

Another major problem concerns the reactions of aldehydes. Although smog chamber data suggests a 50-50 mixture of CH$_2$O/CH$_3$CHO when propylene is the only hydrocarbon, this is not the case with n-butane nor with propylene/n-butane mixtures. This has consequences for the reaction products of Reactions 13 and 14, and for the rate constant of Reaction 13. Table 2 shows the expected distribution among the products of Reactions 13 and 14 at different initial hydrocarbon distributions; the derivation of these data is discussed in Appendix 8.
Table 2. Distribution of products of Reactions 13 and 14 at different initial n-butane/propylene ratios.

\[ \text{RCHO} + h\nu_4 \xrightarrow{13} a \text{HO} + b \text{RO}_2 + c \text{RCO}_3 + d \text{CO} \]

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>( k_{h\nu_4}^* )</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( 1.1 \times 10^{-3} )</td>
<td>0.636</td>
<td>0.045</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>( 7.5 \times 10^{-4} )</td>
<td>0.633</td>
<td>0.089</td>
<td>0.033</td>
<td>0.967</td>
</tr>
<tr>
<td>9</td>
<td>( 5.9 \times 10^{-4} )</td>
<td>0.614</td>
<td>0.127</td>
<td>0.064</td>
<td>0.932</td>
</tr>
<tr>
<td>( \infty )</td>
<td>( 4.3 \times 10^{-4} )</td>
<td>0.581</td>
<td>0.141</td>
<td>0.116</td>
<td>0.872</td>
</tr>
<tr>
<td>&quot;average&quot;</td>
<td>( 7 \times 10^{-4} )</td>
<td>0.6</td>
<td>0.1</td>
<td>0.05</td>
<td>1</td>
</tr>
</tbody>
</table>

\[ \text{RCHO} + \text{HO} \xrightarrow{14} a \text{HO}_2 + b \text{RO}_2 + c \text{RCO}_3 + d \text{CO} \]

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>0.25</td>
<td>0.67</td>
<td>0.33</td>
</tr>
<tr>
<td>9</td>
<td>0.25</td>
<td>0.37</td>
<td>0.75</td>
<td>0.25</td>
</tr>
<tr>
<td>( \infty )</td>
<td>0.17</td>
<td>0.5</td>
<td>0.87</td>
<td>0.17</td>
</tr>
<tr>
<td>&quot;average&quot;</td>
<td>0.3</td>
<td>0.3</td>
<td>0.7</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\[ ^\dagger \alpha = \frac{n\text{-butane}}{\text{propylene}} \text{ at } t = 0 \]

\[ ^* \text{in } \text{min}^{-1} \text{ for } Z = 65^\circ \]
Finally, it is assumed that only 20% of the products of Reaction 10 consists of radicals (Calvert et al. 1978). This is also in line with the mechanism of Herron and Huie (1977) for the $O_3 + \text{ethylene}$ reaction, in which they suggest that only 10% radical formation occurs. The usual procedure is adopted, applied to other short mechanisms in writing the products of Reaction 10 as $\text{HO}$, $\text{HO}_2$, and $\text{RCO}_3$ rather than as a biradical, as suggested by Calvert et al. (1978).

A much more detailed scheme for the $O_3 + \text{olefin}$ reaction has recently been proposed (Dodge and Arnts 1979). The scheme appears to be able to dramatically improve predictions concerning minor products. Since the $O_3 + \text{olefin}$ reaction is of minor importance for plume chemistry, and the new scheme would lead to additional species to be included in the model, its applicability here was not pursued.

2.5 RADICAL TERMINATION REACTIONS

The main radical termination reactions are with NO and NO$_2$ (Reactions 4, 7, and 17 to 19). Reactions 30 to 36 are included in the mechanism but they are not important until late in the plume dilution. Reactions 30 to 32 yield peroxy acids which could potentially photolyze; however, the photolysis rate of H$_2$O$_2$, the only experimentally determined photochemical reaction, will be very small in the atmosphere and, hence, these products are considered to be (pseudo-) stable.

The peroxy nitrates, produced from peroxy radical + NO$_2$ reactions, are thermally unstable and their decomposition has to be included. The overall mechanism could be shortened by deleting Reactions 17, 18, 20, and 21 for summertime calculations, since the decomposition rate of PNA (peroxy nitric acid) and PAIN (peroxy alkyl nitrate) is high enough to keep their mixing ratio at insignificant (i.e., less than ppb levels), and deleting Reaction 22 for winter calculations ($k_{22}$-winter $\approx 10^{-4}$ min$^{-1}$).

Reaction 17a, $\text{NO}_2 + \text{HO}_2 + \text{HNO}_2$ (+ O$_2$), has been deleted, although it has been suggested that this reaction should occur under atmospheric conditions, with $k_{17a}/k_{17} \approx 0.01$ (Uselman et al. 1978).
This report has not been substantiated, and earlier references to its importance are now believed to be erroneous.

2.6 THE HOMOGENEOUS OXIDATION OF SO₂

At first glance it might be surprising that only four reactions are included. Two questions have to be addressed specifically: (1) the product channel of Reaction 23; and (2) the oxidation by HO₂ and RO₂.

2.6.1 Product Channel of Reaction 23

Rather extensive hypotheses have been suggested with regard to the reactions ensuing from Reaction 23 (Calvert et al. 1978; Davis et al. 1979). It is generally agreed that the initially resulting HOSO₂⁻ radical should react exclusively with O₂ to yield an HSO₅⁻ radical which would resemble an HO₂ radical in its reactivity (Benson 1978). Since HSO₅ would predominantly oxidize NO to NO₂, yielding an HSO₄⁻ radical which presumably would resemble an HO radical, it appears that writing the products of Reaction 23 as HO₂ + sulphate is acceptable.

Davis et al. (1979) gave a re-evaluation of the radical propagation subsequent to the HO + SO₂ addition reaction. Their conclusions were that the kinetics are complicated by the fact that hydrated radical clusters are formed that may further oxidize NOₓ and/or SO₂, reinforcing the usefulness of the way in which Reaction 23 is written here. However, Niki et al. (1980) reported no detection of nitrogen-containing aerosols in their FTIR study involving mixtures of Cl₂, H₂, NO, and SO₂ in air. The products appeared to be solely of the form H₂SO₄⁻(H₂O)ₓ. It has to be realized that, in its present form, Reaction 23 will probably overestimate the extent of radical propagation (HO → HO₂). In fact, using the full Calvert Mechanism, including such species as HSO₅ and HSO₄ with reasonable estimates for rate constants (Bottenheim and Strausz 1978), resulted in an initial SO₂ oxidation rate under plume conditions ca. 40% lower than estimated with Reaction 23. For smog chamber simulation studies, the form of Reaction 23 is of minor importance, since radical propagation is obtained by NOₓ chemistry.
It should be noted that Davis and Klauber (1975) have suggested that high ozone levels downwind from an \( \text{SO}_2 \)-containing plume might be due to an additional oxidation chain of \( \text{NO} \) involving the \( \text{HSO}_4 \) radical:

\[
\begin{align*}
\text{HSO}_4 + \text{O}_2 & \rightarrow \text{HSO}_6 \quad 23a \\
\text{HSO}_6 + \text{NO} & \rightarrow \text{HSO}_5 + \text{NO}_2 \quad 23b \\
\text{HSO}_5 + \text{NO} & \rightarrow \text{HSO}_4 + \text{NO}_2 \quad 23c
\end{align*}
\]

This mechanism has been rejected by Calvert (1975) and by Benson (1978) on the basis of the large endothermicity of Reaction 23a. However, there is experimental evidence indicating that some form of interaction between \( \text{O}_2 \) and one of the \( \text{HSO}_x \) radicals does take place, resulting in additional oxidation of \( \text{SO}_2 \) (unpublished results of R.A. Cox, Harwell, U.K., 1978). No mechanistic consequences can be deduced from these data at this time.

2.6.2 Other Homogeneous Oxidation Reactions of \( \text{SO}_2 \)

It has been commonly assumed that the reactions

\[
\begin{align*}
\text{HO}_2 + \text{SO}_2 & \rightarrow \text{HO} + \text{SO}_3 \quad 24 \\
\text{RO}_2 + \text{SO}_2 & \rightarrow \text{RO} + \text{SO}_3 \quad 25
\end{align*}
\]

do occur and contribute to the oxidation of \( \text{SO}_2 \) (Calvert et al. 1978). Although the thermodynamics of these reactions are favourable (Benson 1978), it is puzzling that the comparable reaction

\[
\text{O}_3 + \text{SO}_2 \rightarrow \text{O}_2 + \text{SO}_3 \quad 24a
\]

does not occur to any measurable extent, even though this reaction is also highly exothermic. When this study was initiated, the recommendations of Calvert et al. (1978) were followed and the reactions were included accordingly.

Reports published since that time have considerably complicated the picture. Graham et al. (1979) found \( k_{24} \) to be several orders of magnitude lower than the questionable value of Payne et al. (1973), a value which, due to lack of other experimental data, has been applied for \( k_{24} \). This report by Graham et al. substantiated the earlier direct determination of \( k_{24} \) using laser magnetic resonance (B. Thrush, Cambridge, U.K., personal communication, 1978), and it
would appear that Reaction 24 has to be deleted from the mechanism. On the other hand, Sanhueza et al. (1979) and Kan et al. (1979) independently found a value for $k_{25}$ somewhat higher than the estimate of Whitbeck et al. (1976), used in the 1978 Calvert review, while Simonaitis and Heicklen (1979) also refer to a value for $k_{24}$ somewhat higher than the Payne et al. (1973) result.

The above discussion serves to illustrate the uncertainty in making the right decision concerning Reactions 24 and 25, since, a priori, one should expect these rate constants to be of comparable magnitude (as has now been shown the case for the reactions of HO$_2$ and CH$_3$O$_2$ with the NO$_x$ species). Calvert (personal communication, 1980) has suggested that Reactions 24 and 25 might well have to be compared with Reactions 17 and 18, rather than 8 and 15. The peroxy-SO$_2$ adduct could then either decompose into its original reactants (SO$_2$ + peroxy radical), thus leading to no reaction, or react further to some oxidized product with presumably the formation of an HO type radical.

In the present model, Reactions 24 and 25 were originally included with rate constant data as proposed by Calvert et al. (1978) and Sanhueza et al. (1979), respectively. The rationale for this decision came from the smog chamber simulation experiments. As will be shown, deletion of Reactions 24 and 25 from the model results in a severe underestimation of the rate of oxidation of SO$_2$, compared to experimental smog chamber data. This effect is most noticeable after the NO$_2$ maximum has been reached, precisely at the time when Reactions 24 and 25 would be expected to become more prominent (see, however, the discussion in Section 5.3).
3. SIMULATION OF SMOG CHAMBER DATA

The compact model described in Section 2 has been used to simulate smog profiles from several different research groups. It is well known that in smog chamber experiments several experimental problems exist which are difficult to control, and a perfect match between smog chamber data and simulation results should not be expected. The main use of such comparisons is to identify trends in the chemistry and identify glaring discrepancies between chamber and simulation profiles.

The most up-to-date smog chamber is probably the facility of the Statewide Air Pollution Research Centre (SAPRC) at the University of California, Riverside (Pitts et al. 1977). The data from this source were used to initially test the reliability of the NOx-hydrocarbon section of the mechanism. These data were recently modelled by two other groups, from SAI (Systems Applications Inc., Whitten and Hogo 1977) and SRI (Stanford Research Institute, Hendry et al. 1978), using a detailed chemical mechanism. Since comparison with the SRI data was made, the procedures adopted by SRI in order to take into account the peculiar chamber effects in the SAPRC data were followed. In this section, comparisons between chamber and simulation data will be discussed, the methods used to obtain the simulated profiles are indicated, and some of the discrepancies and potential shortcomings of the chemical model are briefly discussed.

3.1 SMOG CHAMBER PECULIARITIES

The major discrepancies between a smog chamber and the real atmosphere are the much higher surface to volume ratio and the somewhat different spectroscopic distribution of the photolyzing source of a smog chamber. As a result of the high surface to volume ratio, wall effects are known to be important in smog chamber chemistry, the so-called "dirty chamber" effect. Hendry et al. (1978) have found that this effect can be best incorporated by assuming an extra radical source in simulating the SAPRC data:

\[
\text{constant source} \rightarrow \text{H}_2\text{O}_2 \quad k = 2 \times 10^{-6} \text{ min}^{-1}
\]

where the type of radical formed is irrelevant in view of the rapid interconversion between H2O2 and HO. Hence, this procedure was followed here and slightly better results were obtained by assuming that the
radical formed was HO. Since, in essence, all chambers can be considered "dirty", this extraneous radical source was then used in all subsequent smog chamber modelling studies.

A second factor is the initial HNO$_2$ mixing ratio. Smog chamber reports do not quote an initial HNO$_2$ mixing ratio, but all smog profiles implicitly show that this must be present; otherwise, an induction period in the NO-NO$_2$ conversion should be observed, which is not the case. The initial HNO$_2$ mixing ratio is probably due to the method of preparing the reaction mixture: during injection of an NO-NO$_2$ mixture into the air in the chamber, the NO$_x$ mixing ratio is locally high, favouring the build-up of HNO$_2$ via Reaction 37 (H$_2$O will be present as humidity of the air). In these simulations, an initial HNO$_2$ mixing ratio of one-half the equilibrium value expected from Reactions 37 and 38 was assumed, except in the case of the simulation of the SAPRC data, where the values deduced by Hendry et al. were employed (these HNO$_2$ mixing ratios are close to what would be expected from one-half the equilibrium value expected from Reactions 37 and 38, and are calculated from the initial rates of NO → NO$_2$ and hydrocarbon oxidation). Finally, some smog chamber data can only be reasonably reproduced by assuming that Reactions 37 and 38 occur mainly in a heterogeneous fashion (i.e., with much higher rate constants).

In all the smog chamber data available to the authors when these simulations were performed, only the rate of Reaction 1 is reported in order to indicate the strength of the light source, and no mention is made of the spectroscopic distribution, other than mentioning the type of light source (black lights, fluorescent lamps, solar simulator, etc.). Rather than performing an extensive analysis to determine photochemical rate constants as accurately as possible on the basis of this limited information, a solar spectral distribution was assumed in all calculations. Thus, from the reported value of $k_{hv1}$, the solar zenith angle that would produce $k_{hv1}$ is determined and, the other photochemical rate constants at this solar zenith angle are calculated. These values are shown in Table 3. Table 4 gives an overview of all experiments that were modelled and the initial values used in these calculations. The figures showing the modelling results are compiled in Appendix 8.2.
Table 3. Photochemical rate constants used for smog chamber modelling.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Relative rate constant&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Reference&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂ + hv $\xrightarrow{1} NO + O_3$</td>
<td>1</td>
<td>Bass et al. 1976</td>
</tr>
<tr>
<td>O₃ + hv $\xrightarrow{3} 2HO$</td>
<td>$1.5 \times 10^{-4}$&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Hampson and Garvin 1978</td>
</tr>
<tr>
<td>HNO₂ + hv $\xrightarrow{5} NO + HO$</td>
<td>0.185</td>
<td>Stockwell and Calvert 1978</td>
</tr>
<tr>
<td>RCHO + hv $\xrightarrow{13} 0.6 HO₂ + 0.1 R0₂ + 0.05 RCO₃ + CO$</td>
<td>$2.6 \times 10^{-3}$</td>
<td>Hampson and Garvin 1978</td>
</tr>
<tr>
<td>NO₃ + hv $\xrightarrow{26} 0.33 NO + 0.67 NO₂ + 0.67 O₃$</td>
<td>3.4</td>
<td>Graham and Johnston 1978</td>
</tr>
</tbody>
</table>

<sup>a</sup> Rate constants relative to $k_{hv1}$, based on $Z = 65^\circ$.
<sup>b</sup> Reference for absorption spectrum and/or quantum yield.
<sup>c</sup> Assuming $[H₂O] = 1.5 \times 10^4$ ppm.
Table 4. Overview of studies modelled and initial values that were used.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Type</th>
<th>Initial mixing ratio used in Calculation (ppm)</th>
<th>Photochemical rate constant (min⁻¹)</th>
<th>Heterogeneity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NO</td>
<td>NO₂</td>
<td>Olefin</td>
<td>Paraffin</td>
</tr>
<tr>
<td>EC-11</td>
<td>NOₓ/propylene</td>
<td>0.115</td>
<td>0.02</td>
<td>0.447</td>
<td>-</td>
</tr>
<tr>
<td>EC-17</td>
<td></td>
<td>0.106</td>
<td>0.014</td>
<td>0.103</td>
<td>-</td>
</tr>
<tr>
<td>EC-18</td>
<td></td>
<td>0.106</td>
<td>0.014</td>
<td>0.972</td>
<td>-</td>
</tr>
<tr>
<td>EC-39</td>
<td>NOₓ/1-butane</td>
<td>0.547</td>
<td>0.06</td>
<td>2.2</td>
<td>-</td>
</tr>
<tr>
<td>EC-41</td>
<td></td>
<td>0.524</td>
<td>0.063</td>
<td>4.03</td>
<td>-</td>
</tr>
<tr>
<td>EC-42</td>
<td></td>
<td>0.542</td>
<td>0.059</td>
<td>0.385</td>
<td>-</td>
</tr>
<tr>
<td>EC-178</td>
<td></td>
<td>0.087</td>
<td>0.011</td>
<td>1.961</td>
<td>-</td>
</tr>
<tr>
<td>EC-106</td>
<td>NOₓ/propylene/1-butane</td>
<td>0.401</td>
<td>0.102</td>
<td>0.402</td>
<td>2.0</td>
</tr>
<tr>
<td>EC-115</td>
<td></td>
<td>0.402</td>
<td>0.104</td>
<td>0.310</td>
<td>2.94</td>
</tr>
<tr>
<td>EC-122</td>
<td>NOₓ/1-butane</td>
<td>0.398</td>
<td>0.103</td>
<td>0.217</td>
<td>0.108</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.217 ppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPA-306</td>
<td>NOₓ/n-butane</td>
<td>0.30</td>
<td>0.03</td>
<td>1.60</td>
<td>-</td>
</tr>
<tr>
<td>EPA-325</td>
<td>NOₓ/propylene</td>
<td>0.32</td>
<td>0.04</td>
<td>0.45</td>
<td>-</td>
</tr>
<tr>
<td>EPA-459</td>
<td></td>
<td>1.14</td>
<td>0.06</td>
<td>0.78</td>
<td>-</td>
</tr>
<tr>
<td>EPA-348</td>
<td>NOₓ/propylene/n-butane</td>
<td>1.23</td>
<td>0.08</td>
<td>0.44</td>
<td>3.39</td>
</tr>
</tbody>
</table>

continued...
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Type</th>
<th>NO</th>
<th>NO₂</th>
<th>Olefin</th>
<th>Paraffin</th>
<th>Aromatic</th>
<th>HNO₂</th>
<th>RCN/O</th>
<th>CO</th>
<th>SO₂</th>
<th>Relative Humidity (%)</th>
<th>Photochemical rate constant (min⁻¹)</th>
<th>Heterogeneity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA-352</td>
<td>NOₓ/propylene/ n-butane</td>
<td>0.27</td>
<td>0.07</td>
<td>0.26</td>
<td>3.29</td>
<td>-</td>
<td>0.015</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>0.27</td>
<td>+</td>
<td>Hecht et al. 1974</td>
</tr>
<tr>
<td>DB-2</td>
<td>NOₓ/1-butene (9 ppm)</td>
<td>3.1</td>
<td>0.35</td>
<td>9.1</td>
<td>4.5</td>
<td>-</td>
<td>0.14</td>
<td>-</td>
<td>2.9</td>
<td>-</td>
<td>50</td>
<td>0.27</td>
<td>+</td>
<td>Dodge &amp; Bufalini 1972</td>
</tr>
<tr>
<td>DB-2000</td>
<td>''</td>
<td>3.1</td>
<td>0.35</td>
<td>9.1</td>
<td>4.5</td>
<td>-</td>
<td>0.14</td>
<td>-</td>
<td>2000</td>
<td>-</td>
<td>50</td>
<td>0.27</td>
<td>+</td>
<td>Grablicki &amp; Nebel 1971</td>
</tr>
<tr>
<td>GN</td>
<td>NOₓ/propylene SO₂</td>
<td>1.8</td>
<td>0.2</td>
<td>4.5</td>
<td>-</td>
<td>-</td>
<td>0.06</td>
<td>-</td>
<td>55</td>
<td>1.25</td>
<td>0.25</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SU-1</td>
<td>NOₓ/propylene SO₂</td>
<td>-</td>
<td>0.85</td>
<td>6.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.09</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>+</td>
<td>+</td>
<td>Smith &amp; Urmie 1974</td>
</tr>
<tr>
<td>SU-2</td>
<td>''</td>
<td>-</td>
<td>1.7</td>
<td>6.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.06</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>SU-3</td>
<td>''</td>
<td>-</td>
<td>5.1</td>
<td>6.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.06</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>SU-4</td>
<td>''</td>
<td>-</td>
<td>10.2</td>
<td>6.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.06</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>SU-5</td>
<td>''</td>
<td>-</td>
<td>1.7</td>
<td>3.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.06</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>SU-6</td>
<td>''</td>
<td>-</td>
<td>1.7</td>
<td>12.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.06</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>WL-33</td>
<td>NOₓ/1-butene/ SO₂ (4 ppm)</td>
<td>0.96</td>
<td>0.04</td>
<td>3.8</td>
<td>3.8</td>
<td>-</td>
<td>0.003</td>
<td>-</td>
<td>0.75</td>
<td>0.5</td>
<td>0.35</td>
<td>+</td>
<td>Wilson &amp; Levy 1970</td>
<td></td>
</tr>
<tr>
<td>WL-36</td>
<td>''</td>
<td>1.00</td>
<td>0.03</td>
<td>4.0</td>
<td>4.0</td>
<td>-</td>
<td>0.003</td>
<td>-</td>
<td>0.25</td>
<td>0.5</td>
<td>0.35</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WL-49</td>
<td>''</td>
<td>1.00</td>
<td>0.05</td>
<td>3.98</td>
<td>3.98</td>
<td>-</td>
<td>0.003</td>
<td>-</td>
<td>0.53</td>
<td>0.5</td>
<td>0.35</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WL-55</td>
<td>''</td>
<td>1.00</td>
<td>0.02</td>
<td>3.96</td>
<td>3.96</td>
<td>-</td>
<td>0.025</td>
<td>-</td>
<td>0.52</td>
<td>0.5</td>
<td>0.35</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AP-23</td>
<td>NOₓ/hydrocarbon mixture/ SO₂</td>
<td>0.499</td>
<td>0.101</td>
<td>0.261</td>
<td>1.55</td>
<td>2.04</td>
<td>0.017</td>
<td>-</td>
<td>15</td>
<td>0.1</td>
<td>50</td>
<td>0.27</td>
<td>+</td>
<td>Miller 1978</td>
</tr>
</tbody>
</table>

continued...
**Table 4. Concluded.**

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Type</th>
<th>Initial mixing ratio used in calculation (ppm)</th>
<th>Relative Humidity (%)</th>
<th>Photochemical rate constant ($k_{\text{H}_1}$)</th>
<th>Heterogeneity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP-26</td>
<td>NO$_x$/hydrocarbon mixture/SO$_2$</td>
<td>0.125 0.025 0.051 0.225 0.262 0.0042 - 15.1 50</td>
<td>0.27</td>
<td>-</td>
<td>Miller 1978</td>
<td></td>
</tr>
<tr>
<td>AP-27</td>
<td>&quot;</td>
<td>0.490 0.100 0.019 0.193 0.241 0.017 - 15.1 50</td>
<td>0.27</td>
<td>-</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>AP-29</td>
<td>&quot;</td>
<td>0.250 0.047 0.108 0.741 0.946 0.0081 - 15.1 50</td>
<td>0.27</td>
<td>-</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>AP-30</td>
<td>&quot;</td>
<td>0.249 0.050 0.013 0.183 0.249 0.0084 - 15.1 50</td>
<td>0.27</td>
<td>-</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>AP-35</td>
<td>&quot;</td>
<td>0.252 0.052 0.257 1.54 2.00 0.0086 - 15.1 50</td>
<td>0.27</td>
<td>-</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>AP-36</td>
<td>&quot;</td>
<td>0.125 0.025 0.199 0.814 0.978 0.0042 - 15.1 50</td>
<td>0.27</td>
<td>-</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>AP-37</td>
<td>&quot;</td>
<td>1.000 0.200 0.247 1.24 1.94 0.017 - 15.1 50</td>
<td>0.27</td>
<td>-</td>
<td>&quot;</td>
<td></td>
</tr>
</tbody>
</table>

a In "dry" experiments, the relative humidity was assumed to be ≤ 0.5%.

b All modelling studies assume a constant MU source of $2 \times 10^{-4}$ ppm·min$^{-1}$. In some studies the rate constants of Reactions 37 and 38 were increased by factor of 10U; these cases are indicated by a + sign.
3.2 SIMULATION OF NO\textsubscript{X}-HYDROCARBON SMOG CHAMBER DATA

3.2.1 Statewide Air Pollution Research Centre Data

Several representative runs were modelled from the extensive data set originating from the Statewide Air Pollution Research Centre (SAPRC) at the University of California in Riverside, including data involving NO\textsubscript{X}/propylene mixtures, NO\textsubscript{X}/\textit{n}-butane mixtures, NO\textsubscript{X}/propylene/\textit{n}-butane mixtures, and NO\textsubscript{X}/1-butene mixtures (Figures 11 to 20). A comparison with the results obtained by Hendry et al. (1978), who modelled the same data base using a detailed chemical mechanism, shows the condensed model to function quite well.

