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*Kinetics Programs for Simulation of
Tropospheric Photochemistry
on the Global Scale*

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TABLE OF CONTENTS

ABSTRACT.....	2
I. INTRODUCTION.....	3
II. WHY BUILD GLOBAL-SCALE TROPOSPHERIC CHEMISTRY MODELS?.....	4
A. Greenhouse Forcing by Photochemically Active Gases.....	4
B. The Kinetic Web.....	5
C. Zonal Resolution.....	5
D. A Global Change Grid.....	6
E. The Atmospheric Chemical Species.....	7
III. MATHEMATICAL FRAMEWORK FOR GLOBAL PHOTOCHEMISTRY.....	10
A. Continuity Equations and Differencing Representations.....	11
B. Matrix Iterative Solutions.....	12
C. Stiffness.....	12
D. Improvement in Species-segregated Calculations.....	13
E. Families.....	17
IV. OPTIMIZATION OF THE CHEMICAL OPERATOR.....	19
A. The Integrator.....	19
B. Parallelism.....	22
C. Reaction Set Selection and Automation.....	25
V. SUMMARY AND CONCLUSION.....	27
ACKNOWLEDGEMENTS.....	29
REFERENCES.....	30
APPENDIX A: BIBLIOGRAPHY.....	52
APPENDIX B: EQUATIONS.....	54

KINETICS PROGRAMS FOR SIMULATION OF TROPOSPHERIC PHOTOCHEMISTRY ON THE GLOBAL SCALE

by

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ABSTRACT

The study of tropospheric kinetics underlies global change because key greenhouse gases are photochemically active. Modeling of tropospheric chemistry on a global scale is essential because some indirect greenhouse gases are short-lived and interact in a non-linear fashion. It is also extremely challenging, however; the global change grid is extensive in both the physical and temporal domains, and critical lower atmospheric species include the organics and their oxidized derivatives, which are numerous. Several types of optimization may be incorporated into kinetics modules to enhance their ability to simulate the complete lower atmospheric gas phase chemical system.

- (1) The photochemical integrator can be accelerated by avoiding matrix and iterative solutions and by establishing families. Accuracy and mass conservation are sacrificed in the absence of iteration, but atom balancing is restorable post hoc.
- (2) Chemistry can be arranged upon the massive grid to exploit parallel processing, and solutions to its continuity equations can be automated to permit experimentation with species and reaction lists or family definitions. Costs in programming effort will be incurred in these cases.
- (3) Complex hydrocarbon decay sequences can be streamlined either through structural lumping methods descended from smog investigations, which require considerable calibration, or by defining surrogates for classes of compounds, with a loss in constituent detail.

From among the available options, the most advantageous permutations will vary with the specific nature of any eventual global scale study, and there is likely to be demand for many approaches. Tracer transport codes serve as a foundation upon which tropospheric chemistry packages will be tested. Encroachment of the NO_x sphere of influence upon tropical rain forests and the upper free troposphere are two examples of specific problems to which full three-dimensional chemical simulations might be applied.

I. INTRODUCTION

The era of global change is for all intents and purposes upon us [Kerr, 1992 a; Rowland, 1992; Hammitt *et al.*, 1992]. Ozone depletions of greater than 50% in the Antarctic stratosphere have been attributed unequivocally to anthropogenic chlorine inputs [Solomon, 1988; Anderson *et al.*, 1991; Brune *et al.*, 1991; Brune, 1991] and both ground based and satellite instruments detect losses at mid-latitudes as well [WMO, 1989 a and b]. Concentrations of the major greenhouse forcer carbon dioxide have risen steadily for over thirty years [Keeling *et al.*, 1976, 1989 a and b] and will continue to do so [Niehaus and Williams, 1979; Niehaus, 1981; Houghton *et al.*, 1990]. Panels of distinguished scientists conclude that, although its precise forms are as yet beyond prediction, alteration of the terrestrial climate is nonetheless imminent [Houghton *et al.*, 1990; Kerr, 1992 a].

Tropospheric photochemistry will comprise a key link in the study of global change, because many of the direct and indirect greenhouse gases are kinetically active [Crutzen, 1988; Houghton *et al.*, 1990; IPCC, 1992]. Their trace concentrations influence one another in a complex and feedback-intensive web of reactions which can only be understood through photochemical modelling [Crutzen, 1988; Kerr, 1992 b]. Primary participants in the kinetic greenhouse system are ozone, methane, the non-methane hydrocarbons (NMHC), and the nitrogen and hydrogen oxides (NO_x and HO_x). While details of the processes relating them are understood on a local level [Thompson *et al.*, 1989 a and b; Atherton and Penner, 1990; Donahue and Prinn, 1990], the shorter lived species enter into critical nonlinear interactions and so can only be adequately simulated in three dimensions [Chatfield and Crutzen, 1984; Zimmerman *et al.*, 1989]. Tropospheric chemistry promises to be difficult to model on full global grids, however, because of the large number of coupled tracers [Thompson, 1992], and this will be especially true on greenhouse effect time scales. Even in the stratosphere, where the constituents are mainly inorganic, three-dimensional kinetics programs have been slow to develop [Kaye and Rood, 1989; Kao *et al.*, 1990]. Below the tropopause, they are only just appearing, and so far without any allowance for the pressure organics [Crutzen and Zimmerman, 1991].