The model appears to be able to predict the experimental profiles remarkably well. Note that several different hydrocarbon/NO\textsubscript{X} mixing ratios were chosen but the results do not appear to be sensitive to the value chosen. It is especially gratifying that consistent results are obtained when combining the propylene and \textit{n}-butane mechanism in modelling mixtures of these hydrocarbons.

The model appears to slightly overestimate the rate of NO + NO\textsubscript{2} oxidation and the NO\textsubscript{2} maximum. The ozone maxima also appear to be higher than those experimentally observed; this is occasionally observed when the exact chemical model is used and might indicate the absence of some important ozone loss reaction. It should be remembered that the model is expected to overestimate the peroxyl radical concentration late in the run, and hence the ozone levels are predicted to be higher than those calculated from the exact model. The model predicts RCHO and PAN levels surprisingly well when \textit{n}-butane is present, but somewhat less satisfactorily when only olefin is present.

Run EC-122, involving 1-butene as olefin, was modelled applying the CBM procedure (Whitten and Hogo 1977) to translate the present mechanism, which was set up for propylene and/or \textit{n}-butane only. In this particular case, the procedure involves the assumption of a mixing ratio of paraffin (= \textit{\textit{n}}-butane) equal to [\textit{\textit{n}}-butane] + 0.5 \times [propylene]. [According to the CBM, 1-butene should be considered as consisting of one double bond, which reacts at a rate comparable to propylene, and two single C-bonds, reacting with a rate constant equal to 0.25 k\textsubscript{10} (Whitten and Hogo 1977)]. The NO + NO\textsubscript{2} oxidation period then is
reasonably reproduced by the model (see Figure 20), but serious devia-
tions occur after that period; the rates of olefin oxidation and PAN
formation lag behind the experimental values, while the modelled rate
of formation of ozone exceeds the observed rate. A much better match
for the olefin profile can be obtained assuming a larger value for $k_{10}$
in this case, but the data of Huie and Herron (1975) do not substantiate
such an assumption. Nevertheless, this procedure was also used in model-
ling the data of Wilson and Levy (1970) involving NO$_x$/1-butene/SO$_2$
mixtures (Section 3.3.2).

3.2.2 Environmental Protection Agency Data

As an independent test for the reliability of the mechanism,
some of the smog chamber data from the EPA facility, reported by Hecht
et al. (1974), were modelled (see Figures 21 to 25). As indicated
before, the constant HO source was kept in the mechanism, but here
the additional assumption was made that heterogeneous formation of HNO$_2$
took place in these experiments (its importance becomes relatively
minor with the presence of the extraneous HO source). In view of the
fact that these data, which involve older work with less sophisticated
analytical methods, are probably less reliable, the model is able to
reproduce the EPA profiles remarkably well. It is especially gratifying
to note the higher quality of the results as compared to those obtained
by Hecht et al.

3.2.3 Dodge and Bufalini Data on NO$_x$/1-butene Mixtures

The early work of Dodge and Bufalini (1972) represents an
alternative option to check the reliability of modelling NO$_x$/1-butene
mixtures with the C-bond mechanism. The results are presented in Figures
26 and 27. The same trend as found from earlier modelling studies of
the SAPRC data can be observed: the NO $\rightarrow$ NO$_2$ oxidation rate is satis-
factorily reproduced, but the rate of 1-butene oxidation after the NO$_2$
maximum becomes too low. The experiments of Dodge and Bufalini were
specifically directed towards determining the increase in the NO $\rightarrow$ NO$_2$
oxidation rate due to large concentrations of CO. As can be seen from
the figures, the calculations are in reasonable agreement with the ex-
perimental observations in this respect.
3.3 SIMULATION OF NO\textsubscript{x}-HYDROCARBON-SO\textsubscript{2} SMOG CHAMBER DATA

Unfortunately, only very few smog chamber studies involving NO\textsubscript{x}-hydrocarbon-SO\textsubscript{2} mixtures are available for modelling studies. Moreover, with the exception of the recent work of Miller (1978) on the Battelle smog chamber, all studies were performed several years ago, and the results have to be considered with caution. In this section, the focus will be on the rate of SO\textsubscript{2} oxidation and the modelling results using Reaction 23 only will be compared with those including Reactions 24 and 25.

3.3.1 Groblicki and Nebel's Experiments

These experiments involved several different hydrocarbons, and the influence of the type of hydrocarbon on aerosol formation was studied. Unfortunately, little information is provided concerning the oxidation rate of SO\textsubscript{2}; since most data refer to "aerosol" without specifying the type of aerosol (sulfate?, carbonaceous?), no oxidation rates can be deduced from the data. The only experiment for which the time/concentration profiles were reported was simulated with the present model (see Figure 28). Generally, satisfactory reproduction of the NO\textsubscript{x} and hydrocarbon profiles was obtained; the rate of SO\textsubscript{2} loss, however, was calculated to be much slower than the experimental data suggest. Since heterogeneous loss of SO\textsubscript{2} most probably played a role in these experiments, no conclusions can be based on this observation.

3.3.2 Wilson and Levy's Experiments

These experiments, for which time/concentration profiles were reported, were the only ones available to Sander and Seinfeld (1976) when they attempted to model NO\textsubscript{x}/hydrocarbon/SO\textsubscript{2} experimental data. These authors noted inconsistencies in the data and, furthermore, suggested that the very large (up to 100\%) loss of SO\textsubscript{2} could be due to dissolution of SO\textsubscript{2} in aerosol droplets.

The data of Wilson and Levy involve 1-butene as hydrocarbon, and in this work, the C-bond procedure as discussed earlier was used to model the data (see Table 5 and Figure 29). From Figure 29, it can be seen that again the NO\textsubscript{x}-hydrocarbon chemistry is reasonably well reproduced. Experimentally, the ozone mixing ratio is again lower
Table 5. Results of modelling of Wilson-Levy experiments.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>NO\textsubscript{2} (ppm)</th>
<th>Rel. Hum. (%)</th>
<th>NO\textsubscript{2} t\textsubscript{max} (min)</th>
<th>NO\textsubscript{2} \textsubscript{-max} (ppm)</th>
<th>O\textsubscript{3} t\textsubscript{max} (min)</th>
<th>O\textsubscript{3} \textsubscript{-max} (ppm)</th>
<th>ΔNO\textsubscript{2}, σ</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>WL-33</td>
<td>0.75</td>
<td>0.5</td>
<td>80</td>
<td>70 (65)</td>
<td>0.78</td>
<td>0.86 (0.78)</td>
<td>129</td>
<td>150 (108)</td>
</tr>
<tr>
<td>WL-49</td>
<td>0.53</td>
<td>0.5</td>
<td>92</td>
<td>65 (65)</td>
<td>0.78</td>
<td>0.91 (0.82)</td>
<td>137</td>
<td>150 (105)</td>
</tr>
<tr>
<td>WL-36</td>
<td>0.25</td>
<td>0.5</td>
<td>87</td>
<td>65 (70)</td>
<td>0.82</td>
<td>0.89 (0.81)</td>
<td>130</td>
<td>150 (105)</td>
</tr>
<tr>
<td>WL-55</td>
<td>0.52</td>
<td>65</td>
<td>34</td>
<td>30 (40)</td>
<td>0.68</td>
<td>0.87 (0.65)</td>
<td>68</td>
<td>110 (75)</td>
</tr>
</tbody>
</table>

\[ a \] Percent NO\textsubscript{2} loss over a period of 200 min.

\[ b \] Number between brackets is the predicted value of Sander and Seinfeld (1976).

\[ c \] First column: Reaction 23 only; second column: Reactions 23, 24, and 25 in mechanism.
than modelling suggests. It is remarkable that Sander and Seinfeld predicted much lower ozone levels than the experiments suggested. Only one experiment at high humidity was modelled in view of the probability of heterogeneous factors playing a dominant role in the $\text{SO}_2$ loss in this case, and three runs at different initial $\text{SO}_2$ mixing ratios at very low (0.5%) relative humidity. It is well-known that 0% relative humidity is almost impossible to obtain in a smog chamber; the chosen value, 0.5%, gives a good match for the $\text{NO}_x$-hydrocarbon variables such as $\text{NO}_2$-$t_{\text{max}}$ and $\text{O}_3$-$t_{\text{max}}$ (see Table 5). Note the large difference in the percent $\text{SO}_2$ loss when Reactions 24 and 25 are included or deleted in the calculations. It is also noteworthy that inclusion of these reactions reproduces to some extent the increase in the percent $\text{SO}_2$ loss at lower initial $\text{SO}_2$ mixing ratios and the increase in the relative humidity. Most of the $\text{SO}_2$ loss in the calculations occurs after the $\text{NO}_2$ maximum (see Figure 30). (Note that for reasons of clarity, the computed profiles in this figure are indicated by symbols, and the experimental profile by a line). Although, as indicated earlier, the present model tends to overpredict peroxy radical mixing ratios after the $\text{NO}_x$ maximum, the data of Figure 30 and Table 5 suggest that $\text{HO}_2/\text{RO}_2$ reactions with $\text{SO}_2$ should be included, yet the oxidation of $\text{SO}_2$ is underestimated.

### 3.3.3 Smith and Urone's Experiments

These investigators did not use an initial $\text{NO}-\text{NO}_2$ mixture but $\text{NO}_2$ only as the initial oxide of nitrogen. Hence, these experiments should provide an additional test as to the desirability of including Reactions 24 and 25 in the mechanism. No time/concentration profiles were given but the initial rates of $\text{SO}_2$ oxidation were reported (in terms of $\Delta\text{SO}_2/\Delta t$, where $\Delta t = 30$ min). The experimental and calculated results are shown in Table 6. Figure 31 shows a comparison of the computed $\text{SO}_2$ profiles, with and without the inclusion of Reactions 24 and 25, and the experimental profile for Run SU-1. Also shown is the computed profile using only Reaction 23 but including the $\text{O}_3 + \text{olefin}$ interaction, which is described as follows:
Table 6. Results of modeling of Smith and Urone's experiments.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>-d(SO₂)/dt</th>
<th>-d(C₃H₅)/dt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm min⁻¹ x 10³</td>
<td>ppm min⁻¹ x 10²</td>
</tr>
<tr>
<td>obs.</td>
<td>pred⁹</td>
<td>obs.</td>
</tr>
<tr>
<td>SU-1</td>
<td>15 0.61 3.5 (6.0)</td>
<td>9 7.2 (2.2)</td>
</tr>
<tr>
<td>SU-2</td>
<td>12 0.71 2.0 (3.7)</td>
<td>13 8.0 (6.3)</td>
</tr>
<tr>
<td>SU-3</td>
<td>5.6 0.71 1.05 (3.8)</td>
<td>12 8.2 (11.8)</td>
</tr>
<tr>
<td>SU-4</td>
<td>3.7 0.71 0.88 (2.2)</td>
<td>8.3 8.4 (15.0)</td>
</tr>
<tr>
<td>SU-5</td>
<td>6.6 0.54 0.80</td>
<td>6.6 3.0</td>
</tr>
<tr>
<td>SU-6</td>
<td>21 0.66 6.1</td>
<td>23 16.8</td>
</tr>
</tbody>
</table>

⁹ First column assuming HO + SO₂ only; second column assuming HO, HO₂, RO₂ + SO₂. Number between brackets is the predicted value of Sander and Seinfeld (1976).
\[
\begin{align*}
O_3 + \text{olefin} & \xrightarrow{10} 0.2 \text{RCHO} + 0.2 \text{RCHO} & k_{10} = 1.5 \times 10^{-2} \\
\text{RCHO} + \text{SO}_2 & \xrightarrow{10a} \text{RCHO} & k_{10a} = 1.5 \times 10^3 \\
\text{RCHO} + \text{NO} & \xrightarrow{10b} \text{RCHO} + \text{NO}_2 & k_{10b} = 1 \times 10^4 \\
\text{RCHO} + \text{olefin} & \xrightarrow{10c} \text{RCHO} + [\text{olefin-O}^•] & k_{10c} = 4 \times 10^4 \\
[\text{olefin-O}^•] & \rightarrow \text{RO}_2 + 0.5 \text{RCO}_3 + 0.5 \text{HO}_2 + 0.5 \text{CO}
\end{align*}
\]

\(k_{10a} - k_{10c}\) are assumed values, which are probably upper limits. It can be seen from Figure 31 that the latter mechanism gives only a marginal improvement over the short mechanism which assumes Reaction 23 as the only oxidation step for SO\(_2\).

In agreement with the modelling studies of Sander and Seinfeld (1976), good agreement was obtained in the propylene oxidation rate, but considerably lower initial rates of oxidation of SO\(_2\) than experimentally determined were calculated. The inhibition of SO\(_2\) oxidation at larger initial NO\(_2\) mixing ratios of smaller initial olefin mixing ratios was reproduced by the model only when Reactions 24 and 25 were included. This gives a further indication that some reaction between SO\(_2\) and peroxy radicals must have occurred in these experiments.

### 3.3.4 Miller's Experiments

Miller's current smog chamber studies on the homogeneous oxidation of SO\(_2\) are the only recent data that were available for testing the chemical mechanism. The problem here was that, rather than using one hydrocarbon component, Miller used a mixture of 17 hydrocarbons, including paraffins, olefins, and aromatics. Hence, the CBM procedure had to be applied to represent the hydrocarbon fraction in these mixtures. Reaction 12 was added to the reaction scheme here. The only different parameter in the CBM was the value used for \(k_{12}\); in this work, the measured rate constant for the reaction between HO + toluene was used (Hampson 1980) rather than the suggested value of 3 \(\times k_{12}\), where Reaction 12 refers to the reaction between HO and C\(_2\)H\(_4\) (Whitten and Hogo 1977), since most of the aromatic fraction consists of the much more reactive alkyl substituted aromatics. The results of
modelling selected experiments of Miller are shown in Table 7 and Figures 32 to 35. As can be seen in Figures 32 and 33, the NO$_x$-ozone profiles are remarkably well-reproduced with the model, but the tabulated data on hydrocarbon disappearance show rather large deviations. It is obvious that the C-bond mechanism needs further refinements before it can be generally applied.

The reasonable match between the NO$_x$ and the ozone profiles is encouraging, and lends credence to the radical mixing ratios predicted from the model and, hence, the data on the oxidation of SO$_2$ in these experiments can be meaningfully compared with the experimental data of Miller.

The following observations can be made:

1. The calculations using Reaction 23, 24, and 25 suggest a continued increase in SO$_2$ loss with increasing HC/NO$_x$ ratios. The data of Miller also suggest this up to HC/NO$_x$ \( \lesssim 20 \), but indicate a rapid decrease at higher HC/NO$_x$ ratios. This could be due partly to an overestimate of the importance of Reaction 25; it is known that this reaction occurs for \( R = \text{CH}_3 \) but not for \( R = \text{t-butyl} \). The RO$_2$ in these experiments consist largely of higher order alkyl peroxy radicals, and at higher HC/NO$_x$ ratios, oxidation via Reaction 25 becomes more important. No distinguishable pattern appears in the modelling results when Reactions 24 and 25 are deleted. It should be noted that at higher HC/NO$_x$ ratios, the NO$_2$ maximum occurs earlier and, hence, Reactions 24 and 25 become more important for the overall loss of SO$_2$ (note that all \( \Delta \text{SO}_2 \) values refer to percent SO$_2$ loss after a period of 6 h).

2. The modelling data appears to reproduce the experimental observations quite well at low HC/NO$_x$ ratios (i.e., the loss of SO$_2$ over a 6 h period and the maximum fractional oxidation rate of SO$_2$ in Runs AP-27 and AP-30 are in good agreement). This observation is gratifying for two reasons. First, at this ratio, almost all of the oxidation of SO$_2$ occurs via Reaction 23, since the peroxy radical
Table 7. Results of modelling Miller's experiments.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>HC ( \frac{b}{NO_x} ) (ppm)</th>
<th>NO(_x) (ppm)</th>
<th>( \Delta SO_2 ) (%)</th>
<th>( \Delta SO_2)-rate(^d) (5 h)</th>
<th>( \Delta olefin)(^e) (%)</th>
<th>( \Delta paraffin)(^e) (%)</th>
<th>( \Delta aromatic)(^e) (%)</th>
<th>( \Delta hydrocarbon)(^e) (%)</th>
<th>NO(_2)-rate(^f) (ppb/min)</th>
<th>NO(_2)-rate(^g) (ppb/min)</th>
<th>O(_3)-max(^h) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP-35</td>
<td>40</td>
<td>0.304</td>
<td>6.7</td>
<td>2.7</td>
<td>22.7</td>
<td>7.5</td>
<td>0.75</td>
<td>1.6</td>
<td>95</td>
<td>85</td>
<td>9</td>
</tr>
<tr>
<td>AP-36</td>
<td>40</td>
<td>0.150</td>
<td>6.6</td>
<td>3.1</td>
<td>24</td>
<td>10.5</td>
<td>+</td>
<td>2.0</td>
<td>99</td>
<td>86</td>
<td>17</td>
</tr>
<tr>
<td>AP-23</td>
<td>20</td>
<td>0.600</td>
<td>12.2</td>
<td>3.2</td>
<td>14</td>
<td>7.8</td>
<td>0.65</td>
<td>1.5</td>
<td>100</td>
<td>86</td>
<td>21</td>
</tr>
<tr>
<td>AP-29</td>
<td>20</td>
<td>0.297</td>
<td>8.6</td>
<td>4.0</td>
<td>13.9</td>
<td>6.2</td>
<td>0.82</td>
<td>1.8</td>
<td>98</td>
<td>85</td>
<td>17</td>
</tr>
<tr>
<td>AP-26</td>
<td>10</td>
<td>0.150</td>
<td>10.8</td>
<td>5.9</td>
<td>13.9</td>
<td>3.6</td>
<td>1.3</td>
<td>1.3</td>
<td>100</td>
<td>86</td>
<td>21</td>
</tr>
<tr>
<td>AP-37</td>
<td>10</td>
<td>1.200</td>
<td>8.6</td>
<td>2.7</td>
<td>3.5</td>
<td>2.3</td>
<td>0.66</td>
<td>1.3</td>
<td>96</td>
<td>74</td>
<td>20</td>
</tr>
<tr>
<td>AP-27</td>
<td>3</td>
<td>0.590</td>
<td>7.7</td>
<td>3.8</td>
<td>3.9</td>
<td>1.8</td>
<td>1.0(^i)</td>
<td>1.5</td>
<td>92</td>
<td>62</td>
<td>10</td>
</tr>
<tr>
<td>AP-30</td>
<td>5</td>
<td>0.299</td>
<td>8.3</td>
<td>5.1</td>
<td>5.8</td>
<td>2.0</td>
<td>1.6</td>
<td>1.8</td>
<td>96</td>
<td>77</td>
<td>10</td>
</tr>
</tbody>
</table>

\(^a\) Where applicable, the experimental value is given first, followed by the calculated value(s).

\(^b\) Initial ratio of total hydrocarbons as CH\(_x\), over NO\(_x\).

\(^c\) Percent of initial [SO\(_2\)] lost during first 6 h of irradiation, corrected for smog chamber dilution. First predicted value is with HO + SO\(_2\) only; second predicted value with HO, HO\(_2\), SO\(_2\) + SO\(_2\).

\(^d\) Maximum oxidation rate for SO\(_2\). First predicted value is maximum sometime after the first 10 min. of the run; second predicted value occurs within the first 10 min. of the run. \(^+\): rate decreases continually after early maximum; \(^\mp\): no second maximum reached after 10 h.

\(^e\) Percent loss during first 6 h, corrected for smog chamber dilution. (Olefins: excluding C\(_2\)H\(_4\) and C\(_3\)H\(_6\); aromatics: excluding benzene).

\(^f\) Time to reach the maximum [NO\(_2\)].

\(^g\) \(\frac{[NO_2]_{max} - [NO_2]_{initial}}{time to [NO_2]_{max}}\).

\(^h\) Maximum ozone mixing ratio. \(^\ast\): still increasing after 10 h.
concentration is low (peroxy radicals are used up mainly in Reactions 8 and 15). Thus, the mechanism appears to satisfactorily take into account oxidation by HO radicals. Second, it can be anticipated that in the application of the model on plume dilution, the HC/NO\textsubscript{x} ratio will be low and, hence, the model should perform better in this particular case.

3. The experimental data suggest an increase in the maximum fractional oxidation rate of SO\textsubscript{2} with the HC/NO\textsubscript{x} ratio; the model suggests the opposite trend. Note that the calculations show two maxima, an early maximum (within the first 5 min) which is due to the initial buildup of radical (corresponding to turning on the light in the experiments), and a much later maximum which presumably corresponds to the data reported by Miller. It is remarkable that the absence or presence of Reactions 24 and 25 did not lead to a noticeable difference in the (second) maximum oxidation rate of SO\textsubscript{2} (i.e., the maximum appears to be determined by Reaction 23 only). In fact, inspection of Miller's aerosol profiles, from which the oxidation rate of SO\textsubscript{2} had to be determined, suggests that the maximum oxidation rate of SO\textsubscript{2} always occurs in the time regime when Reaction 23 will be more important than Reactions 24 and 25. Either an important SO\textsubscript{2} oxidation reaction, which attains importance at high HC/NO\textsubscript{x} ratios, is missing (the species responsible is unlikely to be one of the products from the HC + O\textsubscript{3} reaction since this interaction only becomes important at a later time in the run) or some unspecified increased rate of reaction between SO\textsubscript{2} and aerosol might be responsible (at high HC/NO\textsubscript{x} ratios, buildup of carbonaceous aerosol is more rapid and abundant).

Figures 34 and 35 show the computed profiles for sulphate buildup, assuming that Reactions 23 or 23 + 24 + 25 all yield sulphate. Both the corrected and uncorrected profiles for smog chamber dilution
are shown, as well as the experimental profile, deduced from Miller's aerosol data (it is not clear from these data whether uncorrected or corrected data are involved). It can be seen that the modelled curves show an increase in sulphate formation after approximately 200 min, when Reactions 24 and 25 are included in the mechanism; the experimental profiles do not show this increase.

3.4 CONCLUSIONS

The compact chemical model developed in Section 2 has been shown to be able to reproduce recent smog chamber data involving mixtures of NO$_x$, propylene, and/or n-butane reasonably well. This is the more gratifying since some simplifications involved were a priori expected to be acceptable under plume conditions but not necessarily when dealing with smog chamber experiments. Some use of the CBM procedure developed by Whitten and Hogo (1977) was made to adjust the mechanism for modelling 1-butene/NO$_x$ or hydrocarbon mixture/NO$_x$ data. The limitations of the CBM were obvious and improvements appear warranted. However, the method is a definite improvement over the older Hecht-Seinfeld-Dodge scheme (1974), and simpler to apply than the evolved procedure recommended by Gelinas and Skewes-Cox for LIRAQ (1977).

Application of the model to smog chamber work involving NO$_x$/hydrocarbon/SO$_2$ mixtures strongly suggests that reactions between peroxy radicals (RO$_2$, HO$_2$) and SO$_2$ have to be included in the mechanism to explain observed oxidation rates of SO$_2$ after the NO$_2$ maximum. This part of the mechanism has to be considered temporary until more experimental data become available related to the peroxy radical-SO$_2$ chemistry.

In general, then, the model appears to satisfactorily predict the rate of NO + NO$_2$ conversion, and tends to overestimate ultimate oxidant levels and underestimate SO$_2$-oxidation rates, particularly at high HC/NO$_x$ ratios after the NO$_2$ maximum.
4. **THE DISPERSION MODEL**

The dispersion model that was used for the overall model has been extensively described elsewhere (Freiberg 1976; Lusis 1976). Hence, only a summary of the essential features will be given here. Atmospheric dispersion of a plume is assumed to obey the Gaussian dispersion formula, without ground reflection. At any downwind location, the plume cross-section is then divided in a number of concentric elliptic rings (see Figure 1). The surface of each ring is determined by the requirement that each ring contains an equal mass of an inert pollutant. Within each ring the concentration is uniform; hence, the air mass is homogeneously mixed. Turbulent exchange between adjacent rings is taken into account, as well as entrainment of ambient air in the outermost ring as the plume moves downwind. This procedure is equivalent to a discrete approximation of a Gaussian concentration distribution for an inert species, and is acceptable for reactive species as long as the rates of their chemical reactions are not so fast that effects of turbulent fluctuations on plume chemistry are significant.

Freiberg (1976) has shown that the area \( A_i \) of each ring then becomes a function of the index of the ring \( i \), the total number of rings considered \( N \), and the Gaussian dispersion parameters \( \sigma_y \) and \( \sigma_z \):

\[
A_i = 2\pi \sigma_y \sigma_z \ln \left( \frac{N-i+1}{N-i} \right) \tag{1}
\]

Lusis (1976) has shown that turbulent exchange between adjacent rings can then be taken into account by equating the mass transfer from ring \( i \) to ring \( i+1 \), with the entrainment of a slice of ring \( i+1 \) by ring \( i \) as the plume moves downwind:

\[
K_i (C_i - C_{i+1}) = C_{i+1} \frac{d}{dt} \left( \sum_{m=1}^{i} A_m \right) \tag{2}
\]

where \( K_i \) is the diffusion coefficient from ring \( i \) to ring \( i+1 \), \( \sum_{m=1}^{i} A_m \) the total area of rings 1 to \( i \), and the \( C_i \) stand for species concentration. Hence, with \( A_i C_i = A_{i+1} C_{i+1} \) (by definition):

\[
K_i = \frac{A_i}{A_{i+1} - A_i} \frac{d}{dt} \left( \sum_{m=1}^{i} A_m \right) \tag{3}
\]
Figure 1. Division of plume cross-section downwind from the stack.
Boundary conditions have to be set for the outermost ring (i=N). Firstly, $A_N$ is not determined by Equation 1 and, following Lusis:

$$A_N = 2A_{N-1} \quad (4)$$

Secondly, since all emitted pollutant mass is within the plume, by definition $K_N=0$ (there is no transport outside of ring N).

For a pollutant $X$, the mass balance equation per unit length of plume for ring $i$ now becomes:

$$\frac{d}{dt} ([X]_iA_i) = -K_i([X]_i-[X]_{i+1}) + K_{i-1}([X]_{i-1}-[X]_i)$$

$$+ [X]_{i+1} \frac{d}{dt} \left( \sum_{m=1}^{i} A_m \right) - [X]_i \frac{d}{dt} \left( \sum_{m=i}^{i-1} A_m \right) + R_i A_i \quad (5)$$

In Equation 5, the left hand side term represents the net change of mass of $X$ in ring $i$; the right hand side term consists of two terms representing diffusion to ring $i+1$ and from ring $i-1$; two terms represent gain from ring $i+1$ and loss to ring $i-1$ due to ring expansion; and finally, a term representing formation of $X$ due to chemical reactions in ring $i$ (note that $R_i$ stands for the net rate of formation of $X$ per unit volume of plume). Equation 5 can be transformed via some algebraic manipulation to the more convenient formulation:

$$\frac{d}{dt} [X]_i = \lambda(t) \cdot (\alpha_i[X]_{i-1} + \beta_i[X]_i + \gamma_i[X]_{i+1}) + R_i \quad (6)$$

In deriving Equation 6, use is made of Equation 7:

$$\frac{d}{dt} \left( \sum_{m=1}^{i} A_m \right) = \left( \sum_{m=1}^{i} A_m \right) \frac{d}{dt} \ln \sigma \sigma_z \quad (7)$$

and the coefficients $\lambda(t)$, $\alpha_i$, $\beta_i$, and $\gamma_i$ are determined by:

$$\lambda(t) = \frac{d}{dt} \ln \sigma \sigma_z \quad (8)$$

$$\alpha_i = \frac{1}{A_i} \frac{A_{i-1}}{A_{i-1}} \left( \sum_{m=1}^{i-1} A_m \right) \quad (9)$$

$$\gamma_i = \frac{1}{A_i} \frac{A_{i+1}}{A_{i+1}} \left( \sum_{m=i+1}^{i} A_m \right) \quad (10)$$

$$\beta_i = - (\alpha_i + \gamma_i) \quad (11)$$
For the first ring, it can be shown that $\alpha_1 = 0$; while for ring $N$, $A_{N+1} = \infty$, hence, $\gamma_N = \frac{1}{A_N} \left( \sum_{m=1}^{N} A_m \right)$ and $[X]_{N+1}$ is the ambient concentration of species $X$. Finally, the radius of each ring is determined by:

$$r_i = \sqrt{2 \ln\left(\frac{N}{N-i}\right)} \quad (12)$$

while for the outermost ring:

$$r_n = \sqrt{2 \ln 4N} \quad (13)$$

The plume boundaries are consequently determined by the equation $\gamma_N, Z_N = \sqrt{2 \ln 4N} \cdot \sigma_y, \sigma_z$. Note that the plume edge extends beyond the commonly invoked 10% limit ($y_e, z_e = \pm 2.15 \cdot \sigma_y, \sigma_z$) (Strom 1976) even for $N = 3$. Hence, it is to be expected that the outermost ring will rapidly indicate the chemistry in the ambient air in which the plume is dispersing.
5. **CALCULATIONS USING THE COMPLETE MODEL**

Combination of the chemistry model described in Section 2 with the dispersion model outlined in Section 4 constitutes the complete plume chemistry model developed in this work. The purpose of this development was to determine whether recent field measurements on (1) the rate of oxidation of SO$_2$ during sunny summer days, 1 to 5% h$^{-1}$; and (2) the occurrence, under certain circumstances, of an "ozone bulge" downwind from the stack, can be quantitatively understood. Unfortunately, it appeared next to impossible to assess the applicability of the model properly, since several necessary parameters were not determined during the field experiments for which data were available. Hence, assumptions had to be made that could substantially influence the modelling results. Therefore, a "standard" plume was defined and the effect of variation of important assumed parameters delineated. Next, the plume model was applied to the data from two recent field studies during which the oxidation rate of SO$_2$ was estimated and an ozone-bulge downwind was observed. During a field study in the current year (1980), an attempt will be made to collect data for most of the parameters expected to influence plume chemistry. These data, and application of the present plume chemistry model, will be published in a separate report.

5.1 **"STANDARD" PLUME CALCULATIONS**

The standard plume was modelled from measured and assumed conditions of the GCOS (Great Canadian Oil Sands)\textsuperscript{1} power plant plume of 19 June 1977. Thus, the emission rate was taken as 2 kg·s$^{-1}$ SO$_2$ and 0.05 g NO$_x$ per g SO$_2$ (Lusis et al. 1978). Since no field data for ambient air were reported, it was assumed here to consist of a 1:1 mixture of C$_3$H$_6$ and n-C$_4$H$_{10}$ and at 60 ppb each, NO$_2$/NO = 2.5 with [NO] = 6 ppb and [O$_3$] = 50 ppb. For these calculations, the mixing ratios in ambient air were kept constant, as were the photochemical rate constants at their mid-day values, estimated by the procedure of Schere and Demerjian (1977). At the start of the calculation, the rigorous assumption that no entrainment of ambient air takes place during the first 2.5 min after emission was made. Rather than describing the chemistry during this period, it was assumed that the plume cross-section after 2.5 min was Gaussian with

\textsuperscript{1} now Suncor, Inc.
the in-plume ratio $\text{NO}_2/\text{NO}_x = 0.1$ and HNO$_2$ formation was 10% of its equilibrium value from Reactions 37 and 38 (i.e., $[\text{HNO}_2]_{t=2.5} = 0.1 \times [\text{HNO}_2]_{eq}$). Finally, the product of the dispersion parameters $\sigma_y$ and $\sigma_z$ was estimated to be $10^4 \text{ t}^{0.8}$ (next section), and the ambient temperature and average wind speed were, as reported, $291^0 \text{K}$ and 350 m$\cdot$min$^{-1}$, respectively.

For the calculations in this section, a three-ring model was used, and the oxidation rate of SO$_2$ at time $t$ was determined as:

$$\text{Rate (\% h}^{-1}) = \left[\frac{\text{sulphate}}{\text{SO}_2 + \text{sulphate}} \right]_t - \left[\frac{\text{sulphate}}{\text{SO}_2 + \text{sulphate}} \right]_{t_0} \times \frac{60}{(t-t_0)} \times 100$$

where $t_0 = 2.5 \text{ min}$ and the total mass of SO$_2$ and sulphate in the plume was used. This expression is simple to use and the rate calculated is within 5% of that estimated with rigorous first order kinetics. Moreover, many experimental rates are actually estimated using this equation. (Note that in the final form of computer code RPLM, rigorous first order kinetics are implemented).

Starting the calculations at $t = 2.5 \text{ min}$ after emission is admittedly crude but not without foundation. It is well known that dispersion of a plume from a power plant immediately after emission is hardly determined by the ambient turbulence but, instead, is dominated by source-originating effects; hence, starting the calculation at $t = 2.5 \text{ min}$ circumvents large deviations from the Gaussian formulation due to these effects. Moreover, this procedure conforms with the practice of field measurements where oxidation rates of SO$_2$ are usually obtained from the variation in the sulphate/SO$_2$ ratio with time; this ratio is determined at several distances downwind from the stack with the first measurement point, effectively the zero point, normally located ~0.5 to 1 km downwind.

Figure 2 shows the calculated oxidation rate of SO$_2$ in different segments of the standard plume. As can be seen, the model predicts substantially faster oxidation rates in the outermost part of the plume. This result is undoubtedly due to entrainment of hydrocarbon-rich ambient air which promotes radical buildup and, hence,
Figure 2. Calculated oxidation rate of SO$_2$ in different rings as a function of plume age for "standard" plume conditions (3 is the outermost ring).
homogeneous oxidation of $\text{SO}_2$. Interestingly, the calculations show that during the first hour more than 90% of the oxidation is due to reaction with $\text{HO}$ radicals, even in the outer part of the plume.

Figure 3 shows the ozone buildup and again this is predicted to be initially much more rapid in the outer ring, although eventually it is the innermost ring which attains the highest ozone level. These results are in agreement with the data of Hegg et al. (1977) who showed that conversion of NO to NO$_2$ (related to O$_3$ via the photostationary state) occurs in a reactive zone which shifts from the edges of the plume inwards as it moves downwind. In this regard, the calculations also show that the photostationary state with

$$\psi = \frac{k_1[\text{NO}_2]}{k_2[\text{NO}][\text{O}_3]} = 1$$

is attained much earlier in each separate ring ("zone") than in the overall plume using average values for [NO$_x$] and [O$_3$].

Note that the ozone levels in our calculations reach higher values than the assumed 50 ppb in ambient air. Since the in-plume NO$_x$ level is calculated to be higher than the ambient level after 1 h, this ozone buildup must be due to interaction between in-plume NO$_x$ and entrained hydrocarbons. It would therefore appear that these calculations substantiate the early suggestion by Altshuller (1974) that an ozone bulge downwind can be due to entrainment of hydrocarbons.

An important parameter in these calculations is the initial concentration of HNO$_2$ at $t = 2.5\ \text{min}$. Chan et al. (1976) have argued that HNO$_2$ formation, due to the homogeneous Reaction 37, can be an important process at the very early stages of a plume. However, in many instances, in particular in the GCOS plume with its large particle loading and high water content, HNO$_2$ formation might well be accelerated by heterogeneous processes, and 0.1 x [HNO$_2$]$_{eq}$ is certainly a conservative estimate. Thus, assuming the following average conditions describe the plume during the first minute after emission, [NO] = 50 ppm, [NO$_2$]/[NO$_x$] = 0.01 and [H$_2$O] = 0.1 atm., and increasing $k_{37}$ by two orders of magnitude to represent heterogeneous conditions, it can be calculated that 46% of [HNO$_2$]$_{eq}$ will be obtained after 1 min [using formulae discussed by Leighton (1961)].
Figure 3. Calculated ozone mixing ratio in different rings as a function of plume age for "standard" plume conditions (3 is the outermost ring).
The importance of the initial HNO₂ concentration can be seen from Figure 4, from which it appears that there is a threshold value for the initial HNO₂ concentration. When the HNO₂ level is taken larger than this value, then the rate of the ensuing photolysis (Reaction 5), and hence formation of HO radicals, is sufficiently large to instantaneously initiate a substantial rate of oxidation of SO₂ (≥ 1% h⁻¹) for our conditions; below the HNO₂ threshold, the rates of radical buildup and oxidation depend on the rate of hydrocarbon entrainment (See Figure 5). For the standard plume conditions, the threshold value is 0.26 x [HNO₂]eq, and this seems well attainable in view of the above calculation.

Unfortunately, the available field data do not permit an evaluation of the importance of this mechanism. A clear distinction between a very rapidly attained oxidation rate of 1% h⁻¹ and a slowly increasing rate might be observable by measuring plume profiles at a few points within the first hour after emission, but this is not the common practice. Note, however, that the results from the MISTT study (Wilson 1978) indicated that in the Labadie power plant plume, which is low in particle loading, the SO₂ oxidation rate was found to increase further downwind, seemingly suggesting the importance of entrainment of ambient air in that plume.

The sensitivity of the calculated oxidation rates of SO₂ towards ambient air composition and dispersion parameters was determined in terms of the time after emission before the average oxidation rate was 1% h⁻¹. Figure 6 shows the influence of the hydrocarbon/NOₓ ratio in the ambient air. It appears that when HC/NOₓ ≥ 10, then the time required to attain an oxidation rate of 1% h⁻¹ is relatively insensitive towards the NOₓ or HC mixing ratio. The time required to reach high ozone levels in smog chemistry at HC/NOₓ ≥ 10 is equally insensitive towards the HC mixing ratio, but sensitive towards NOₓ (Dimitriades 1977). The insensitivity towards ambient NOₓ in plume chemistry must be due to the fact that in-plume NOₓ is more important in determining the ongoing chemistry. This fact is more clearly shown in Figure 7, where it can be seen that in-plume NOₓ in fact inhibits the oxidation of SO₂. Hence, the rate of attainment of an oxidation rate of 1% h⁻¹ is directly proportional to the ambient hydrocarbon concentration and inversely proportional to the in-plume NOₓ mixing ratio.
Figure 4. Time required to reach an average oxidation rate of SO$_2$ of 1% h$^{-1}$ as a function of the ratio between the assumed initial mixing ratio of HNO$_2$, and its equilibrium value from Reactions 37 and 38 of Table 1.
Figure 5. Calculated average oxidation rate of $SO_2$ as function of the initial mixing ratio of HNO$_2$ for "standard" plume conditions. A: $HNO_2_{\text{init}} = 0.1 \times HNO_2_{\text{eq}}$; B, C: $HNO_2_{\text{init}} = 0.3 \times HNO_2_{\text{eq}}$; A, B: hydrocarbons in ambient air; C: no hydrocarbons in ambient air.
Figure 6. Time required to reach an average oxidation rate of $SO_2$ of $1\%$ h$^{-1}$ as a function of the HC/NO$_x$ ratio in ambient air.
Figure 7. Time required to reach an average oxidation rate of SO$_2$ of 1% h$^{-1}$ as a function of the NO$_x$/SO$_2$ ratio in the plume.
Miller et al. (1978) have suggested that the buildup of an ozone bulge is related to the $\text{HC}_{\text{ambient}}/\text{NO}_x$ plume ratio. With plume age, the NO$_x$ level will decrease, while entrainment of ambient air increases the HC level. Consequently, at some downwind distance, the $\text{HC}_{\text{ambient}}/\text{NO}_x$ plume ratio can attain the critical level of ca. 5 to 10 (Dimitriades 1977) where efficient ozone formation is to be expected. Furthermore, Gillani and Wilson (1979) have shown empirically that a good correlation usually exists between the SO$_2$ oxidation rate and concurrent ozone levels. Both these theories appear to be well in line with the results obtained here.

The sensitivity towards dispersion parameters is shown in Figure 8. The functional form of both $\sigma_y$ and $\sigma_z$ is expected to be $d^x$, with $x = \bar{u}t$, and hence the product $\sigma_y\sigma_z$, appearing in Equation 8, is of the form $P^x Q^y$. Thus, Figure 8 illustrates the effect of variations of $P$ and/or $Q$ on the oxidation rate. The standard plume, with $\sigma_y\sigma_z = 10^4 t^{-0.8}$, correlates with relatively neutral atmospheric conditions, and Figure 8 shows that under those, as well as unstable conditions (increase in $Q$), the time required to attain an oxidation rate of 1% h$^{-1}$ is not very sensitive towards variations in $\sigma_y\sigma_z$. The oxidation rate is, however, expected to be sensitive towards dispersion under stable conditions (decrease in $P$ and/or $Q$).

5.2 MODELLING OF THE GCOS POWER PLANT PLUME, DD. 19 JUNE 1977

The GCOS power plant plume has been the subject of three intensive field studies (Fanaki 1978, 1979a,b). Although emphasis was on the physics of the plume, the oxidation rate of SO$_2$ and the potential for ozone formation was determined (Lusis et al. 1978). We wish to focus here on the observations of Lusis et al. concerning the early afternoon plume on 19 June 1977. All input data employed for the modelling are shown in Table 8.

The oxidation rate of SO$_2$ was found to be 0.9% h$^{-1}$ over the first hour, and a slight ozone bulge was observed at a point 24 km downwind of the stack. Pollutant emission, ambient temperature, and average windspeed were determined as mentioned in Section 5.1. This leaves, however, additional parameters to be determined for which scant data are available.
Figure 8. Time required to reach an average oxidation rate of SO$_2$ of 1% h$^{-1}$ as a function of the dispersion parameter product $\sigma_y \sigma_z$. 

\[ \sigma_y \sigma_z = 10^4 t^x \]

\[ \sigma_y \sigma_z = x \times 10^4 t^{0.8} \]
Table 8. Input data for modelling GCOS power plant plume, dd. 19 June 1977.