With global change looming, pressure will naturally be exerted upon the geosciences community to quantify its manifestations. Models of the total terrestrial system blending oceanic, atmospheric, and biospheric routines are already under discussion [Brost *et al.*, 1991; Kao *et al.*, 1992 a; EPA, 1992 a], and photochemistry will be a vital component. There will likely be room for a variety of gas phase kinetics efforts in the arena. Lower dimensionality atmospheric chemistry models proliferated at least partially because of the needs for intercomparison [Jackman *et al.*, 1989; Lashof and Tirpak, 1990; WMO, 1991] and replication/sensitivity analysis [Stolarski *et al.*, 1978; Thompson and Stewart, 1991; EPA, 1992 b]. These requirements extend logically to three dimensions as well [Thompson, 1992].

In the present work, we survey the computational aspects of investigating global scale tropospheric chemistry by outlining the options available to photochemists in tailoring large gas kinetic reaction sets to the global change mesh. Some of the concepts delineated are adapted directly from early applications to large areas in the stratosphere, but many are specialized to handle the abundance of organic components existing uniquely at lower altitudes. Our motivation is to organize some of the reference information which will be essential to selection of chemical numerical strategies appropriate for the troposphere. For example, here at Los Alamos National Laboratory, Kao *et al.* [1992 a and b] have constructed and tested a chemical tracer model (CTM) to which kinetics could be attached, and we are currently evaluating several of the integrators described below as candidates for insertion. Our text is designed largely to function as a review and so is fairly comprehensive and reference intensive. The major topics are itemized in brief in the contents and in narrative form below.

We begin by offering background material on the need for global tropospheric chemical modelling. Greenhouse forcings by photochemically active gases are commented upon, and examples of their networking kinetics are given. The weaknesses of zonal averaging are underscored, and in parallel, the difficulties in attaining longitudinal resolution are demonstrated through simple back-of-the-envelope calculations conducted on a generic global change grid. The richness of tropospheric organic chemistry is sketched so that the ways in which it compounds the chemical modelling problem may be appreciated.

Next, a mathematical history of atmospheric photochemical computations is laid out as a framework for more quantitative portions of the text. We open with the full tracer transport continuity equations, and describe early solutions conducted through the method of lines and iterative matrix inversions. A semi-

rigorous definition of stiffness flows logically once the Jacobian of partials has been defined. The desire to bolster computation rates soon led photochemists away from matrix inversions and iterations, and toward species conglomerates known as families. A key step in this evolution was an increasing willingness to split operators. The assumptions and limitations behind splitting techniques are explored, but only briefly; we take the position that it should currently be viewed as a necessary expedient. Adopting time splitting as a starting point provides a clean theoretical connection with published reviews on advection schemes [e. g., Chock and Dunker, 1983; Thompson, 1984; Chock, 1985; Prather *et al.*, 1987], but in particular, with Rood [1987], which begs a chemical follow up. Once the photochemical equations have been segregated, the nature of the classical stiffness property is developed and solutions to it are classified as they have arisen within the field of atmospheric chemistry. Key explanatory papers are collected first in this section, and a more complete bibliography is tabulated later in supplemental format.

Following these two types of preliminary, we elaborate upon the methods available for optimization of the chemical operator for the global scale. The photochemical integrator itself is our lead. At maximum chemical time steps, there is necessarily a conflict between speed and accuracy, and the potential resolutions are collected. "Integration" of the integrator is also stressed, however. Many paths can be imagined for pushing chemistry along the global grid, but not all take real advantage of parallel processing within modern computing facilities. As a subset of the vectorization arguments, it is shown that chemistry can be rate-limiting relative to advection. Other forms of optimization regard the processing of the kinetic data set, and reach their greatest relevance in the troposphere, which is the focus here. Divergent schemes are available for both the streamlining of intricate reaction sets, and the automation of adjustments in those sets to facilitate experimentation with poorly known chemistries.

We finish the text with a summary tabulation of the outstanding points which emerge from our analysis. No attempt is made to evaluate merits of the many numerical techniques a tropospheric modeller might employ to accomplish his mission in studying the kinetics behind global change. In fact, we conclude that the features contained in a global kinetics package will depend heavily on the nature of the task at hand. As denouement, we touch upon some intriguing real projects from among the plethora to which global scale tropospheric chemical simulations will someday be applied.