<table>
<thead>
<tr>
<th>Stack emission:</th>
<th>0 km</th>
<th>10 km</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SO}_2 ) ( \text{ppm min}^{-1} ) ( \approx 2.1 \text{ kg s}^{-1} )</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>( \text{NO} ) ( \text{ppm min}^{-1} )</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>( \text{NO}_2 ) ( \text{ppm min}^{-1} ) ( = 0.1 \times \text{SO}_2 )</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>( \text{HNO}_2 ) ( \text{ppm min}^{-1} )</td>
<td>45.0</td>
<td>40.0</td>
</tr>
<tr>
<td>( \text{CO} ) ( \text{ppm} )</td>
<td>500.0</td>
<td>500.0</td>
</tr>
<tr>
<td>( \text{Paraffin} ) ( \text{ppm} )</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( \text{Olefin} ) ( \text{ppm} )</td>
<td>10.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( \text{Aromatic} ) ( \text{ppm} )</td>
<td>15.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Plume age at start calculation: 1 min
Time of day at start calculation: 1300 MST
Average windspeed: 350 m min\(^{-1}\)
Ambient temperature: 19°C
Plume dispersion function \( (\sigma_y, \sigma_z) \): \( 8.5 \times 10^3 t^{0.81} \)
The dispersion parameter product $\sigma_y \sigma_z$ was estimated by assuming the plume to be Gaussian and $\sigma_y \sigma_z = Pt^0$. From the reported (approximate) average $SO_2$ concentration at $t = 6.5$ and 68 min, one can solve for $P$ and $Q$ assuming for the moment that $SO_2$ is chemically inert. As a result, $\sigma_y \sigma_z = 8.5 \times 10^3 t^{0.81}$. This estimate is of course crude and has to be considered with caution for the following reasons. Firstly, it was observed that the plume was brought down to the ground well upwind of sampling locations, thus rendering a purely Gaussian description questionable. Secondly, Lusis et al. emphasize that their reported concentrations of $SO_2$ from filter pack measurements were not accurate since sampling was not halted once their helicopter flew outside the plume boundaries. Hence, it would first appear more appropriate to perform the calculations using the $SO_2$ concentrations from the figure of Lusis et al.'s paper (1978) (see Figure 9). However, there are some serious drawbacks to this procedure as well. Firstly, Davison and Grandia (1979) reported a maximum $SO_2$ mixing ratio at plume height of only 0.18 ppm at 3.2 km from the stack (using an identical $SO_2$ monitor) for the GCOS plume during the early afternoon of 19 June 1977; Figure 9 would suggest an $SO_2$ mixing ratio of more than 5 ppm at 2.3 km from the stack. Secondly, using the data from Figure 9 would result in the equation $\sigma_y \sigma_z = 1.35 t^{1.78}$. This formula is at odds with the analysis of Davison and Leavitt (1979), who analyzed all plume dispersion parameters obtained during the June 1977 field studies. Unfortunately, the measured values for $\sigma_y$ and $\sigma_z$ from different experiments appear to be unreliable for 19 June. However, it appears clear that $\sigma_z$ is essentially independent of time, while $\sigma_y$ must be a function of $t^Q$ where $0.5 < Q < 1$. Obviously, the value for $\sigma_y \sigma_z$ of $8.5 \times 10^3 t^{0.81}$ does fit this analysis contrary to the value derived from Figure 9. The cause of the apparent discrepancy between the data for $SO_2_{max}$ of Lusis et al. (1978) and Davison and Grandia (1979) is not known. Conceivably, the plume transversal shown by Lusis et al. constituted an atypical high concentration puff. It is well known that consecutive plume transversals at the same downwind location can show widely varying maximum levels of pollutant levels. Hence, it appears reasonable to use average $SO_2$ levels (averaged over several plume transversals) rather than instantaneous $SO_2$ levels to estimate average plume dispersion parameters.
Figure 9. Crosswind $\text{SO}_2$ and $\text{O}_3$ profiles near the stack and downwind, 19 June 1977, 1300 to 1515 h LST (from Fanaki 1979b).
Even less information concerning ambient air is available. From Figure 9, the ambient ozone mixing ratio appeared to be 45 ppb and 40 ppb at 2.3 km and 24 km, respectively. Strosher (1978) originally reported ground level monthly averages for June 1977 of NMHC (0.24 ppm), ozone (32 ppb), and NO\textsubscript{x} (20 ppb) at ca. 35 km from the GCOS plant ("Bitumount"). The values for NMHC are not mentioned in his later report, apparently because of the unreliability of the detector employed (Strosher 1980). Furthermore, during the 1980 field study, hydrocarbon levels in the ambient air were consistently found to be in the low ppb range, while NO\textsubscript{x} was found to be below the detection limit of ca. 5 ppb (Bottenheim, unpublished results). Within the plume, hydrocarbons were found close to the stack (ca. 2 to 5 mi), but almost exclusively consisting of paraffins, ethylene, and potentially aromatics (no detailed analysis for aromatic hydrocarbons was made). The source of these hydrocarbons is presumed to be the flare stack of the plants. In view of the above discussion, the following (admittedly) arbitrary procedure was adopted to describe ambient air effects.

During the first 10 km of plume travel, refinery operations of the GCOS plant are assumed to influence the ambient air, with $[O_3] = 45$ ppb, $[\text{paraffin}] = 100$ ppb\textsubscript{C}, $[\text{olefin}] = 10$ ppb\textsubscript{C}, and $[\text{aromatics + ethylene}] = 15$ ppb\textsubscript{C}. Beyond 10 km from the stack, hydrocarbon levels in ambient air are assumed negligible: $[\text{paraffin}] = [\text{olefin}] = [\text{aromatics}] = 0$, while $[O_3] = 40$ ppb. The potential effect of 2 ppm CH\textsubscript{4} was determined and found to be less than 1\% on the oxidation rate of SO\textsubscript{2} or ozone formation. Finally, ambient NO\textsubscript{x} levels were assumed to be at 0.1 ppb (Bottenheim and Strausz 1980) with the ratio NO\textsubscript{2}/NO determined by the ambient ozone level via the photostationary state equation.

The results of the model calculations predict an oxidation rate of SO\textsubscript{2} from 2.4 to 2.8\% h\textsuperscript{-1}, depending on whether Reactions 24 and 25 are excluded or included in the mechanism, respectively. Figure 10 shows a comparison between experimental and calculated plume profiles for O\textsubscript{3} using $\sigma_y$ values estimated from Figure 9. The agreement between experimental and calculated data is quite encouraging. In particular, it is interesting to note that the assumption of entrainment of mainly
Figure 10. Comparison between experimental and computed plume profiles for $O_3$ on 19 June 1977, in the GCOS plume.
moderately reactive paraffinic and aromatic hydrocarbons over a limited time period and at moderate levels, in effect, predicts excess ozone formation. Several further refinements can be applied to these calculations, but lacking experimental data, such efforts seem rather inappropriate.

5.3 MODELLING OF A POWER PLANT PLUME FROM MILWAUKEE, WISCONSIN DD. 20 JULY 1977.

On 20 July 1977, a power plant plume dispersing in the Milwaukee urban plume was followed over Lake Michigan by a research aircraft from the Battelle Institute, as part of the MAP3S program (Miller et al. 1978; Miller and Alkezweeny 1979). The stabilizing influence of the lake made the plume dispersion relatively uniform and caused virtual "decoupling" of the plume from the boundary layer. Hence, the observations made in this plume should yield an ideal data set to test the present model. As was the case with the GCOS plume described in Section 5.2, several input parameters were not available but from the data reported in the two papers by Miller and others, as well as some printouts of the original data kindly supplied by Dr. Alkezweeny, a complete set of input data could be derived (see Table 9).

As far as ambient pollutant levels are concerned, the most important question is the hydrocarbon mixing ratio. For the day in question, no experimental data were obtained, but from experience on other days, it appeared that no great variation was observed. Hence, the ambient air was modelled first to estimate the contents of the air to be entrained by the plume (see Table 10). (A similar procedure was adopted by Miller et al. 1978). During the plume calculation, the ambient air conditions were then upgraded with 5 min intervals. Secondly, no data were available pertaining to cloud levels. Miller et al. (1978) suggested a value for $k_1$ of between 0 and 0.39 min$^{-1}$, and hence, in this work, photochemical rate constants were adjusted such that $k_1 = 0.39$ min$^{-1}$ at noon. To accomplish this adjustment, a 20% attenuation from clear sky conditions had to be assumed. Finally, no information on source emission rate was available and only plume cross-section data for one transversal (presumably at plume centre height) per downwind location. The following procedure was therefore developed. According
Table 9. Input data for modelling a power plant plume over Lake Michigan, dd. 20 July 1977.

| Plume age at start calculation: | 1 min |
| Time of day at start calculation: | 12.30 C.D.T. |
| Average windspeed: | 1020 m·min$^{-1}$ |
| Ambient temperature: | 28°C |

**Stack emission**

Plume dispersion see text:

$$\frac{Q}{2\pi \sigma_y \sigma_z u} = \alpha't^{-\beta}$$

$$\alpha'SO_2 = 429 \text{ ppb·min}^{-1}$$
$$\alpha'NO = 80 \text{ ppb·min}^{-1}$$
$$\alpha'NO_2 = 60 \text{ ppb·min}^{-1}$$
$$\alpha'HNO_2 = 2 \text{ ppb·min}^{-1}$$

$$\beta = 0.46$$

**Ambient air data:** see Table 10.
Table 10. Estimated air composition, entrained by a power plant plume over Lake Michigan, dd. 20 July 1977.

<table>
<thead>
<tr>
<th>Time (C.D.T.)</th>
<th>1230</th>
<th>1330</th>
<th>1430</th>
<th>1530</th>
<th>1630</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>7.0</td>
<td>0.44</td>
<td>0.21</td>
<td>0.16</td>
<td>0.14</td>
</tr>
<tr>
<td>NO₂</td>
<td>3.0</td>
<td>3.6</td>
<td>2.0</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>NO₃</td>
<td>-</td>
<td>$9.7 \times 10^{-4}$</td>
<td>$8.0 \times 10^{-4}$</td>
<td>$7.7 \times 10^{-4}$</td>
<td>$9.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>HNO₂</td>
<td>-</td>
<td>$2.6 \times 10^{-2}$</td>
<td>$4.8 \times 10^{-3}$</td>
<td>$2.6 \times 10^{-3}$</td>
<td>$2.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>HNO₃</td>
<td>-</td>
<td>2.1</td>
<td>2.6</td>
<td>2.9</td>
<td>3.1</td>
</tr>
<tr>
<td>PAN</td>
<td>-</td>
<td>3.6</td>
<td>5.0</td>
<td>5.0</td>
<td>4.8</td>
</tr>
<tr>
<td>PNA</td>
<td>-</td>
<td>$6.5 \times 10^{-2}$</td>
<td>$3.7 \times 10^{-2}$</td>
<td>$3.0 \times 10^{-2}$</td>
<td>$2.7 \times 10^{-2}$</td>
</tr>
<tr>
<td>PAN</td>
<td>-</td>
<td>$5.4 \times 10^{-2}$</td>
<td>$3.3 \times 10^{-2}$</td>
<td>$2.8 \times 10^{-2}$</td>
<td>$2.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>olefin (C₃H₆)</td>
<td>20.0</td>
<td>7.8</td>
<td>4.9</td>
<td>3.4</td>
<td>2.5</td>
</tr>
<tr>
<td>paraffin (C₄H₁₀)</td>
<td>70.0</td>
<td>64.</td>
<td>61.</td>
<td>60.</td>
<td>58.</td>
</tr>
<tr>
<td>aromatic (C₇H₈)</td>
<td>10.0</td>
<td>8.0</td>
<td>7.4</td>
<td>6.9</td>
<td>6.6</td>
</tr>
<tr>
<td>RCHO</td>
<td>1.0</td>
<td>35.</td>
<td>39.</td>
<td>39.</td>
<td>39.</td>
</tr>
<tr>
<td>O₃</td>
<td>20.0</td>
<td>80.</td>
<td>103.</td>
<td>117.</td>
<td>128.</td>
</tr>
<tr>
<td>SO₂</td>
<td>15.0</td>
<td>14.</td>
<td>13.3</td>
<td>12.7</td>
<td>12.2</td>
</tr>
<tr>
<td>Sulphate</td>
<td>-</td>
<td>0.96</td>
<td>1.7</td>
<td>2.3</td>
<td>2.8</td>
</tr>
<tr>
<td>CO</td>
<td>500.0</td>
<td>500.</td>
<td>500.</td>
<td>510.</td>
<td>510.</td>
</tr>
<tr>
<td>NO</td>
<td>-</td>
<td>$2.3 \times 10^{-4}$</td>
<td>$1.3 \times 10^{-4}$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$8.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>NO₂</td>
<td>-</td>
<td>$6.2 \times 10^{-2}$</td>
<td>$6.1 \times 10^{-2}$</td>
<td>$5.7 \times 10^{-2}$</td>
<td>$5.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>NO₃</td>
<td>-</td>
<td>$5.1 \times 10^{-2}$</td>
<td>$5.5 \times 10^{-2}$</td>
<td>$5.2 \times 10^{-2}$</td>
<td>$4.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>RCO₃</td>
<td>-</td>
<td>$2.6 \times 10^{-2}$</td>
<td>$4.2 \times 10^{-2}$</td>
<td>$4.6 \times 10^{-2}$</td>
<td>$4.3 \times 10^{-2}$</td>
</tr>
<tr>
<td>NOₓᵇ</td>
<td>10.0</td>
<td>9.9</td>
<td>9.9</td>
<td>9.9</td>
<td>9.9</td>
</tr>
<tr>
<td>NMHCᶜ</td>
<td>410.0</td>
<td>335.0</td>
<td>310.0</td>
<td>298.0</td>
<td>286.0</td>
</tr>
</tbody>
</table>

Experimental observations, at approximate coincidental times:

| NOₓ           | -    | 10.4 | 10.  | -    | 10.  |
| O₃            | -    | 95.  | 98.  | -    | 102. |
| sulphateᵈ     | -    | 8.6  | 9.3  | -    | -    |
| NMHC, 27/8    | -    | 420. | 274. | 219. | -    |
| NMHC, 28/8    | -    | 270. | 245. | 227. | 220. |

ᵃ All values in ppb, unless otherwise indicated.
ᵇ NOₓ as sum of NO + NO₂ + HNO₃ + PAN + PNA + PAN.
ᶜ NMHC in ppbC.
ᵈ Based on 1 μg·m⁻³ SO₄²⁻ = 0.25 ppb sulphate.
to the Gaussian dispersion formula, at plume height, the pollutant concentration, \( c \), is given by:

\[
c(x, y, z = 0) = \frac{Q}{2\pi \sigma_y \sigma_z \bar{u}} e^{-\frac{y^2}{2\sigma_y^2}}
\]

where \( Q \) is the source emission rate, \( \sigma_y \) and \( \sigma_z \) are plume dispersion parameters, \( \bar{u} \) is the average wind speed, and \( y \) is the distance from the plume centre line. Furthermore, at plume centre, the maximum pollutant level is found as:

\[
c_m(x) = \frac{Q}{2\pi \sigma_y \sigma_z \bar{u}}
\]

and \( \sigma_y \sigma_z \) has to be of the functional relationship:

\[
\sigma_y \sigma_z = a \beta
\]

Combination of Equations 14 and 15 results in:

\[
c(y, t) = c_m(t) e^{-\frac{y^2}{2\sigma_y^2}}
\]

where:

\[
c_m(t) = a' t^{-\beta}
\]

From the reported cross-sections, \( c_m(t) \) can then be calculated with (17) and next, the parameters \( a' \) and \( \beta \) with Equation 18. Such calculations were performed for the data reported for \( \text{SO}_2 \) and \( \text{NO}_x \) (see Table 11). It can be seen that good agreement was obtained for the values found from both data sets. Since \( \text{SO}_2 \) can more reasonably be considered to be a pseudo-conservative species, it was decided to use the \( \beta \) value from the \( \text{SO}_2 \)-data set in the model calculations. An independent test of the procedure followed here can be obtained from a comparison of the \( \sigma_y \) values determined with Equation 18 and the standard procedure of integrating the area under the experimental plume profile for \( \text{SO}_2 \) (Davison and Grandia 1979). The \( \sigma_y \) values are also compared in Table 11, showing better than 10\% agreement.

The results of the plume modelling are presented in Tables 12 to 14. The following observations can be made from these data:

1. Contrary to the case of modelling the GCOS plume, the oxidation rate of \( \text{SO}_2 \) appears to be somewhat underestimated. Inclusion of Reactions 24 and 25 in the mechanism more closely reproduces the experimental oxidation rates.
Table 11. Experimental and estimated maximum levels of $\text{SO}_2$ and $\text{NO}_x$, and derived dispersion parameters for a power plant plume over Lake Michigan, dd. 20 July 1977.

A. Maximum mixing ratio

<table>
<thead>
<tr>
<th>Species</th>
<th>Plume age (min)</th>
<th>Estimated mixing ratio (ppb)</th>
<th>Experimental mixing ratio (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SO}_2$</td>
<td>52</td>
<td>67.9</td>
<td>69.7</td>
</tr>
<tr>
<td></td>
<td>141</td>
<td>44.6</td>
<td>75.7</td>
</tr>
<tr>
<td></td>
<td>233</td>
<td>33.5</td>
<td>41.4</td>
</tr>
<tr>
<td>$\text{NO}$</td>
<td>52</td>
<td>28.2</td>
<td>31.6</td>
</tr>
<tr>
<td></td>
<td>141</td>
<td>19.1</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td>233</td>
<td>15.5</td>
<td>20.2</td>
</tr>
</tbody>
</table>

B. Plume dispersion parameters $\alpha^t$ and $\beta$, Equation 18.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\alpha^t$ (ppb)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SO}_2$</td>
<td>429</td>
<td>0.46</td>
</tr>
<tr>
<td>$\text{NO}$</td>
<td>136</td>
<td>0.40</td>
</tr>
</tbody>
</table>

C. Plume dispersion parameter $\sigma_y$.

<table>
<thead>
<tr>
<th>Calculation method</th>
<th>$\sigma_y$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t = 52$</td>
<td>$t = 141$</td>
</tr>
<tr>
<td>Equation 17, $\text{SO}_2$</td>
<td>657</td>
</tr>
<tr>
<td>Equation 17, $\text{NO}_x$</td>
<td>655</td>
</tr>
<tr>
<td>Area integration, $\text{SO}_2$</td>
<td>690</td>
</tr>
</tbody>
</table>

$^a$ The data for $\text{SO}_2$ were corrected for the apparent calibration offset. No correction (if any) was applied to the $\text{NO}_x$ data.
Table 12. Calculated and experimental oxidation rate of SO$_2$ and the O$_3$ level at plume centre for a power plant plume over Lake Michigan, dd. 20 July 1977.

<table>
<thead>
<tr>
<th>Input</th>
<th>SO$_2$ oxidation rate ($%$ h$^{-1}$)</th>
<th>O$_3$ level at plume centre (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t = 52</td>
<td>t = 141</td>
</tr>
<tr>
<td>As from Table 10</td>
<td>5.2</td>
<td>5.8</td>
</tr>
<tr>
<td>Same, but Reactions 24 and 25 deleted</td>
<td>4.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Experimental</td>
<td>-</td>
<td>8.2</td>
</tr>
</tbody>
</table>
Table 13. Experimental and calculated data on average pollutant levels in a power plant plume over Lake Michigan, dd. 20 July 1977.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>t = 52</th>
<th>t = 141</th>
<th>t = 233</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{x}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Plume</td>
<td>20.4</td>
<td>17.8</td>
<td>15.4</td>
</tr>
<tr>
<td>Ambient</td>
<td>10.0</td>
<td>9.9</td>
<td>10.0</td>
</tr>
<tr>
<td>Net Plume</td>
<td>10.4</td>
<td>7.9</td>
<td>5.4</td>
</tr>
<tr>
<td>O\textsubscript{3}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Plume</td>
<td>89.0</td>
<td>68.0</td>
<td>112.0</td>
</tr>
<tr>
<td>Ambient</td>
<td>95.0</td>
<td>73.5</td>
<td>98.0</td>
</tr>
<tr>
<td>Net Plume</td>
<td>-6.0</td>
<td>-5.5</td>
<td>14.0</td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Plume</td>
<td>42.0</td>
<td>40.0</td>
<td>28.0</td>
</tr>
<tr>
<td>Ambient</td>
<td>15.0</td>
<td>14.2</td>
<td>14.0</td>
</tr>
<tr>
<td>Net Plume</td>
<td>27.0</td>
<td>27.8</td>
<td>14.0</td>
</tr>
</tbody>
</table>
Table 14. Calculated data on average levels of NO\textsubscript{x} species in a power plant plume over Lake Michigan, dd. 20 July 1977.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>t = 52</th>
<th>t = 141</th>
<th>t = 233</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsuperscript{a}</td>
<td>Total Plume</td>
<td>1.7</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Ambient</td>
<td>0.5</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Net Plume</td>
<td>1.2</td>
<td>0.04</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>Total Plume</td>
<td>9.4</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>Ambient</td>
<td>4.1</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>Net Plume</td>
<td>5.3</td>
<td>1.0</td>
</tr>
<tr>
<td>HNO\textsubscript{3}</td>
<td>Total Plume</td>
<td>3.6</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>Ambient</td>
<td>2.1</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>Net Plume</td>
<td>1.5</td>
<td>2.3</td>
</tr>
<tr>
<td>PAN</td>
<td>Total Plume</td>
<td>3.1</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>Ambient</td>
<td>3.1</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>Net Plume</td>
<td>0.0</td>
<td>1.7</td>
</tr>
<tr>
<td>NO + NO\textsubscript{2}</td>
<td>\frac{\text{Total Plume}}{\text{NO\textsubscript{x}}}, %</td>
<td>62.</td>
<td>21.</td>
</tr>
<tr>
<td></td>
<td>Ambient</td>
<td>47.</td>
<td>21.</td>
</tr>
<tr>
<td></td>
<td>Net Plume</td>
<td>81.</td>
<td>21.</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Mixing ratios in ppb.
2. The experimentally observed excess ozone formation is well reproduced by the simulations. It can be seen in Table 13 that the net ozone production due to plume chemistry is calculated to be first observable at the second downwind location. The rather large discrepancy between excess ozone observed and calculated at the third downwind location is due largely to the ambient ozone level. In Table 10, it can be seen that the calculated ozone level is considerably larger than the observed level at this location. To a lesser extent, the excess ozone, observed and calculated at the third downwind location, should be different since the calculations are based on truly Lagrangian conditions, where, in fact, the air parcel monitored was emitted more than 1 h earlier than the other two air parcels.

3. In the calculations, NO\textsubscript{x} is assumed to be the sum of NO, NO\textsubscript{2}, PAN, PNA, PAIN, and HNO\textsubscript{3}. As can be seen, this procedure gives good agreement between experimental and calculated data. This calculation procedure was followed since it is well known that commercial NO-NO\textsubscript{2}-NO\textsubscript{x} detectors respond to peroxynitrates and nitric acid in their NO\textsubscript{x}-mode (Winer et al. 1974). In Table 14, the calculated average levels of the individual NO\textsubscript{x} components are presented. It can be seen that the plume causes net PAN and nitrate formation. In this respect, it is interesting to note that PAN formation follows the same pattern as ozone formation (i.e., excess PAN formation is suggested to be found only from the second observation point). On the other hand, net HNO\textsubscript{3} formation appears to start at a much earlier time.

4. The most interesting result from Table 14 is probably shown in the last line, where it can be seen that the model calculations suggest almost 90% conversion of initially emitted NO\textsubscript{x} into more stable compounds, mainly PAN and HNO\textsubscript{3} (in the approximate ratio of 2:3). This conversion
occurs for the particular plume under study within a time span of 4 h. During the same time, the calculations predict a 10 to 18% conversion of S02 to sulphate (depending on whether one includes Reactions 24 and 25 in the chemical mechanism or not; this inclusion has a rather minor effect on the NO_X conversion rate). The implications of this result, in the context of acid rain formation due to power plant emission, are obvious, but their discussion falls outside the scope of this work.

5.4 CONCLUSIONS

The plume model developed in this work has been shown to satisfy the initial goals, i.e., it reproduces well experimentally observed oxidation rates of S02 in the 1 to 5% h⁻¹ range, and predicts the formation of excess ozone within the plume boundaries as was found in two unrelated studies. However, it is important to realize its strength and weakness.

The model developed here is a hybrid between plume physics and chemistry, and the requirement to keep it useful without having to spend large amounts of CPU-time necessitated simplifications that are difficult to accept from either a physical or a chemical point of view alone. In particular, the assumption of purely Gaussian dispersion is rather remote from current dispersion theories. On the other hand, the lumped version of the hydrocarbon chemistry is too simple to be palatable to atmospheric chemists. Throughout this text, moreover, the large uncertainty in the S02 oxidation chemistry has been emphasized. In this respect, it should be reiterated that liquid phase chemistry has been completely ignored.

On the positive side, one has to remember that the present effort was initiated to understand some chemical observations in a plume. Hence, it is in the chemical predictions where the strength of the model has to be found. Here, the model not only has fulfilled its objectives but, moreover, has given important additional insight into plume chemistry. Thus, it was found that the oxidation of S02 might well be enhanced due to initial HNO2 formation, as suggested by Chan et al. (1976). It
appears that if, as assumed in the model, the fly ash from stack emissions catalyzes HNO$_2$ formation, then the HNO$_2$ concentration can surpass a critical level above which homogeneous oxidation of SO$_2$ takes off almost instantaneously with rates of more than 1% h$^{-1}$. Secondly, sensitivity studies showed that the oxidation rate of SO$_2$ and the excess ozone formation are related to the ratio of in plume NO$_x$ versus ambient hydrocarbon. This is precisely the theory proposed by Miller et al. (1978) concerning the origin of excess ozone formation. Thirdly, it was predicted that emitted NO$_x$ is almost totally converted into PAN and nitrate in a plume where excess ozone formation is observed. Moreover, excess ozone formation in this respect appears to be accompanied by excess PAN formation. Finally, it is tempting and quite possible to improve the simulation of experimental plume studies. In view of the uncertainty in some of the input parameters for the simulation, this cannot amount to much more than glorified curve fitting at the present time.
6. SUMMARY AND RECOMMENDATIONS

A reactive plume model was developed, describing the chemistry in a dispersing plume. The plume was thought to originate from a pseudo point source, such as the chimney of a power plant, and to consist typically of large amounts of SO$_2$ and NO$_x$. A simplified chemical mechanism was designed and its ability to simulate smog chamber experiments involving mixtures of NO$_x$, hydrocarbons, and SO$_2$ in air was tested. The discrete, Gaussian dispersion model of Freiberger (1976), expanded by Lusis (1976), was chosen to describe the concurrent plume dispersion. The complete model was tested to determine how changes in input parameters change the modelling results. Finally, the application of the model to experimental data from two recent plume studies was described. It was shown that the model reproduces the experimental oxidation rate of SO$_2$ of ca. 1 to 5% h$^{-1}$, and the formation of excess ozone in the plume.

The present model creates a theoretical framework within which important observations related to chemistry in plume studies of recent years can be quantitatively understood. It also suggests chemical phenomena for which no experimental data are as yet available. Based upon these considerations and conclusions reached in earlier sections of this report, the following recommendations are presented.

6.1 OXIDATION MECHANISM OF SO$_2$

The largest uncertainty in the chemical mechanism remains the oxidation mechanism of SO$_2$ in the atmosphere. Not only is the interaction of SO$_2$ with peroxy radicals more uncertain than before, but also the follow-up of the radical-SO$_2$ interaction remains as unknown as ever. Undoubtedly, this is due to the fact that simple gas phase kinetics studies do not suffice. Gas liquid interactions have to be taken into account and the basic chemical methodology for this type of studies is in its infancy. Concerted studies into this field should actively be stimulated, in view of the importance of such reactions with respect to oxidation of SO$_2$ and potential influence on excess ozone formation.
6.2 EXPERIMENTAL PLUME DATA FOR HNO$_3$ AND PAN

It was deduced that most NO$_x$ from a power plant will be converted to PAN and nitrate if excess ozone formation occurs. Since there is now a growing consensus that excess ozone formation in power plant plumes is actually a very common event during the summer, the modelling result has serious implications with respect to acid rain formation. It is therefore recommended that development of techniques for in situ monitoring of PAN and nitrate (mainly HNO$_3$) be actively stimulated, and when possible, experimental data collected. It might be restated here that the modelling data suggest that nitrate formation precedes PAN formation. As a first start, moreover, it is suggested to verify whether (excess) PAN formation accompanies excess ozone formation.

6.3 EXPERIMENTAL PLUME DATA FOR HYDROCARBONS

The theory of the mechanism of excess ozone formation is heavily dependent on the entrainment of reactive hydrocarbons by a dispersing plume. Although this theory appears attractive, and the present modelling study confirms its applicability, most experimental studies appear to have either ignored hydrocarbon analyses or experienced great difficulties in establishing hydrocarbon levels. It is recommended with great emphasis that any field study which is undertaken to understand chemical events in an airshed, be it plume study or a long range effects study, should include determination of hydrocarbon levels. This is especially important since a common key in all current theories is ozone formation, which does not only depend on the NO$_2$/NO ratio, but also on the ability of the total air mass to convert NO to NO$_2$. Hydrocarbons play an essential role in this process, as is well known from urban pollution ("smog") studies.

6.4 EXPERIMENTAL PLUME DATA IMMEDIATELY AFTER EMISSION

The model has suggested an alternative mechanism for the effect of fly ash from a power plant stack with respect to oxidation of SO$_2$. Rather than heterogeneous oxidation of SO$_2$, it is deduced that fly ash might well catalyze the formation of HNO$_2$ at an early stage of plume
dispersion, thereby triggering a rapid buildup of HO radicals that can then oxidize SO₂. It is recommended that this initiation mechanism for SO₂ is studied further. Some avenues for such a study would be the determination of HNO₂ levels in plumes at an early time, whenever sensitive in situ monitors for HNO₂ become available, or the determination of the SO₂ oxidation rate at short distances from the stack. Since this mechanism would be light sensitive, an indication of its importance relative to truly heterogeneous oxidation of SO₂ might be deduced from SO₂ oxidation rates in particle-rich plumes during day versus night.

6.5 COMPARISON WITH OTHER REACTIVE PLUME MODELS
In view of the severe limitations of using an ideal Gaussian plume model, it is recommended that a comparison be made with other reactive plume models. One model that comes to mind has recently been described by Yocke et al. (1980), and it seems worthwhile to investigate whether the present model can be more generalized by incorporating some of the techniques used in Yocke's model.

6.6 USE OF THE MODEL FOR POLLUTION CONTROL
It is recommended that the present model not be used as a primary tool for the design of control strategies. Rather, it should be applied as a sub-model to the larger air shed models, which, due to their nature, tend to ignore chemical effects and concentrate almost exclusively on the physics of atmospheric motion. Unpleasant surprises will be experienced if one designs a strategy purely on the basis of where "S" and "N" might be encountered without knowledge whether "S" is in the form of SO₂ or SO₄, and "N" is NO + NO₂ or NO₃⁻ and PAN. In this respect, it may be added here that, in principle, it is possible to extend air shed models to include relatively detailed chemistry. However, such models would require large amounts of CPU-time, and the question becomes whether it is reasonable to design a model which predicts effects on the same time scale as their occurrence in the actual world. The accuracy of such models is potentially excellent, but to predict what is actually occurring at the same time is a rather useless effort. It appears that a combination of sub-models, as recommended
here, will give similarly useful results with only a fraction of the cost in money and time involved.
7. REFERENCES CITED


8. APPENDICES

8.1 DETERMINATION OF THE FATE OF RCHO

In Section 2.4, it was outlined that in the chemical mechanism all aldehydes and ketones are lumped in one species, RCHO. In this section, the derivation of the product channels of the reactions of RCHO is presented.

Smog chamber data suggest that, with propylene as the hydrocarbon, approximately equal amounts of CH$_2$O and CH$_3$CHO are produced, while with n-butane, the production of CH$_2$O, CH$_3$CHO, and CH$_3$COC$_2$H$_5$, in the ratio of 1:2:3, can be expected (Pitts et al. 1977). Since

$$k(\text{HO} + C_3H_6)/k(\text{HO} + n-C_4H_{10}) = 9,$$

the aldehyde-ketone fraction ("RCHO") in C$_3$H$_6$-n-C$_4$H$_{10}$ mixtures is then approximated as:

$$\text{CH}_2\text{O}:\text{CH}_3\text{CHO}:\text{CH}_3\text{COC}_2\text{H}_5 = (1 + \frac{9}{a}):(2 + \frac{9}{a}):3,$$

where:

$$a = \frac{\left[n-C_4H_{10}\right]}{C_3H_6} \text{ at } t = 0.$$

The product distribution from the reactions of RCHO and the photochemical rate constant $k_{hv4}$ are estimated taking the reaction products and rates of the individual reactions of the components of RCHO into account (see Table 15). Whereas the rate constants for reactions with HO are more or less equal ($k \sim 2.1 \times 10^4$ ppm$^{-1}$ min$^{-1}$), they differ for the individual photochemical reactions. Many smog chamber experiments report $k_{hv1} = 0.27$ min$^{-1}$, which correlates with a solar zenith angle $z = 65^\circ$. This seems to be a reasonable value for an average solar zenith angle, and the photolytic rate constants at $z = 65^\circ$, calculated with the procedure of Schere and Demerjian (1977), are also shown in Table 15. The composite rate constant $k_{hv4}$ is determined from the formula:

$$k_{hv4} = \frac{3 \times k_{13d} + (2 + \frac{9}{a})k_{13c} + (1 + \frac{2}{a})(k_{13a} + k_{13b})}{6 + \frac{18}{a}}$$

and by variation of $a$, it can be shown that at $z = 65^\circ$, a good approximation will be $k_{hv4} \approx k_{13b}$. The products of the composite Reactions 13 and 14 can also be determined as functions of $a$ and the photolytic rate constants, as shown in Table 16. Variation of $a$ has led to the "average" product fractions which are tabulated in Table I in the main text.
Table 15. Reactions determining the reactivity of RCHO.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$O + hv → H$_2$ + CO</td>
<td>1.4 x 10$^{-3}$</td>
</tr>
<tr>
<td>CH$_2$O + hv → H + HCO $\rightarrow$ 2HO$_2$ + CO</td>
<td>6.5 x 10$^{-4}$</td>
</tr>
<tr>
<td>CH$_3$CHO + hv → CH$_3$ + HCO $\rightarrow$ HO$_2$ + RO$_2$ + CO</td>
<td>1.0 x 10$^{-4}$</td>
</tr>
<tr>
<td>CH$_3$COC$_2$H$_5$ + hv → CH$_3$CO + C$_2$H$_5$ $\rightarrow$ RCO$_3$ + RO$_2$ + CO</td>
<td>1.0 x 10$^{-4}$</td>
</tr>
<tr>
<td>CH$_2$O + HO $\rightarrow$ HO$_2$ + CO</td>
<td>2.1 x 10$^{-4}$</td>
</tr>
<tr>
<td>CH$_3$CHO + HO $\rightarrow$ RCO$_3$</td>
<td>2.2 x 10$^{-4}$</td>
</tr>
<tr>
<td>CH$_3$COC$_2$H$_5$ + HO $\rightarrow$ RCO$_3$ + RO$_2$</td>
<td>$\sim$ 1 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reactions 13a to 13d are in min$^{-1}$, based on z = 65°; Reactions 14a to 14c, in ppm$^{-1}$ min$^{-1}$, from Demerjian et al. (1974).
Table 16. Product distribution for Reactions 13 and 14.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>13</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>(\frac{(2p k_{13b} + q k_{13c})}{r k_{hv_4}})</td>
<td>(p/r)</td>
</tr>
<tr>
<td>b</td>
<td>(\frac{(q k_{13c} + 3k_{13d})}{r k_{hv_4}})</td>
<td>(3/r)</td>
</tr>
<tr>
<td>c</td>
<td>(\frac{3k_{13d}}{r k_{hv_4}})</td>
<td>(p/r)</td>
</tr>
<tr>
<td>d</td>
<td>(\frac{[p(k_{13a} + k_{13b}) + q k_{13c}]}{r k_{hv_4}})</td>
<td>(\frac{(3 + q)}{r})</td>
</tr>
</tbody>
</table>

\(^a\) \(p = 1 + \frac{9}{\alpha}, \ q = 2 + \frac{9}{\alpha}, \ r = 6 + \frac{18}{\alpha}\).
8.2 FIGURES OF SMOG CHAMBER SIMULATION STUDIES

The figures in this section are the results of the smog chamber simulations described in Section 3 of this report. The appropriate information on the origin of the experimental data and the input data used for the simulations, can be found in Table 4. In these figures, symbols refer to experimental data points, while drawn lines are calculated results, unless otherwise indicated.
Figure 11. Simulation of Run EC-II.
Figure 12. Simulation of Run EC-17.
Figure 13. Simulation of Run EC-18.
Figure 14. Simulation of Run EC-39.
Figure 15. Simulation of Run EC-41.
Figure 16. Simulation of Run EC-42 (continued).
Figure 16. Concluded.
Figure 17. Simulation of Run EC-178 (continued).
Figure 17. Concluded.
Figure 18. Simulation of Run EC-106 (continued).
Figure 18. Concluded.
Figure 19. Simulation of Run EC-115 (continued).
Figure 19. Concluded.
Figure 20. Simulation of Run EC-122.
Figure 21. Simulation of Run EPA-306.
Figure 22. Simulation of Run EPA-325.
Figure 23. Simulation of Run EPA-459.
Figure 24. Simulation of Run EPA-348.
Figure 25. Simulation of Run EPA-352.
Figure 26. Simulation of Run DB-2.
Figure 27. Simulation of Run DB-2000.
Figure 28. Simulation of Run GN.
Figure 29. Simulation of Run WL-33.
Figure 30. Profiles of SO$_2$, experimental (---) and calculated (symbols), with different mechanistic assumptions, of Run WL-33.
Figure 31. Profiles of SO₂, experimental (-----) and calculated (symbols), with different mechanistic assumptions, of Run SU-1.
Figure 32. Simulation of Run AP-30.
Figure 33. Simulation of Run AP-37.
Figure 34. Profiles of sulphate formation, experimental (---) and calculated (symbols), with different mechanistic assumptions of Run AP-30. Experimental profile not on scale.
Figure 35. Profiles of sulphate formation, experimental (---) and calculated (symbols), with different mechanistic assumptions of Run AP-37. Experimental profile not on scale.
8.3 COMPUTER CODE RPLM

The computer code RPLM was written based on Gear's original algorithm DIFSUB, developed for the integration of a stiff set of ordinary differential equations. Its basic framework is similar to the code AAPM, written for the simulation of a set of chemical equations, as described in an earlier report (Bottenheim and Strausz 1978). As before, the IMSL-library version of DIFSUB is employed. In the newer editions of this library, the subroutine DGEAR is now supplied, superceding the older version DVOGER, and RPLM is written to use DGEAR (IMSL 1980). A short description of the successive sections of RPLM follows. (For more detailed information, consult the listing of RPLM.)

8.3.1 Main

The function of the Main-routine is to direct the order of manipulations from input via integration to output. Additionally, the Main routine instructs DGEAR when to stop (parameter XEND), and follows this with the appropriate action (either record data, change input parameters, or stop integration).

8.3.2 Subroutine INPUTS

This subroutine manages the bulk of input data. The only other subroutines requiring input are RMECH and PRATE1, which read and manipulate the input for the chemical mechanism and photochemical rate constants, respectively, and REPORT, which is in charge of printing the results. RMECH and PRATE1 are called by INPUTS. All input requirements are fully documented in the listing. A sample input listing follows in Section 8.3.9.

8.3.3 Subroutine RMECH

This subroutine is slightly changed from the version in the earlier code AAPM to allow for more than three products that are not necessarily formed with unit efficiency. This expansion became necessary due to the lumping of some reactions such as
Reactions 13 and 14, Section 2. Each reaction is now represented by two cards instead of one.

8.3.4 Subroutine PRATE 1
Again, this subroutine is slightly changed from the earlier version in Code AAPM, but the input format is unchanged.

8.3.5 Subroutine LOADA
This routine determines the coefficients $a_i$, $b_i$, and $\gamma_i$ as outlined in the description of the plume model (Section 4).

8.3.6 Subroutines DIFFUN and DJAC
Contrary to DVOGER, the new version of Gear's integration program, DGEAR, requires separate subroutines for the creation of the set of differential equations and the Jacobian. DIFFUN is the first part of DFUN in AAPM, modified to include the dispersion parameters. Matrix AA consists of the coefficients $a_i$, $b_i$, and $\gamma_i$ (see LOADA), multiplied by the time dependent coefficient $\lambda(t)$. DJAC now determines the Jacobian.

8.3.7 Subroutine REPORT
The code RPLM has been arranged such that all potentially useful information, including the calculation results, is stored in a temporary scratch file (File 8). File 8 is set up sequentially in binary code so that it uses the minimal amount of space for this operation. File 8 therefore might be saved for later reference. Subroutine REPORT is equally designed such that it can be run independently from code RPLM with minimal modifications, thereby allowing, in conjunction with a saved File 8, data manipulation at a later time.

REPORT begins with printing the title of the calculation, and then asks for indication of which output is required. Calculation results can be printed in two different ways:
1. A mass balance calculation is performed whereby correction for entrainment is incorporated. This calculation also shows the average concentration in the plume. In addition, the percent conversion of one set of species to another may be calculated, and the rate at which this takes place (in % h$^{-1}$, assuming first order kinetics), e.g.:

$$\text{SO}_2 + \text{sulphate} \ [\% \ \text{conversion}] = \frac{\text{sulphate}}{\text{SO}_2 + \text{sulphate}} = \beta$$

$$[\text{Rate in } \% \ h^{-1}] = \frac{\ln (1-\beta)_{t_0}}{\ln (1-\beta)_t} \cdot (t-t_0) \cdot 60 \cdot 100$$

2. The concentration in each ring as function of time is printed. This mode allows for inspection of change in plume cross section.

A sample output from the sample input (Section 8.3.9) follows in Section 8.3.10.

8.3.8 **Listing of Code RPLM**

See following pages.
PROGRAM CODE RPLM

THIS PROGRAM WILL SIMULATE THE CHEMISTRY IN A DISPERSING PLUME. IT WAS DEVELOPED ON THE AMDahl 470/V7 COMPUTER AT THE UNIVERSITY OF ALBERTA BY JAN WILLEM BOTTENHEIM. THE CODE IS WRITTEN IN FORTRAN-4 AND USES DOUBLE PRECISION FOR ALL REAL VARIABLES EXCEPT THOSE WITH THE PREфикс P.

ACTUAL INTEGRATION IS PERFORMED NUMERICALLY BY CALLING THE DOUBLE PRECISION VERSION OF SUBROUTINE DGEAR FROM THE IMSL-LIBRARY, EDITION 8. SUMMER 1980. THE PROGRAM ASSUMES ACCESS TO THE IMSL-LIBRARY.