II. WHY BUILD GLOBAL-SCALE TROPOSPHERIC CHEMICAL MODELS?

A. Greenhouse Forcing by Photochemically Active Gases

Although the single most important greenhouse gas, CO₂, is inert up to the mesosphere [Lauerman and Spreiter, 1983; Brasseur and Solomon, 1984], contributions to radiative forcing by other species are nontrivial, and photochemical players are chief among them. Terrestrial surface warming is generally estimated at about 2° for carbon dioxide doubling, a standard climatic yardstick expected to be reached by the end of the twenty-first century [NAS, 1983; Houghton *et al.*, 1990]. The sum of changes resulting from all non-CO₂ gases should be about the same, and O₃ and CH₄, the photochemically active direct forcers, account for roughly half of the total [Ramanathan *et al.*, 1987; Ramanathan, 1988; Lacis *et al.*, 1990]. Crudely, then, over the CO₂ doubling time scale, ozone and methane alone hold the potential for a degree or so of surface temperature change. This is clearly not a secondary effect; it is perhaps less than well recognized only because photochemistry confounds simulation [IPCC, 1992].

Several of the most important indirect greenhouse gases are photochemically active as well [Houghton *et al.*, 1990; Lelieveld and Crutzen, 1992]. The indirect forcers are not radiatively crucial in or of themselves; they are either present at low levels or else do not fall in windows along the earth's infrared spectrum. However, their chemistries are linked with and influence those of other molecules which do. The nitrogen oxides are prime examples, and it should be noted that some compounds operate on the radiation field both directly and indirectly; methane's dual role has recently been examined in some detail [Lelieveld and Crutzen, 1992].

B. The Kinetic Web

The interwoven fates of the photochemical forcers are amply witnessed by the identification of intricate feedback loops in which they take part [Sze, 1977; Chameides *et al.*, 1977; Thompson and Cicerone, 1986; Crutzen, 1988; Khalil and Rasmussen, 1988; Guthrie, 1989]. Recent reviews of tropospheric chemistry trace the reaction set in some depth [Logan *et al.*, 1981; Crutzen, 1988; Jacob, 1991; Thompson, 1992], but it is probably best dealt with in short order by citing examples. We begin with methane; concentrations are observationally on the rise [Craig and Chou, 1982; Stauffer *et al.*, 1985; Blake and Rowland, 1986 a] and will necessarily alter those of the dominant atmospheric oxidants HO_x [Levy, 1971; Crutzen, 1973; Crutzen, 1988]. The direction of the alteration, however, depends on local NO_x levels [Crutzen, 1988; Thompson, 1992]. There are titration points embedded in the CH₄ oxidation sequence which are controlled by the species NO. If its concentrations are greater than roughly 10 ppt, it can abstract an oxygen atom from the methyl peroxy radical and short circuit HO_x destructive cycles leading out to the stable methyl hydroperoxide. Thus, the methane increase will be self-enhancing in some localities and self-inhibiting in others. One of the games in modelling of global tropospheric chemistry will be to sort out relative volumes occupied by the two distinct regimes.

Oxidation of the non-methane hydrocarbons produces analogous effects on HO_x [Thompson and Cicerone, 1986; Crutzen, 1988; Thompson, 1992], and as if this weren't enough, tropospheric ozone is either produced or removed along all carbon chain decompositions, again subject to control by NO_x [Crutzen, 1973 and 1974; Fishman and Crutzen, 1978; Crutzen *et al.*, 1979; Chameides *et al.*, 1987; Crutzen, 1988; Crutzen and Andreae, 1990]. Ozone and NO_x are considerably shorter lived than methane and so are more difficult to measure, but their concentrations also seem to be rising [Logan, 1983; Marland and Rotty, 1984; Logan, 1985; Bojkov, 1986; Volz and Kley, 1988; Oltmans *et al.*, 1989; Fishman *et al.*, 1990; Sandroni *et al.*, 1992]. The hydroxyl radical, the more reactive member of the HO_x family, is so ephemeral that measurements remain elusive [Platt *et al.*, 1988; Dorn *et al.*, 1988; Perner *et al.*, 1989; Brune, 1992; Mount and Eisele, 1992; Mount, 1992] and modelling of trends has thus far yielded no clear consensus [Prinn *et al.*, 1987; Taylor *et al.*, 1991; Butler *et al.*, 1991; Thompson, 1992; Kao *et al.*, 1992 a and b].