IMPLICIT REAL*8 (A-H,Q-Z)
EXTERNAL DIFFUN,DJAC
LOGICAL PHTFLG
DIMENSION Y(200),WK(42200),IWK(200)
COMMON /CHEM/ R1(41),R2(41),SPECIE(21),YO(20),PC2(40,20),IC1(40).
-IC11(3,40),IC2(20),IC22(40,20)
COMMON /MATA/ A(30),BYZ
COMMON /NUMBRS/ NS,NRI,NR,NRIM1,NRI2,NRI3,NI1P1,NSRNSR,NSR
COMMON /WORK/ Z(650)
COMMON /INTEGR/ METH,MITER,TOL,H,TST,TF,TIME1(260),TIME2(100)

CALL INPUTS(Y)

CALL LOADA

PARAMETERS FOR FIRST STEP

CALL LOADMA

INTRODUCTION

MATRIX A DETERMINES CONCENTRATIONS IN THE RINGS. SEE TEXT

CALL LOADA

INTRODUCTION

10 CALL DGEAR(NSR,DIFFUN,DJAC,T,H,Y,XEND,TOL,METH,...

IF(IER.NE.0) GO TO 999

IF CALCULATION STOPPED FOR DATA RECORDING WRITE ON SCRATCH FILE 8. OTHERWISE UPDATE PHOTOCHEMICAL RATE CONSTANTS
C CHECK IF CALCULATION IS FINISHED
C
IF(XEND.EQ.TF) GOT050
KNT1 = KNT1 + 1
C UPDATE PHOTOCHEMICAL RATE CONSTANTS IF REQUIRED
C
30 IF(XEND.LT.TIME2(KNT2)) GOT040
CALL PRATE2
KNT2 = KNT2 + 1
C CHECK WHEN NEXT TO STOP CALCULATION
C
40 XEND = DMIN1(TIME1(KNT1),TIME2(KNT2))
GOTO10
C END OF INTEGRATION LOOP
C
50 ENDFILE 8
CALL REPORT
CALL EXIT
C ERROR MESSAGES
C
999 IF(IER.GT.33) GOT0920
998 IF(MITER.NE.1) GOT0910
997 IIER = IIER + 1
996 IF(IER.GT.10) GOT0910
995 GOT0920
990 WRITE(6,901) MITER, IIER
989 WRITE(6,902)
988 WRITE(6,903)
987 PAUSE
986 GOT020
985 WRITE(6,904) IER, T, H
984 WRITE(6,903)
983 PAUSE
982 GOT020
981 WRITE(6,904) IER, T, H
980 WRITE(6,903)
979 PAUSE
978 GOT020
977 WRITE(6,904) IER, T, H
976 WRITE(6,903)
975 PAUSE
974 GOT020
973 WRITE(6,904) IER, T, H
972 WRITE(6,903)
971 PAUSE
970 GOT020
969 WRITE(6,904) IER, T, H
968 WRITE(6,903)
967 PAUSE
966 GOT020
965 WRITE(6,904) IER, T, H
964 WRITE(6,903)
963 PAUSE
962 GOT020
961 WRITE(6,904) IER, T, H
960 WRITE(6,903)
959 PAUSE
958 GOT020
957 WRITE(6,904) IER, T, H
956 WRITE(6,903)
955 PAUSE
954 GOT020
953 WRITE(6,904) IER, T, H
952 WRITE(6,903)
951 PAUSE
950 GOT020
949 WRITE(6,904) IER, T, H
948 WRITE(6,903)
947 PAUSE
946 GOT020
945 WRITE(6,904) IER, T, H
944 WRITE(6,903)
943 PAUSE
942 GOT020
941 WRITE(6,904) IER, T, H
940 WRITE(6,903)
939 PAUSE
938 GOT020
937 WRITE(6,904) IER, T, H
936 WRITE(6,903)
935 PAUSE
934 GOT020
933 WRITE(6,904) IER, T, H
932 WRITE(6,903)
931 PAUSE
930 GOT020
929 WRITE(6,904) IER, T, H
928 WRITE(6,903)
927 PAUSE
926 GOT020
925 WRITE(6,904) IER, T, H
924 WRITE(6,903)
923 PAUSE
922 GOT020
921 WRITE(6,904) IER, T, H
920 WRITE(6,903)
919 PAUSE
918 GOT020
917 WRITE(6,904) IER, T, H
916 WRITE(6,903)
915 PAUSE
914 GOT020
913 WRITE(6,904) IER, T, H
912 WRITE(6,903)
911 PAUSE
910 GOT020
909 WRITE(6,904) IER, T, H
908 WRITE(6,903)
907 PAUSE
906 GOT020
905 WRITE(6,904) IER, T, H
904 WRITE(6,903)
903 PAUSE
902 GOT020
901 FORMAT(' IER = ', I2, ' AT TIME ', F10.3/}
900 FORMAT(' ' THIS ERROR OCCURRED ', I3, ' TIMES')
900 FORMAT(' CHECK IMSL MANUAL FOR POTENTIAL REMEDY')
901 FORMAT(' IF THIS IS A TERMINAL RUN, CONTINUATION IS ',
902 FORMAT(' POSSIBLE BY A COMMAND RESTART')
903 FORMAT(' IER = ', I3, ' AT TIME ', F10.3, ' WITH H = ', F10.3)}
SUBROUTINE INPUTS(Y)

INPUTS READS ALL INPUT INFORMATION REQUIRED BEFORE START OF THE CALCULATION, EXCEPT THE REACTION MECHANISM AND THE PHOTOCHEMICAL RATE CONSTANT DATA. THE LATTER TWO ARE MANAGED BY SUBROUTINES RMECH AND PRATEI RESPECTIVELY.

THE REQUESTED OUTPUT AFTER THE CALCULATION REQUIRES ALSO INPUT WHICH IS MANAGED BY SUBROUTINE REPORT.

IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION Y(200)
COMMON /CHEM/R(41),P2(41),SPECIE(21),YO(20),PC2(40,20),IC1(40),
*IC11(3,40),IC2(20),PC22(40,20)
COMMON /MATA/A(30),BYZ
COMMON /NUMBERS/NS,NRI,NR,NR1M1,NR12,NR13,NRI1P1,NSRNSR,NSR
COMMON /WORK/TITLE(I0),TT(II),SAVE(10,40),PSAVE(7,40),
*T(210),Q(20),SP(20)
COMMON /INTEGR/METH,MITER,TOL,H,TST,TF,TIME1(260),TIME2(100)

C TITLE AND COMMENTS
ONE LINE OF 80 CHARACTERS IS ALLOWED

C********** INPUT 1 : FORMAT(10A8)**********
10 READ(5, 1) TITLE

C CONTROL PARAMETERS FOR CALCULATION
THES PARAMETERS DETERMINE CALCULATION METHOD IN SUBROUTINE OGEAR, SEE EXPLANATION IN IMSL HANDBOOK

C RECOMMENDED VALUES ARE: METH=2, MITER=1, TOL=1.E-3, H=.1 E-4

C********** INPUT 2 : FORMAT(4Gl0.3) **********
READ(5,2) METH,MITER,TOL,H

C TIME VARIABLES AND TEMPERATURE
TF : FINAL TIME OF CALCULATION IN MINUTES
TA : TIME INTERVAL FOR REPORTING CALCULATION RESULTS
TST: TIME OF DAY AT TO IN FORMAT XX.YY WHERE XX=HOURS AND YY=MINUTES
TT : VECTOR OF TIMES IN THE CALCULATION THAT CALCULATION RESULTS ARE REQUESTED BEYOND THE TA INTERVALS
NOTE IN SUBROUTINE REPORT THAT THE TT VALUES ARE USED AS REFERENCE POINTS FOR CONVERSION RATE CALCULATIONS
KNT: NUMBER OF POINTS IN TT (MAXIMUM 10)
TK : TEMPERATURE IN DEGREES K

C********** INPUT 3 : FORMAT(BG10.3) **********
READ(5,2) TO,TA,TST,KNT,(TT(I), 1=I,KNT),TK

C CALCULATE THE TIMES AT WHICH CALCULATION RESULTS ARE TO BE PRINTED AND PUT IN VECTOR TIME!

C NOTE THAT AT THE END OF THE CALCULATION ONLY AT THESE TIMES DATA WILL BE AVAILABLE

KNT+1
T+TO
113

181  J=1
182  TIME1(1)=T+H
183  DO 50 I=1,260
184  T=T+TA
185  IF(T.GT.TF) T=TF
186  20 IF(T.LT.TT(J)) GOTO30
187  KNT1=KNT1+1
188  TIME1(KNT1)=TT(J)
189  J=J+1
190  IF(TIME1(KNT1).EQ.T) GOTO40
191  GOTO20
192  30 KNT1=KNT1+1
193  TIME1(KNT1)=T
194  40 IF(T.EQ.TF) GOTO60
195  IF(KNT1.EQ.260) GOTO90
196  50 CONTINUE
197
198  C DETERMINE TTK = 298./TK
199  C 60 TTK=298./TK
200
201  C REACTION MECHANISM AND RATE CONSTANTS
202  C PHTFGL IS AN INDICATOR WHETHER TIME DEPENDENT PHOTO CHEMICAL
203  C RATE CONSTANTS ARE USED (.TRUE.: YES. FALSE.: NO)
204  C RATE CONSTANTS ARE USED (.TRUE.: YES. FALSE.: NO)
205  C
206  C*********** INPUT 4: SEE SUBROUTINE RMECH ***********
207  CALL RMECH(PHTFGL)
208  C CALCULATE RATE CONSTANTS AT TEMPERATURE TK
209  C REMEMBER THAT R1(J) IS TO BE IN PPM-PRESSURE AT 298 DEGREE K
210  C
211  DO 70 J=1,NR
212  IF(IC1(J).GE.0) R1(J)=R1(J)*TTK**(IC1(J)-1)*DEXP(-R2(J)/TK)
213  70 CONTINUE
214
215  C PLUME PARAMETERS AND NUMBER OF RINGS
216  C NR1: NUMBER OF CONCENTRIC RINGS DIVIDING PLUME CROSS SECTION
217  C VEL: WIND SPEED IN M/MIN
218  C AYZ,BYZ: PLUME DISPERSION PARAMETERS ACCORDING TO THE
219  C FORMULA SIGMA(Y)*SIGMA(Z) = AYZ**2*BYZ
220  C WHERE SIGMA(Y) AND SIGMA(Z) IN METERS
221  C
222  C*********** INPUT 5: FORMAT(4G10.3) ***********
223  C
224  C READ(5.2) NRI,VEL,AYZ,BYZ
225  C
226  C DERIVED NUMBERS
227  C
228  C
229  C
230  C
231  C
232  C
233  C
234  C
235  C
236  C
237  C
238  C
239  DO 80 I=1,NRI
240  VN=DFLOAT(NRI-1)
C SOURCE EMISSION AND INITIAL PLUME PROFILE
C SPEC : SPECIES IDENTITY, E.G. "SO2", "NO"
C QQ : EMISSION RATE IN UNITS OF PPM/MIN. THE
C CONVERSION FACTOR FROM KG/S IS:
C 1 KG/S = 4.92E+6 * (T/M) PPM/MIN
C T IN DEGREE K AND M = MOLECULAR WEIGHT
C LAST CARD MUST BE $ENDFILE
C
C ========== INPUT 6 : FORMAT(8B,2X,G10.3) ===========
DO 90 I=1,NSR
90 Y(I)=0.
KZ=0
100 READ(5,3,END=140) SPEC,QQ
DO 110 I=1,NS
IF (SPEC.EQ.SPECIE(I)) GO TO 120
110 CONTINUE
WRITE(6,903) SPEC
CALL EXIT
120 DO 130 M=NRI
130 Y(M)+=QQ/Q(M)
KZ=KZ+1
Q(KZ)=QQ
SP(KZ)=SPEC
GO TO 100
C AMBIENT CONCENTRATIONS
C SPEC : SPECIES IDENTITY
C YY : AMBIENT CONCENTRATION IN PPM-PRESSURE
C LAST CARD MUST BE $ENDFILE
C
C ========== INPUT 7 : FORMAT(8B,2X,G10.3) ===========
DO 140 I=1,NS
140 YO(I)=0.
150 READ(5,3,END=190) SPEC,YY
DO 170 I=1,NS
IF (SPEC.EQ.SPECIE(I)) GO TO 180
170 CONTINUE
WRITE(6,903) SPEC
CALL EXIT
180 YO(I)+=YY
GO TO 160
C ALL INPUT DATA ARE STORED ON SEQUENTIAL SCRATCH FILE 8
C ON ONE LINE.
C ALL CALCULATION RESULTS ARE ALSO STORED ON THIS FILE WITH
C EACH LINE REPRESENTING DATA AT A REPORTING TIME AS
C SPECIFIED IN VECTOR TIME1. SCRATCH FILE 8 MAY BE SAVED
C FOR LATER REFERENCE SINCE IT WILL CONTAIN ALL RELEVANT
C INFORMATION FROM THE CALCULATION
C REWIND 8
WRITE(8) TITLE,NS,NR,NRI,NSR,KNT,METH,MTER,TOL,H,TF,TA,
*(TS),KNT,T(I(I)),I=1,KNT),TK,VEL,AY2,AYZ,(SPECIE(I),I=1,NS),
*(Y(I),I=1,NSR),(YO(I),I=1,NS),KZ,(Q(I),SP(I),I=1,KZ),
$ENDFILE
C
*!(SAVE(I,J),I=1,10),R1(J),(PSAVE(I,J),I=1,7),J=1,MR)

RETURN

C ERROR MESSAGES

999 WRITE(6,901)

CALL EXIT

998 WRITE(6,902)

CALL EXIT

1 FORMAT(10A8)

2 FORMAT(8G10.3)

3 FORMAT(A8,2X,G10.3)

901 FORMAT(' ERROR: MORE THAN 10 VALUES FOR VECTOR TT')

902 FORMAT(' ERROR: COMBINED DATA FOR TO,TF,TA AND TT RESULT IN MORE',RPLM0314

903 FORMAT(' ERROR: INITIAL SPECIES ',A8,' DOES NOT APPEAR', RPLM0317

' IN MECHANISM')

END
SUBROUTINE RMECH(PHTFLG)

C RMECH READS THE CHEMICAL MECHANISM AND DERIVES THE PARAMETERS
C TO CONSTRUCT THE DIFFERENTIAL EQUATIONS IN SUBROUTINES DIFFUN
C AND DJAC

IMPLICIT REAL*8 (A-H,O-Z)
LOGICAL PHTFLG

COMMON /CHEM/ R(41),R2(41),SPECIE(21),YO(20),PC2(40,20),IC1(40),
IC1(3,40), IC11(3,40), IC2, IC22(40,20)
COMMON /NUMBERS/ NS,NRI,NR,NRIM1,NRI2,NRI3,NRIP1,NSRNSR,NSR
COMMON /WORK/
OUMMY(21),SAVE(400),PSAVE(200),S(10),PF(7)

DATA BLANK /8H /
PHTFLG=. FALSE.
NS=1
NR=0

00 10 IC1(J)=0

DO 10 1=1,20 PC2(J,N)=0.

SPECIE( 1 )=BLANK

READ IN 'REACTION-CARDS'; TWO AT A TIME
INPUT ON FIRST CARD: S(I,J),I=1,10
INPUT ON SECOND CARD: R1(J),R2(J),(PF(I,J),I=1,7)
5(1),5(2),5(3): REACTANTS
5(4) - 5(10) PRODUCTS
R1(I) PREEXPONENTIAL TERM OF RATE CONSTANT
R2(I) ACTIVATION ENERGY OF THE REACTION DIVIDED BY AVOGADRO'S NUMBER R
MULTIPLICATION FACTORS FOR PRODUCTS IF DIFFERENT FROM 1
THE VALUES FOR R1(J) SHOULD BE IN UNITS OF PPM-PRESSURE AT 298 DEGREE K,
IF PHOTOCHEMICAL REACTION THEN R1(J) SHOULD BE A MULTIPLE OF -1,
WHERE THE ABSOLUTE VALUE OF R1(J) IS THE 'ID' INDICATING WHICH OF THE (MORE THAN ONE)
IF APPLICABLE) PHOTOCHEMICAL REACTIONS OF S(1) IS MEANT. E.G. O3 -> 0(3P) OR O3 -> O(1D).
MATCH WITH THE INPUT DATA READ IN SUBROUTINE PRATE1
FURTHERMORE R2(I)/1000. WILL BE THE ATTENUATION FACTOR FOR THE PHOT. R. C. (E.G. DUE TO CLOUDS,
or IN CASE OF A COMPOSITE REACTION SUCH AS O3-> 2HO).
THE LAST CARD OF THIS SET MUST BE 'END OF FILE' OR A COMPLETELY BLANK CARD

*********** INPUT RM1 : FORMAT(10A8/2E12.4,7F8.4) ***********

20 NR=NR+1

READ(S(1),END=90) S(1),I=1,10,R1(NR),R2(NR),(PF(I),I=1,7)
IF(R(NR),EQ.0.) GO TO 90
IF(NR.GT.40) GO TO 999

DO 30 J=1,10

30 SAVE(I+NR-1)*10+I=1

DO 40 I=1,7

40 PSAVE(I+NR-1)*10+PF(I)

IJ=0

DO 50 I=1,9

50 DO J=1,NS

IF(S(I).EQ.BLANK) GO TO 80

DO 50 J=1,NS
J\text{J}=\text{J}
\text{I} f(S(\text{I}).\text{E}.S\text{PECIE(J))} \text{GO TO 60}
\text{S}C\text{EICIE(\text{NS})}=S(\text{I})
\text{NS}=\text{NS}+1
\text{I} f(\text{NS}.G{T}.21) \text{GO TO 998}
\text{S}P\text{ECIE(\text{NS})}=\text{BLANK}
\text{J} O\text{I} (\text{\text{I}.}G{T}.3) \text{GO TO 70}
\text{P}\text{C2(NR,JJ)} \text{PC2(NR,JJ)}}-\text{1}
\text{C} D\text{ETERMINE THE COMPOSITE CODE FOR THE REACTANTS}
\text{C} OF THE REACTION, IC11(I). IC1(J) IS THE SUM OF THE REACTANTS
\text{C} 11-11.1
\text{I} \text{C1(NR)}-\text{I I}
\text{I} \text{C11(I,NR)}-\text{JJ}
\text{GO TO 80}
\text{70 I} f(PF(\text{I-3)).\text{E}.O.) PF(\text{I-3)}=1.
\text{PC2(NR,JJ)} \text{PC2(NR,JJ)}}+PF(\text{I-3)}
\text{80 C} CONTINUE
\text{C} \text{I F THIS IS A PHOTOCHEMICAL REACTION (R1(I) .LT. 0.)}
\text{C} \text{SET IC1} = -IC1
\text{C} \text{I} f(\text{R1(NR)}=0.) \text{GO TO 20}
\text{I} \text{C1(NR)}=\text{-IC1(NR)}
\text{PHTFLG}=\text{TRUE}.
\text{GO TO 20}
\text{90 NS=NS}-1
\text{NR=NR}-1
\text{C} D\text{ETERMINE REACTION MATRIX IC22(K,J),}
\text{C} WHEN IC22(K,J)=1, THEN SPECIES I PARTICIPATES IN REACTION J, AND
\text{C} PC2(K,J) IS THE MULTIPLICATION FACTOR IN THE REACTION EQUATION
\text{C} WITH PC2(K,J)=1 FOR REACTANTS, AND PC2(K,J) IS POSITIVE.
\text{C} 10 \text{LE. 10}
\text{DO 110 J=1,NS}
\text{K=0}
\text{DO 100 I=1,NR}
\text{I} f(PC2(\text{I,J)}=0.) \text{GO TO 100}
\text{K}=K+1
\text{IC22(K,J)}=1
\text{PC2(K,J)}=PC2(\text{I,J)}
\text{100 CONTINUE
\text{110 IC2(J)}=K
\text{C} \text{ENTER TABLE OF PHOTOCHEMICAL RATE CONSTANTS}
\text{C} \text{IF PHOTOCHEMICAL RATE CONSTANTS ARE}
\text{C} \text{CONSTANT FOR THIS CALCULATION, THIS CALL IS IGNORED IF THE}
\text{C} \text{CORRECT VALUES ARE ALREADY READ FROM THE REACTION CARDS}
\text{C} \text{C} \text{ERROR MESSAGES
\text{C} 999 \text{WRITE(6,901)}}
CALL EXIT
998 WRITE(6, 902)
CALL EXIT
1 FORMAT(10A8/2E12.4,7F8.4)
901 FORMAT(' ERROR; ONLY 40 REACTIONS ARE ALLOWED. ')
902 FORMAT(' ERROR; ONLY 20 SPECIES ARE ALLOWED. ')
END
END OF FILE
SUBROUTINE PRATE1

PRATE1 READS THE TABLE OF PHOTOCHEMICAL RATE CONSTANTS IF NO CONSTANT VALUES ARE TO BE USED IN THE MECHANISM, AND PLACES THEM IN ARRAY RTCNST, IN THE ORDER OF CALLING DETERMINED IN SUBROUTINE RMECH. AT EVERY TIME DURING THE CALCULATION THAT THE PHOTOCHEMICAL RATE CONSTANTS NEED TO BE UPDATED, THE MAIN PROGRAM CALLS THE ENTRY POINT PRATE2 IN THIS SUBROUTINE, AND THE APPROPRIATE VALUES FROM ARRAY RTCNST ARE SUBSTITUTED IN THE RATE CONSTANT VECTOR RI(I).

IMPLICIT REAL*8 (A-H,Q-Z)

COMMON /CHEM/ R1(41), R2(41), SPECIE(21), YO(20), PC2(40,20), IC1(40), IC1(3,40), IC2(20), IC2(20)

COMMON /NUMBRS/ NS, NRI, NR, NRI1, NRI2, NIRP1, NRSR, NSR, NRSRNSR, NSR

COMMON /WORK/ DUMMY(561), SPECPH(20), F(20), ISPECP(20), II(20)

COMMON /INTEGR/ METH, MITER, TOL, H, TST, TF, TIME1(260), TIME2(100)

DIMENSION RTCNST(100,20)

DO 10 I = 1, 20
   RTCNST(I,1) = 20

C READ IN TABLE OF PHOTOCHEMICAL RATE CONSTANTS

FIRST CARD:
"JFIRST, JLAST, JINC, NPR"

JFIRST: REAL TIME OF FIRST PHOTOCHEMICAL RATE CONSTANT
JLAST: TOTAL NUMBER OF RATE CONSTANTS GIVEN PER REACTION
JINC: TIME INTERVAL BETWEEN EACH PHOTOCHEMICAL RATE CONSTANT
NOTE THAT JINC CAN BE LARGER THAN HMAX (SEE MAIN FOR HMAX).
NPR: TOTAL NUMBER OF PHOTOCHEMICAL REACTIONS FOR WHICH DATA ARE IN TABLE

SECOND (AND THIRD, FOURTH IF NECESSARY) CARD:
"REACTANT.ID (FORMAT:A8,I2) - SEE SUBROUTINE RMECH"

A MAXIMUM OF 8 SETS A MAXIMUM OF 20 PHOTOCHEMICAL REACTIONS IS ALLOWED
A MAXIMUM OF 99 RATE CONSTANTS PER REACTION IS ALLOWED

******* INPUT P1 : FORMAT(415) *******

READ(5,1) JFIRST, JLAST, JINC, NPR
IF(JLAST.GT.99) GO TO 999
IF(NPR.GT.20) GO TO 998
IENO = JLAST

******* INPUT P2 : FORMAT(B(AB,12)) *******

READ(5,2) (SPECPH(I), ISPECP(I), I = 1, NPR)

C SORT OUT DATA FROM THE TABLE AND MATCH EACH REACTION WITH ITS
C APPEARANCE IN THE REACTION MECHANISM

KTOT = 0
DO 40 J = 1, NR
   IF(IC1(J).GE.0) GO TO 40

IF THIS IS A PHOTOCHEMICAL REACTION THEN IC1(I,J) IS THE
INDEX OF THE REACTANT, THE ABSOLUTE VALUE OF R1(I,J) IS THE
ID, AND R2(I,J) IS THE ATTENUATION FACTOR. SEE SUBROUTINE RMECH

L = IC1(I,J)

SPEC = SPECIE(L)
LSPEC = IDINT(DABS(R1(I,J)))

IF(SPEC.NE.SPECPH(I)) GO TO 20
510  IF(LSPECP.EQ.ISPECP(I)) GO TO 30
511  20 CONTINUE
512  WRITE(*,903) J,R1(J),R2(J),SPEC
513  CALL EXIT
514  30 KTOT=KTOT+1
515  40 CONTINUE
516  CALL EXIT
517  40 CONTINUE
518  50 CONTINUE
519  60 CONTINUE
520  C
521  C C READ IN THE PHOTOCHEMICAL RATE CONSTANTS TABLE AND PUT IN
522  C C MATRIX RTCNST(I,J), WHERE
523  C C I : TIME INDEX.
524  C C I=1 : PHOT. R.C. AT SUNRISE
525  C C I=K : PHOT. R.C. (K-1)*JINC MINUTES AFTER SUNRISE
526  C C I=LAST : PHOT. R.C. AT SUNSET, BEFORE SUNRISE
527  C C I=JEND : RTCNST=0. AFTER SUNSET, BEFORE SUNRISE
528  C C J : REACTION INDEX, IN ORDER OF APPEARANCE IN THE MECHANISM
529  C C PROGRAM EXPECTS 5 RATE CONSTANTS PER CARD (MAXIMUM)
530  DO 60 I=1,NPR
531  FF=F(I)
532  IF(FF.EQ.0.) FF=1.
533  C******* INPUT P3 ; FORMAT(5E15.4) ********
534  READ(5,3) (RTCNST(L,J),L=1,JLAST)
535  DO 50 L=1,JLAST
536  RTCNST(L,J)=FF*RTCNST(L,J)
537  60 RTCNST(JEND,J)=0.
538  C
539  C DETERMINE VECTOR TIME2, CONTAINING THE TIMES OF DAY WHEN
540  C THE PHOTOCHEMICAL RATE CONSTANTS ARE UPDATED
541  TS1=DFLOAT(IDINT(TST))
542  TS2=100.*(TST-TS1)
543  TSTART=60.*TS1+TS2
544  DINC=DFLOAT(JINC)
545  J1=JFIRST/100
546  J2=JFIRST/100+1
547  TFIRST=60.*DFLOAT(J1)+DFLOAT(J2)
548  T=TFIRST
549  TLAST=TFIRST+DINC+DFLOAT(JLAST)
550  IF(TSTART.LT.TFIRST.OR.TSTART.GE.TLAST) GOTO110
551  DO TO KT=1,JLAST
552  T=T+DINC
553  IF(T.GT.TLAST) GOTO100
554  IF(T.GT.TSTART) GOTO80
555  70 CONTINUE
556  80 T=T-TSTART
557  TIME2(I)=T
558  L=KT+1
559  90 DO 100 L=LJ,LJLAST
560  T=T+DINC
561  LT=LT+1
562  100 CONTINUE
563  IF(LT.GT.JLAST) GOTO997
564  TIME2(LT)=T
565  IF(LT.GT.TFIRST) GOTO120
566  100 CONTINUE
567  LT=LT+1
568  997 IF(LT.GT.JLAST) GOTO997
569  TIME2(LT)=1440.-LAST+TFIRST+T
570  999 CONTINUE
IF (TIME2(LT).GT.TF) GOTO120
L+1
GOTO90
110 KT=0
WRITE(6,GE.TLAST) TSTART+TSTART=1440.
GOTO90
120 IF(KT.EQ.0) KT=JEND
ENTRY PRATE2
C
ENTRY POINT PRATE2
C THIS ENTRY POINT IS CALLED BY THE MAIN PROGRAM WHEN THE
C PHOTOCHEMICAL R.C. NEED UPDATING. BEFORE THE START OF THE
C CALCULATION THE RATE CONSTANTS AT TSTRT (SEE SUBROUTINE
C INPUTS) ARE PLACED IN RATE CONSTANT VECTOR R1(I)
KNT=O
DO 130 K=1, NR
130 R(K)=RKCNST(KT,KNT)
IF(KNT.EQ.KTOT) GOTO140
130 CONTINUE
KT+KT+1
IF(KT.EQ.JEND+1) KT=1
RETURN
C ERROR MESSAGES
997 WRITE(6,904)
998 CALL EXIT
999 WRITE(6,902)
1 CALL EXIT
1 FORMAT(4I5)
2 FORMAT(8(A8,I2))
3 FORMAT(8(E15.5))
901 FORMAT(' ERROR: NPR NOT ALLOWED LARGER THAN 20: ')
902 FORMAT(' ERROR: JLAST NOT ALLOWED LARGER THAN 99: ')
903 FORMAT(' ERROR: FOUND PHOTOCHEMICAL REACTION IN MECHANISM: ')
904 FORMAT(' ERROR: MAXIMUM OF 100 PHOTOCHEMICAL RATE CONSTANT UPDATES: ')
905 FORMAT(' ERROR: MAXIMUM OF 100 PHOTOCHEMICAL RATE CONSTANT UPDATES: ')
906 " REACTION CARD DATA (RATES AND REACTANT): ' ,2E15.4,AB)
907 " ARE ALLOWED: ')
908 END
SUBROUTINE LOAOA
C
C LOAOA DETERMINES THE MATRIX OF COEFFICIENTS ALPHA; SEE TEXT
C
IMPLICIT REAL*8 (A-H,Q-Z)
COMMON /MATA/ A(30)
COMMON /NUMBS/ NS,NRI,NR,NRIM1,NRI2,NRI3,NRIP1,NSRNSR,NSR
COMMON /WORK/ SUMA(10),AREA(10)
VN=DFLOAT(NRIM1)
10 AREA(1)=OLOG((VN+1)/VN)
00 10 M=2,NRIM1
VN=DFLOAT(NRI-M)
10 AREA(M)=OLOG((VN+1)/VN)
00 20 M=2,NRI
20 SUMA(M)=SUMA(M-1)+AREA(M)
AREA(NRI)=2.*AREA(NRIM1)
SUMA(NRI)=SUMA(NRIM1)+AREA(NRI)
C FIRST RING
A(1)=-AREA(2)/(AREA(2)-AREA(1))
A(NRIP1)=-A(1)
C INTERMEDIATE AND OUTSIDE RINGS
DO 30 M=2,NRIM1
30 A(M+NRI)=AREA(M+1)*SUMA(M)/((AREA(M+1)-AREA(M))*AREA(M))
A(NRIP1)=SUMA(NRI)/AREA(NRI)
00 40 M=2,NRI
40 A(M+NRI2)=AREA(M+1)*SUMA(M-1)/((AREA(M)-AREA(M-1))*AREA(M))
A(NRIP1)=A(M+NRI)+A(M+NR12))
RETURN
END
END OF FILE
SUBROUTINE OIFFUN(NSR,T,Y,OY)
OIFFUN CONSTRUCTS THE DIFFERENTIAL EQUATIONS FOR THE CALCULATION AT EACH INTEGRATION STEP. I.E. AT TIME T IN THE INTEGRATION).

IMPLICIT REAL*8 (A-H.O-Z)

DIMENSION Y(1),OY(1)

COMMON /CHEM/ R1(41),R2(41),SPECIE(21),YO(20),PC2(40,20),IC1(40),ICI1(3,40),IC2(20),IC22(40,20)

COMMON /MAT/ A(30),BYZ

COMMON /NUMB/ NS,NRI,NR,NRIM1,NRI2,NRI3,NRIP1,NSRNSR

COMMON /WORK/ RR(400),YY(220),AA(30)

PUT ALL VARIABLES, INCLUDING AMBIENTS IN ONE VECTOR

DO 10 I=1,NSR
10 YY(I)=Y(I)

DO 20 I=1+NSR
20 YY(J)=YO(I)

PREPARE AA MATRIX AT TIME T

VLDA=BYZ/T

DO 30 M=1,NRI3
30 AA(M)=VLDA*A(M)

DETERMINE RATE OF EACH REACTION EQUATION

DO 50 J=1,NR
50 R=R1(J)

11=(M-1)*NS+1
12=M*NS

BETA=AA(M)
GAMMA=AA(M+NRI)

DO 70 I=1,NS
70 S=BETA*YY(I+M2)+GAMMA*YY(I+M3)

DO 90 J=IC2(I)
90 S=S+PC2(J,I)*RR(K+M1)

70 DY(I+M2)=S

DO 80 M=1.NRIM1
80 ALPHA=AA(M+NRI2+1)

11=(M-1)*NS+1
12=M*NS

DO 100 M=1.NRIM1
100 RR(J+M1)=R

CONSTRUCT DIFFERENTIAL EQUATIONS FOR EACH SPECIES

DO 70 M=1,NRI
70 M1=(M-1)*NR
M2=(M-1)*NS

BETA=AA(M)
GAMMA=AA(M+NRI)

DO 90 I=1,NS
90 S=BETA*YY(I+M2)+GAMMA*YY(I+M3)

DO 110 J=IC2(I)
110 S=S+PC2(J,I)*RR(K+M1)

DY(I+M2)=S

DO 120 M=1.NRIM1
120 RR(J+M1)=R
<table>
<thead>
<tr>
<th>Line</th>
<th>Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>713</td>
<td>L=I+NS</td>
<td></td>
</tr>
<tr>
<td>714</td>
<td>80 DY(L)<em>DY(L)+ALPHA</em>YY(I)</td>
<td></td>
</tr>
<tr>
<td>715</td>
<td>RETURN</td>
<td></td>
</tr>
<tr>
<td>716</td>
<td>END</td>
<td></td>
</tr>
</tbody>
</table>

END OF FILE
SUBROUTINE DJAC(NSR,T,V,Y)

DJAC DETERMINES EXPLICITLY THE JACOBIAN AT EACH INTEGRATION STEP. I.E., AT TIME T IN THE INTEGRATION, DJAC IS ONLY CALLED WHEN MITER=1. SEE IMSL MANUAL AND SUBROUTINE INPUTS.

IMPLICIT REAL*8 (A-H,O-Z)

DIMENSION V(*),VY(*),VZ(*),VZ2(*)

COMMON /CHEM/ R1(41),R2(41),SPECIE(21),YO(20),PC2(40,20),IC1(40),IC2(20),IC22(40,20)

COMMON /MATA/ A(30),BYZ

COMMON /NUMBRS/ NS.NRI,NR,NRIM1,NRI2,NRI3,NRI5,NSRNSR

COMMON /WORK/ RR(400),YY(220),AA(30)

PUT ALL VARIABLES, INCLUDING AMBIENTS IN ONE VECTOR

DO 10 I=I,NSR

YY(I)=Y(I)

DO 20 J=I+NSR

YY(J)=YO(I)

PREPARE AA MATRIX AT TIME T

V1DA=BYZ/T

DO 30 M=I,NRI

AA(M)=V1DA*A(M)

DETERMINATION OF THE JACOBIAN

DO 40 I=I,NSR_NS

1(1)=0.

DO 100 M=I,NRI

BETA=AA(M)

GAMMA=AA(M..NRI)

IF(M.LT.NRI) ALPHA=AA(M..NRI+1)

M(M-1)=NS

M2=(M-1)*NS

M3=(NSR+1)*M2

DO 100 I=I,NSR

IM=(IM-1)*NSR

IF(M.GT.1) W(I)=W(I-1)+NSR*W

IF(M.GT.1) W(I)=W(I-1)+NSR*W

DO 70 J=1,NR

R=R+YY(J)*J

DO 60 T=1,NSR

PMULT=0.

DO 50 T=1,NSR

PMULT=PMULT+T

DO 40 T=1,NSR

PMULT=PMULT+T

DO 30 T=1,NSR

PMULT=PMULT+T

R=R+YY(J)*J

GO TO 10

10 CONTINUE
779    DO 80 J=1,J1
780       K=IC22(J,I)
781       S=S+PC2(J,I)*RR(K)
782       W(IW)=S
783    100 CONTINUE
784    RETURN
785    END
SUBROUTINE REPORT

REPORT WRITES THE OUTPUT REQUESTED FOR THE CALCULATION.

INPUT IS REQUIRED TO INDICATE TYPE OF INFORMATION AND CALCULATION RESULTS THAT ARE REQUESTED. THIS SUBROUTINE FUNCTIONS INDEPENDENTLY FROM THE REST OF THE PROGRAM. SINCE ALL DATA ARE STORED ON SCRATCH FILE 8, WHICH IS USED BY REPORT TO WRITE THE OUTPUT, REPORT CAN BE USED INDEPENDENTLY FROM THE REST OF THE PROGRAM TO OBTAIN DATA FROM EARLIER CALCULATIONS IF SCRATCH FILE 8 HAD BEEN SAVED. SEE TEXT AND SUBROUTINE INPUTS.

IMPLICIT REAL*8 (A-H,Q-Z)

COMMON /WORK/ A(10),Q(20).SP(20).
-TEXT( 10).SAVE(10,40).TT(10),S(3.2).PSAVE(7,40).N( 10,2).LBAL(2)
DATA BLANK /8H /
REWIND 8
READ(5,2) TEXT,NS,NR,NRI.NSR,NREC,METH.MITER.TOL,H,TO.TA.(TT(I).I=1.KNT),TK.VEL,AYZ.BYZ,(SPECIE(I),I=1,NS), *(SAVE(I,J),J=1,10),R(J),PSAVE(I,J),J=1,10)
NRIM1=NRI-1
WRITE(6,1) TEXT
C INDICATE WHAT OUTPUT IS DESIRED
C KCONT .NE. 0 CONTROL PARAMETERS, INCLUDING TIMING
C KIN1T .NE. 0 INPUT DATA
C KSPEC .NE. 0 SPECIES IN MECHANISM
C KMECH .NE. 0 CHEMICAL MECHANISM
C KBAL .NE. 0 MASS BALANCE AND/OR CONVERSION PERCENTAGE CALCULATION
C KDAT .NE.0 STRAIGHTDATA
C INPUT R1 FORMAT(6I5) ********
READ(5,2) KCONT,KINIT,KSPEC,KMECH,KBAL,KDAT
IF(KCONT.EQ.0) GOTO20
C PRINT CONTROL PARAMETERS
WRITE(6,3) METH.MITER.TOL,H,TO.TA.(TT(I).I=1.KNT)
20 IF(KINIT.EQ.0) GOTO20
C PRINT INPUT SPECIFICS OF PLUME CALCULATION
WRITE(6,4) TST,TK.VEL,AYZ.BYZ,(SP(I).Q(I).I=1.KZ)
WRITE(6.5) lI,I cl,NRI) R0 40 L·l.KZ
IF(SP(L).EQ.SPECIE(I)) GO TO 40
WRITE(6,6) SPECIE(I),YO(I)
50 CONTINUE
C PRINT CHEMICAL SPECIES LIST
WRITE(6,8) (SPECIE(I),I=1,NS)
C*********** INPUT R1 : FORMAT(6I5) ***********
C MASS BALANCE (M.B.), AND CONVERSION RATE (C.R.) CALCULATION
C M.B. AND C.R. ARE CORRECTED FOR ENTRAINMENT OF AMBIENT AIR
C C.R. IS EXPRESSED IN I HOUR^-1. ASSUMING FIRST ORDER KINETICS
C C.R. IS CALCULATED INITIALLY WITH RESPECT TO T0 (=TREF), AND
C WITH RESPECT TO THE CURRENT VALUE OF TT (=TREF).
C WHEN IN((REACTANTS)/(REACTANTS+PRODUCTS))=A THE FORMULA FOR
C BECOMES:
C
C C.R. = A(TREF)/A(T) • 1/(T-TREF) • 60 • 100
C
C THIS SECTION REQUIRES ADDITIONAL INPUT
C
70 IF(KMECH.EQ.0) GO TO 90
C PRINT CHEMICAL MECHANISM
C DO 80 J=1,NR
C WRITE(6,9) TST,TK
C SUMA=0.
C DO 100 I=1,NRIM1
C V=DFLOAT(NRI-I)
C A(I)=DLOG(V+1.)/V
C SUMA=SUMA+A(I)
C A(NRI)=DLOG(4.0+00)
C SUMA=SUMA+A(NRI)
C F1=6.28·VEL·AYZ
C F2=F1+TO·BYZ·SUMA
C IF MASS BALANCE IS REQUESTED ONLY, ENTER:
C IF CONVERSION RATE IS REQUESTED, ENTER:
C WHEN THE MAXIMUM NUMBER FOR LBAL(1) AS WELL AS LBAL(2) IS 10
C THIS SECTION REQUIRES ADDITIONAL INPUT
C
100 READ(5,2,END=260) LBAl(I),LBAl(2)
C ENTER SPECIES LIST FOR LBAL(1) AND LBAL(2) IF NECESSARY;
C EACH LIST ON SEPARATE LINE
C
260 WRITE(6,10) TEXT(I),I=1,LL
C 110 READ(5,2,END=260) LBAl(1),LBAl(2)
C REWIND 8
C READ(8)
C IND=1
C 120 LL=LBAl(IND)
C READ(5,13) (TEXT(I),I=1,LL)
C S(1,IND)=0.
C S(2,IND)=0.
C DD 150 J=1,LL
DO 130 I = 1, NS
   IF (SPECIE(I).EQ.TEXT(J)) GO TO 140
   WRITE(6,901) TEXT(J)
   IF (IND.EQ.1.AND.LBAL(2).NE.0) READ(5,13)
   GO TO 110
   WRITE(6,903) (TEXT(I),I=1,LL)
   IF (LBAL(2).EQ.0) GO TO 180
   IND = 2
   GO TO 120
RPLM0908
RPLM0909
RPLM0910
RPLM0911
RPLM0912
RPLM0913
RPLM0914
RPLM0915
RPLM0916
RPLM0917
RPLM0918
RPLM0919
RPLM0920
RPLM0921
RPLM0922
RPLM0923
RPLM0924
RPLM0925
RPLM0926
RPLM0927
RPLM0928
RPLM0929
RPLM0930
RPLM0931
RPLM0932
RPLM0933
RPLM0934
RPLM0935
RPLM0936
RPLM0937
RPLM0938
RPLM0939
RPLM0940
RPLM0941
RPLM0942
RPLM0943
RPLM0944
RPLM0945
RPLM0946
RPLM0947
RPLM0948
RPLM0949
RPLM0950
RPLM0951
RPLM0952
RPLM0953
RPLM0954
RPLM0955
RPLM0956
RPLM0957
RPLM0958
RPLM0959
RPLM0960
RPLM0961
RPLM0962
RPLM0963
RPLM0964
RPLM0965
RPLM0966
RPLM0967
GO TO 210
DO 280 I=1,NS
IF(SPEC.EQ.SPECIE(I)) GO TO 290
WRITE(6,20) SPEC,
REWIND 8
READ(8) NSPEC
J=1,NS
READ(8,10) T(Y(I),I=1,NS)
WRITE(6,21) T(Y(I),I=1,NS,NS)
300 CONTINUE
310 RETURN
1 FORMAT(I10.10X,10E8,/' * Signature */)
2 FORMAT(1D15)  
3 FORMAT(1H10,5/,'CONTROL PARAMETERS':/T10,'METH',T40,12/T10,  
'METER',T40,12/T10,'TDL',T40,10.3/T10,'H',T40,10.3/=  
'T10',T-START',T40,10.3/T10,'T-FINAL',T40,10.3/=  
'T10',T-INCREMENT',T40,10.3/T10,'T-REF (VECTOR T)',T40,  
'T(10.3,5X)/T40(5E10.3X))'  
4 FORMAT(1HO,T5,'TIME OF DAY AT TSTART (HRS)',T35,F10.2/)  
5 FORMAT(1HO,T5,'AMBIENT TEMPERATURE (KELVIN)',T35,F10.2/)  
6 FORMAT(1H10,'Initial Plume Profile'/IX,'Species'-T30,'RING NR'/  
7 FORMAT(1X,AB,1X,10E10.3)  
8 FORMAT(1H10,T5,'AMBIENT MIXING RATIOS'/  
9 FORMAT(1H10,T5,'Species List of Chemical Mechanism'/4(IX,5(I2,","),  
"AB',4X/)')  
10 FORMAT(I10,'CHEMICAL MECHANISM'/  
11 FORMAT(I10,T30,'RATE COEFFICIENTS AT TIME ',F6.2,' AND TEMPERATURE ',F6.1,  
12 FORMAT(5E10.3)  
13 FORMAT(12,'Degree K'/1X,'Rate Constants'/  
14 FORMAT(12,4E10.3,2(IX,AB))  
15 FORMAT(1X,1F12.4,3(2X,AB)),  
16 FORMAT(4(1X,1F12.4,1F12.4))  
17 FORMAT(1X,1F12.4,3(2X,AB))  
18 FORMAT(12,4E10.3)  
19 FORMAT(12,3E10.3)  
20 FORMAT(12,4E10.3)  
21 FORMAT(12,4E10.3)  
22 FORMAT(12,4E10.3)  
23 FORMAT(12,4E10.3)  
24 FORMAT(12,4E10.3)  
25 FORMAT(12,4E10.3)  
26 FORMAT(12,4E10.3)  
27 FORMAT(12,4E10.3)  
28 FORMAT(12,4E10.3)  
29 FORMAT(12,4E10.3)  
30 FORMAT(12,4E10.3)  
31 FORMAT(12,4E10.3)  
32 FORMAT(12,4E10.3)  
33 FORMAT(12,4E10.3)  
34 FORMAT(12,4E10.3)  
35 FORMAT(12,4E10.3)  
36 FORMAT(12,4E10.3)  
37 FORMAT(12,4E10.3)  
38 FORMAT(12,4E10.3)  
39 FORMAT(12,4E10.3)  
40 FORMAT(12,4E10.3)  
41 FORMAT(12,4E10.3)  
42 FORMAT(12,4E10.3)  
43 FORMAT(12,4E10.3)  
44 FORMAT(12,4E10.3)  
45 FORMAT(12,4E10.3)  
46 FORMAT(12,4E10.3)  
47 FORMAT(12,4E10.3)  
48 FORMAT(12,4E10.3)  
49 FORMAT(12,4E10.3)  
50 FORMAT(12,4E10.3)  
51 FORMAT(12,4E10.3)  
52 FORMAT(12,4E10.3)  
53 FORMAT(12,4E10.3)  
54 FORMAT(12,4E10.3)  
55 FORMAT(12,4E10.3)  
56 FORMAT(12,4E10.3)  
57 FORMAT(12,4E10.3)  
58 FORMAT(12,4E10.3)  
59 FORMAT(12,4E10.3)  
60 FORMAT(12,4E10.3)  
61 FORMAT(12,4E10.3)  
62 FORMAT(12,4E10.3)  
63 FORMAT(12,4E10.3)  
64 FORMAT(12,4E10.3)  
65 FORMAT(12,4E10.3)  
66 FORMAT(12,4E10.3)  
67 FORMAT(12,4E10.3)  
68 FORMAT(12,4E10.3)  
69 FORMAT(12,4E10.3)  
70 FORMAT(12,4E10.3)  
71 FORMAT(12,4E10.3)  
72 FORMAT(12,4E10.3)  
73 FORMAT(12,4E10.3)  
74 FORMAT(12,4E10.3)  
75 FORMAT(12,4E10.3)  
76 FORMAT(12,4E10.3)  
77 FORMAT(12,4E10.3)  
78 FORMAT(12,4E10.3)  
79 FORMAT(12,4E10.3)  
80 FORMAT(12,4E10.3)  
81 FORMAT(12,4E10.3)  
82 FORMAT(12,4E10.3)  
83 FORMAT(12,4E10.3)  
84 FORMAT(12,4E10.3)  
85 FORMAT(12,4E10.3)  
86 FORMAT(12,4E10.3)  
87 FORMAT(12,4E10.3)  
88 FORMAT(12,4E10.3)  
89 FORMAT(12,4E10.3)  
90 FORMAT(12,4E10.3)  
91 FORMAT(12,4E10.3)  
92 FORMAT(12,4E10.3)  
93 FORMAT(12,4E10.3)  
94 FORMAT(12,4E10.3)  
95 FORMAT(12,4E10.3)  
96 FORMAT(12,4E10.3)  
97 FORMAT(12,4E10.3)  
98 FORMAT(12,4E10.3)  
99 FORMAT(12,4E10.3)  
100 FORMA
17 FORMAT(H0, T10, 'TIME', T23, 'DISTANCE', T39, 'TOTAL MASS', T51, 'AVER. M. R.')
18 FORMAT(1X, 2F15.4, 5X, 6E12.4)
19 FORMAT('MIXING RATIO FOR SPECIES ', A8, ' IN INDICATED RINGS')
21 FORMAT(F10.3, 10E10.3)
901 FORMAT('ERROR: SPECIES ', A8, ' NOT IN MECHANISM; DATAREQUEST')
13 FORMAT('IGNORED')
END
8.3.9 Listing of Sample Input to Code RPLM
See following pages.
<table>
<thead>
<tr>
<th></th>
<th>TEST CALCULATION WITH GCDS PLUME 19-6-77</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2, 1.1E-3, 1E-4;</td>
</tr>
<tr>
<td>2</td>
<td>1.10, 10, 13, 2, 6.57, 5, 291;</td>
</tr>
<tr>
<td>3</td>
<td>NO2 NO O3</td>
</tr>
<tr>
<td>4</td>
<td>0.100E+01 0.0000E+03 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>5</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>6</td>
<td>0.200E+01 0.0780E+03 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>7</td>
<td>NO2 NO2 O3</td>
</tr>
<tr>
<td>8</td>
<td>0.100E+01 0.0000E+03 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>9</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>10</td>
<td>0.100E+01 0.0000E+03 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>11</td>
<td>CH2O CO O2R NO2 RC03</td>
</tr>
<tr>
<td>12</td>
<td>0.100E+01 0.0000E+03 1.0000 0.1000 0.6000 0.0500 0.0 0.0 0.0</td>
</tr>
<tr>
<td>13</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>14</td>
<td>0.200E+01 0.0000E+03 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>15</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>16</td>
<td>0.3400E+04 0.1450E+04 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>17</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>18</td>
<td>0.1000E+05 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>19</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>20</td>
<td>0.1600E+05 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>21</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>22</td>
<td>0.1800E+03 0.2450E+04 0.0000 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>23</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>24</td>
<td>0.2500E+03 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>25</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>26</td>
<td>0.4100E+03 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>27</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>28</td>
<td>0.1200E+05 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>29</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>30</td>
<td>0.3800E+05 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>31</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>32</td>
<td>0.1000E+05 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>33</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>34</td>
<td>0.1100E+05 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>35</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>36</td>
<td>0.2100E+05 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>37</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>38</td>
<td>0.5000E+04 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>39</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>40</td>
<td>0.1000E+02 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>41</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>42</td>
<td>0.1600E+04 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>43</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>44</td>
<td>0.1800E+03 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>45</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>46</td>
<td>0.2000E+03 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>47</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>48</td>
<td>0.1400E+01 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>49</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>50</td>
<td>0.2400E+04 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>51</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>52</td>
<td>0.1700E+04 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>53</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>54</td>
<td>0.1500E+04 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>55</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>56</td>
<td>0.2400E+16 0.1000E+05 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>57</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>58</td>
<td>0.1700E+16 0.1000E+05 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>59</td>
<td>NO3 NO2 O3</td>
</tr>
<tr>
<td>60</td>
<td>0.1200E+19 0.1360E+05 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>121</td>
<td>0.4347E-04</td>
</tr>
<tr>
<td>122</td>
<td>0.2243E-03</td>
</tr>
<tr>
<td>123</td>
<td>0.6080E-04</td>
</tr>
<tr>
<td>124</td>
<td>0.1047E-02</td>
</tr>
<tr>
<td>125</td>
<td>0.1427E-02</td>
</tr>
<tr>
<td>126</td>
<td>0.1688E-02</td>
</tr>
<tr>
<td>127</td>
<td>0.1679E-02</td>
</tr>
<tr>
<td>128</td>
<td>0.1627E-02</td>
</tr>
<tr>
<td>129</td>
<td>0.1328E-02</td>
</tr>
<tr>
<td>130</td>
<td>0.1342E-03</td>
</tr>
<tr>
<td>131</td>
<td>0.4848E-03</td>
</tr>
<tr>
<td>132</td>
<td>0.1501E-03</td>
</tr>
<tr>
<td>133</td>
<td>0.1328E-04</td>
</tr>
<tr>
<td>134</td>
<td>0.3463E-01</td>
</tr>
<tr>
<td>135</td>
<td>0.5579E+00</td>
</tr>
<tr>
<td>136</td>
<td>0.6723E+00</td>
</tr>
<tr>
<td>137</td>
<td>0.7373E+00</td>
</tr>
<tr>
<td>138</td>
<td>0.7725E+01</td>
</tr>
<tr>
<td>139</td>
<td>0.7873E+01</td>
</tr>
<tr>
<td>140</td>
<td>0.7849E+01</td>
</tr>
<tr>
<td>141</td>
<td>0.7646E+01</td>
</tr>
<tr>
<td>142</td>
<td>0.7229E+01</td>
</tr>
<tr>
<td>143</td>
<td>0.6456E+01</td>
</tr>
<tr>
<td>144</td>
<td>0.5087E+01</td>
</tr>
<tr>
<td>145</td>
<td>0.2704E+01</td>
</tr>
<tr>
<td>146</td>
<td>0.8814E-01</td>
</tr>
<tr>
<td>147</td>
<td>0.3500E-04</td>
</tr>
<tr>
<td>148</td>
<td>0.1111E-01</td>
</tr>
<tr>
<td>149</td>
<td>0.1111E-01</td>
</tr>
</tbody>
</table>

END OF FILE
8.3.10 Output Generated by RPLM with Sample Input
See following pages.
**TEST CALCULATION WITH GCOS PLUME 19-6-77**

<table>
<thead>
<tr>
<th>CONTROL PARAMETERS:</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>METH</td>
<td>2</td>
</tr>
<tr>
<td>MITER</td>
<td>1</td>
</tr>
<tr>
<td>TOL</td>
<td>0.100E-03</td>
</tr>
<tr>
<td>H</td>
<td>0.100E-04</td>
</tr>
<tr>
<td>T-START</td>
<td>0.100E+01</td>
</tr>
<tr>
<td>T-FINAL</td>
<td>0.700E+02</td>
</tr>
<tr>
<td>T-INCREMENT</td>
<td>0.100E+02</td>
</tr>
<tr>
<td>T-REF (VECTOR TT)</td>
<td>0.657E+01 0.675E+02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TIME OF DAY AT TSTART (HRS)</th>
<th>AMBIENT TEMPERATURE (KELVIN)</th>
<th>WINDSPEED (M/MIN)</th>
<th>DISPERSION FUNCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.00</td>
<td>291.00</td>
<td>350.00</td>
<td>8500.00*T**0.81</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>EMISSION FROM STACK</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO2 (PPM/MIN)</td>
</tr>
<tr>
<td>0.490E+08</td>
</tr>
<tr>
<td>NO2 (PPM/MIN)</td>
</tr>
<tr>
<td>0.500E+06</td>
</tr>
<tr>
<td>HNO2 (PPM/MIN)</td>
</tr>
<tr>
<td>0.300E+05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>INITIAL PLUME PROFILE</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPECIES</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>SO2</td>
</tr>
<tr>
<td>NO</td>
</tr>
<tr>
<td>NO2</td>
</tr>
<tr>
<td>HNO2</td>
</tr>
<tr>
<td>AMBIENT MIXING RATIOS</td>
</tr>
<tr>
<td>NO2</td>
</tr>
<tr>
<td>NO</td>
</tr>
<tr>
<td>O3</td>
</tr>
<tr>
<td>C0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SPECIES LIST OF CHEMICAL MECHANISM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1=N2</td>
</tr>
<tr>
<td>2=NO</td>
</tr>
<tr>
<td>3=O3</td>
</tr>
<tr>
<td>4=NO</td>
</tr>
<tr>
<td>5=HNO2</td>
</tr>
<tr>
<td>6=CH2O</td>
</tr>
<tr>
<td>7=O2</td>
</tr>
<tr>
<td>8=O2R</td>
</tr>
<tr>
<td>9=NO2</td>
</tr>
<tr>
<td>10=NITRATE</td>
</tr>
<tr>
<td>11=O3</td>
</tr>
<tr>
<td>12=PALN</td>
</tr>
<tr>
<td>13=PA</td>
</tr>
<tr>
<td>14=SULFATE</td>
</tr>
<tr>
<td>15=PNA</td>
</tr>
<tr>
<td>16=NO2</td>
</tr>
<tr>
<td>17=NITRATE</td>
</tr>
<tr>
<td>18=PAN</td>
</tr>
<tr>
<td>19=PA</td>
</tr>
<tr>
<td>20=PAN</td>
</tr>
<tr>
<td>Reaction Equation</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>$\text{NO}_2 \rightarrow \text{NO}_3$</td>
</tr>
<tr>
<td>$\text{NO}_3 \rightarrow \text{NO}_2$</td>
</tr>
<tr>
<td>$\text{NO}_2 \rightarrow \text{NO}_3$</td>
</tr>
<tr>
<td>$\text{NO}_3 \rightarrow \text{NO}_2$</td>
</tr>
<tr>
<td>$\text{HNO}_2 \rightarrow \text{H}_2\text{O} \text{NO}$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O} \rightarrow \text{CO}_2\text{R}$</td>
</tr>
<tr>
<td>$\text{NO}_3 \rightarrow \text{NO}_2$</td>
</tr>
<tr>
<td>$\text{NO}_3 \rightarrow \text{NO}_2$</td>
</tr>
<tr>
<td>$\text{NO}_2 \rightarrow \text{NO}_3$</td>
</tr>
<tr>
<td>$\text{NO}_3 \rightarrow \text{NO}_2$</td>
</tr>
<tr>
<td>$\text{NO}_2 \rightarrow \text{NO}_3$</td>
</tr>
<tr>
<td>$\text{NO}_3 \rightarrow \text{NO}_2$</td>
</tr>
<tr>
<td>$\text{NO}_2 \rightarrow \text{NO}_3$</td>
</tr>
<tr>
<td>$\text{NO}_3 \rightarrow \text{NO}_2$</td>
</tr>
<tr>
<td>$\text{NO}_3 \rightarrow \text{NO}_2$</td>
</tr>
<tr>
<td>$\text{NO}_3 \rightarrow \text{NO}_2$</td>
</tr>
<tr>
<td>$\text{NO}_3 \rightarrow \text{NO}_2$</td>
</tr>
<tr>
<td>$\text{NO}_3 \rightarrow \text{NO}_2$</td>
</tr>
</tbody>
</table>
MASS BALANCE CALCULATION, CORRECTED FOR AMBIENT ENTRAINMENT, AND AVERAGE MIXING RATIO OVER TOTAL PLUME FOR SULFATE SO2 AND THE PERCENTAGE OF THE FOLLOWING SPECIES TOWARDS THIS SUM (*CORRECTED MASS BALANCE AND AVERAGE MIXING RATIO OVER PLUME)

<table>
<thead>
<tr>
<th>TIME</th>
<th>DISTANCE</th>
<th>TOTAL MASS</th>
<th>AVER. M.R.</th>
<th>PART. MASS</th>
<th>AVER. M.R.</th>
<th>PERCENTAGE</th>
<th>CONV. RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.490E+08</td>
<td>0.105E+01</td>
<td>0.555E-03</td>
<td>0.119E-10</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>6.5</td>
<td>350.0035</td>
<td>0.489E+08</td>
<td>0.229E+00</td>
<td>0.249E+05</td>
<td>0.105E-03</td>
<td>0.459E-01</td>
<td>0.494E+00</td>
</tr>
<tr>
<td>11.0</td>
<td>385.0000</td>
<td>0.489E+08</td>
<td>0.151E+00</td>
<td>0.429E+05</td>
<td>0.132E-03</td>
<td>0.876E-01</td>
<td>0.565E+00</td>
</tr>
<tr>
<td>21.0</td>
<td>7350.0000</td>
<td>0.489E+08</td>
<td>0.894E-01</td>
<td>0.102E+06</td>
<td>0.210E-03</td>
<td>0.684E+00</td>
<td>0.849E+00</td>
</tr>
<tr>
<td>31.0</td>
<td>10850.0000</td>
<td>0.489E+08</td>
<td>0.653E+01</td>
<td>0.185E+06</td>
<td>0.247E-03</td>
<td>0.379E+00</td>
<td>0.636E+00</td>
</tr>
<tr>
<td>61.0</td>
<td>14350.0000</td>
<td>0.489E+08</td>
<td>0.521E+01</td>
<td>0.291E+06</td>
<td>0.310E-03</td>
<td>0.981E+00</td>
<td>0.981E+00</td>
</tr>
<tr>
<td>51.0</td>
<td>17850.0000</td>
<td>0.489E+08</td>
<td>0.436E+01</td>
<td>0.421E+06</td>
<td>0.375E-03</td>
<td>0.861E+00</td>
<td>0.110E+01</td>
</tr>
<tr>
<td>61.0</td>
<td>21350.0000</td>
<td>0.488E+08</td>
<td>0.376E+01</td>
<td>0.572E+06</td>
<td>0.441E-03</td>
<td>0.117E+01</td>
<td>0.125E+01</td>
</tr>
<tr>
<td>67.5</td>
<td>23625.0000</td>
<td>0.487E+08</td>
<td>0.346E+01</td>
<td>0.682E+06</td>
<td>0.484E-03</td>
<td>0.139E+01</td>
<td>0.134E+01</td>
</tr>
<tr>
<td>70.0</td>
<td>24500.0000</td>
<td>0.487E+08</td>
<td>0.336E+01</td>
<td>0.725E+06</td>
<td>0.500E-03</td>
<td>0.149E+01</td>
<td>0.220E+01</td>
</tr>
</tbody>
</table>
MASS BALANCE CALCULATION, CORRECTED FOR AMBIENT ENTRAINMENT, AND AVERAGE MIXING RATIO OVER TOTAL PLUME FOR NO₂, NO, NO₃, HN₂O, NITRATE PAN, PNA, PALN, AND THE PERCENTAGE OF THE FOLLOWING SPECIES TOWARDS THIS SUM (+CORRECTED MASS BALANCE AND AVERAGE MIXING RATIO OVER PLUME)

<table>
<thead>
<tr>
<th>TIME</th>
<th>DISTANCE</th>
<th>TOTAL MASS</th>
<th>AVER. M.R.</th>
<th>PART. MASS</th>
<th>AVER. M.R.</th>
<th>PERCENTAGE</th>
<th>CONV. RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0000</td>
<td>350.0035</td>
<td>0.5030E+07</td>
<td>0.1083E+00</td>
<td>0.5687E-04</td>
<td>0.1225E-11</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>6.5700</td>
<td>2298.5000</td>
<td>0.5027E+07</td>
<td>0.2367E-01</td>
<td>0.7733E+04</td>
<td>0.3625E-04</td>
<td>0.1523E+00</td>
<td>0.1651E+01</td>
</tr>
<tr>
<td>11.0000</td>
<td>3850.0000</td>
<td>0.5024E+07</td>
<td>0.1563E-01</td>
<td>0.1928E+05</td>
<td>0.5955E-04</td>
<td>0.3811E+00</td>
<td>0.3099E+01</td>
</tr>
<tr>
<td>21.0000</td>
<td>7350.0000</td>
<td>0.5019E+07</td>
<td>0.3002E-02</td>
<td>0.5776E+05</td>
<td>0.1056E-03</td>
<td>0.1136E+01</td>
<td>0.4113E+01</td>
</tr>
<tr>
<td>31.0000</td>
<td>10850.0000</td>
<td>0.5024E+07</td>
<td>0.6825E-02</td>
<td>0.1135E+06</td>
<td>0.1514E-03</td>
<td>0.2219E+01</td>
<td>0.6134E+01</td>
</tr>
<tr>
<td>41.0000</td>
<td>14350.0000</td>
<td>0.5028E+07</td>
<td>0.9473E-02</td>
<td>0.1960E+06</td>
<td>0.1978E-03</td>
<td>0.3615E+01</td>
<td>0.6149E+01</td>
</tr>
<tr>
<td>51.0000</td>
<td>17850.0000</td>
<td>0.5021E+07</td>
<td>0.4601E-02</td>
<td>0.2747E+06</td>
<td>0.2440E-03</td>
<td>0.5922E+01</td>
<td>0.7799E+01</td>
</tr>
<tr>
<td>61.0000</td>
<td>21350.0000</td>
<td>0.5009E+07</td>
<td>0.3988E-02</td>
<td>0.3779E+06</td>
<td>0.2914E-03</td>
<td>0.7308E+01</td>
<td>0.8196E+01</td>
</tr>
<tr>
<td>67.5000</td>
<td>23625.0000</td>
<td>0.5000E+07</td>
<td>0.3678E-02</td>
<td>0.4521E+06</td>
<td>0.3212E-03</td>
<td>0.8733E+01</td>
<td>0.8848E+01</td>
</tr>
<tr>
<td>70.0000</td>
<td>24500.0000</td>
<td>0.4997E+07</td>
<td>0.3573E-02</td>
<td>0.4817E+06</td>
<td>0.3322E-03</td>
<td>0.9299E+01</td>
<td>0.1493E+02</td>
</tr>
<tr>
<td>TIME (MIN)</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.000</td>
<td>0.102E-06</td>
<td>0.594E-07</td>
<td>0.610E-06</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.570</td>
<td>0.115E-01</td>
<td>0.194E-01</td>
<td>0.202E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.000</td>
<td>0.174E-01</td>
<td>0.250E-01</td>
<td>0.318E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.000</td>
<td>0.249E-01</td>
<td>0.306E-01</td>
<td>0.352E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.000</td>
<td>0.287E-01</td>
<td>0.333E-01</td>
<td>0.367E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41.000</td>
<td>0.310E-01</td>
<td>0.349E-01</td>
<td>0.377E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>51.000</td>
<td>0.327E-01</td>
<td>0.361E-01</td>
<td>0.384E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>61.000</td>
<td>0.340E-01</td>
<td>0.371E-01</td>
<td>0.391E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>67.500</td>
<td>0.348E-01</td>
<td>0.377E-01</td>
<td>0.395E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70.000</td>
<td>0.351E-01</td>
<td>0.379E-01</td>
<td>0.396E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time (Min)</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.000</td>
<td>0.216E+01</td>
<td>0.126E+01</td>
<td>0.631E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.570</td>
<td>0.469E+00</td>
<td>0.274E+00</td>
<td>0.137E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.000</td>
<td>0.309E+00</td>
<td>0.180E+00</td>
<td>0.902E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.000</td>
<td>0.132E+00</td>
<td>0.107E+00</td>
<td>0.539E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.000</td>
<td>0.103E+00</td>
<td>0.778E+00</td>
<td>0.388E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41.000</td>
<td>0.886E-01</td>
<td>0.619E-01</td>
<td>0.309E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>51.000</td>
<td>0.517E-01</td>
<td>0.517E-01</td>
<td>0.258E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>61.000</td>
<td>0.763E-01</td>
<td>0.445E-01</td>
<td>0.222E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>67.500</td>
<td>0.700E-01</td>
<td>0.408E-01</td>
<td>0.203E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70.000</td>
<td>0.679E-01</td>
<td>0.396E-01</td>
<td>0.197E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### LIST OF AOSERP RESEARCH REPORTS

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>HY 3.1</td>
<td>Strosher, M.T., and E. Peake. 1976. The evaluation of waste waters from an oil sand extraction plant. Prep. for the Alberta Oil Sands Environmental Research Program by The University of Calgary, Environmental Sciences Centre (Kananaskis). AOSERP Report 5. 103 pp.</td>
</tr>
<tr>
<td>6</td>
<td>PM</td>
<td>Patterson, R., and A.M. Lansdown. 1976. Housing for the north--the stackwall system: construction report, Mildred Lake tank and pump house. Prep. for the Alberta Oil Sands Environmental Research Program by the University of Manitoba, Faculty of Engineering, Northern Housing Committee. AOSERP Report 6. 36 pp.</td>
</tr>
</tbody>
</table>


41 AF 3.5.1 Sprague, J.B., D.A. Holdway, and D. Stendahl. Acute and chronic toxicity of vanadium to fish. Prep. for the Alberta Oil Sands Environmental Research Program by the University of Guelph. AOSERP Report 41. 92 pp.


49  WS 1.3.3  Hartland-Rowe, R.C.B., R.S. Davies, M. McElhone, and R. Crowther. The ecology of macrobenthic invertebrate communities in Hartley Creek, northeastern Alberta. Prep. for the Alberta Oil Sands Environmental Research Program by Dept. of Biology, the University of Calgary. AOSERP Report 49. 144 pp.


57 LS 2.3.1 Thompson, M.D. 1979. Ecological habitat mapping of the AOSERP study area: Phase 1, aquatic macrophytes. Prep. for the Alberta Oil Sands Environmental Research Program by Intera Environmental Consultants Ltd. AOSERP Report 57. 45 pp.

<table>
<thead>
<tr>
<th>ID</th>
<th>Code</th>
<th>Reference</th>
</tr>
</thead>
</table>


75  WS 1.3.4  Hickman, M., S.E.D. Charlton, and C.G. Jenkerson. 1979. Interim report on a comparative study of benthic algal primary productivity in the AOSERP study area. Prep. for the Alberta Oil Sands Environmental Research Program by Department of Botany, University of Alberta. AOSERP Report 75. 197 pp.


<table>
<thead>
<tr>
<th>Page</th>
<th>Report Code</th>
<th>Reference</th>
</tr>
</thead>
</table>


<table>
<thead>
<tr>
<th>Report</th>
<th>Reference</th>
</tr>
</thead>
</table>