C. Zonal Resolution

Tropospheric ozone can be used as a textbook case in the pitfalls of zonal averaging. Fishman *et al.* [1990, 1991] have shown through a seminal coupling of TOMS and SAGE satellite measurements that biomass burning events in tropical regions of the southern hemisphere create ozone pollution plumes extending to the mesoscale. This is smog chemistry on a grand tableau: the oxidation of non-methane hydrocarbons occurring in conjunction with NO_x release [Crutzen and Andreae, 1990; Chatfield and Delany, 1990]. However, both the precursor classes NO_x and NMHC are short lived with respect to longitudinal mixing; the NO_x lifetime is on the order of a week [Logan, 1983; Penner *et al.*, 1991], and excluding species at the lowest end of their respective homologous series such as methane and ethane [Blake and Rowland, 1986 a, b and 1988], the organics survive on the order of hours to days before hydrogen abstraction [Graedel, 1978; Singh and Zimmerman, 1992].

As rules of thumb, most chemical reactions in the lower atmosphere are bimolecular [Atkinson and Lloyd, 1984; Demore *et al.*, 1990], and so also are most of the rate determining steps (RDS) in the ozone and HO_x production sequences tracking hydrocarbon oxidation. It is likely that RDS in the Fishman burning plumes involve attacks on stable hydrocarbons, which launch the cascade of carbon atoms through chains of increasingly oxidized intermediates. Ignoring for the moment the possibility of initialization via ozone attachment to multiple bonds, we may write as a zeroth order approximation for an arbitrary parcel,

$$dO_3/dt = k(OH)(NMHC), \quad (1)$$

where the oxidation intensive organics remain unnamed. Hydroxyl is in turn a function of local NO_x and NMHC levels, so that generalization is possible as in

$$dO_3/dt = f[(NO_x)^n(NMHC)^m]. \quad (2)$$

To restate, ozone production within the plume may be a function in the broad sense of products of NO_x and NMHC concentrations. The powers *n* and *m* can only be determined through kinetic modelling [Liu *et al.*,

1987; Trainer *et al.*, 1987; Liu *et al.*, 1987; Thompson, 1992]. Purely for illustration purposes here, we postulate that the form of the function is as follows:

$$p = a (\text{NO}_x)(\text{NMHC}), \quad (3)$$

where a is some constant and p now denotes the production.

The Fishman *et al.* plumes tend to sweep with southern hemisphere trade winds along a latitude circle. We may now imagine two disparate techniques for calculation of ozone input rates in a latitude band containing the burning source: either by averaging rates in a resolved manner, or by calculating them at average concentrations. For convenience, we assume that significant NMHC and NO_x decay takes place within two zonal segments whose widths are unspecified, and allow the subscripts h and l to denote high and low concentrations, respectively, along the decay curves. The average of rates in the segments is

$$(p_h + p_l)/2 = a [(\text{NO}_{xh})(\text{NMHC}_h) + (\text{NO}_{xl})(\text{NMHC}_l)]/2, \quad (4)$$

while the rate at overall averages is by contrast

$$p_{av} = a (\text{NO}_{xav})(\text{NMHC}_{av}) \quad (5)$$

$$= a [(\text{NO}_{xh} + \text{NO}_{xl})/2][(\text{NMHC}_h + \text{NMHC}_l)/2] \quad (6)$$

$$= a [(\text{NO}_{xh})(\text{NMHC}_h) + (\text{NO}_{xl})(\text{NMHC}_l) + (\text{NO}_{xh})(\text{NMHC}_l) + (\text{NO}_{xl})(\text{NMHC}_h)]/4 \quad (7)$$

The two calculations are not equivalent, and the result may be capsulized succinctly; the average of products is not necessarily identical with the product of averages. Because the chemistry of tropospheric ozone production is non-linear, and depends on local concentrations of short-lived precursors, it can only be modeled accurately with zonal gradients resolved, or in other words, in three full dimensions.

The precursor species NO_x and NMHC fall into the category of indirect, photochemically active greenhouse gases, and were classified as such by the first report of the IPCC [Houghton *et al.*, 1990]. An attempt was made there to calculate indirect global warming potentials (GWP) for NO_x and NMHC based on low dimensionality radiative chemical modelling [Wuebbles, 1989; Hough and Derwent, 1990]. The GWP values have since been retracted, partially because of the non-linearities dilemma portrayed here [IPCC, 1992]. This can be viewed as further evidence that a market must exist for full global models of tropospheric photochemistry.

It is instructive as an incidental to note that expression (7) collapses to (4) if one of the two components is stable enough to remain at constant concentrations along the plume. For example, with NMHC set to ethane or with methane substituted for NMHC, organic $h = l$. The chemistry is pseudo-first-order in these situations and the system is pseudo-linear. Two dimensional models of stable hydrocarbon-ozone relationships may consequently be allotted some degree of confidence [Isaksen and Hov, 1987; Kanakidou *et al.*, 1991].

D. A Global Change Grid

Although the transience of some indirect greenhouse species renders three dimensional calculations essential, the global mesh upon which they must be placed for photochemical and transport modelling is vast, by any interpretation. The extent of the tropospheric chemistry physical grid can be estimated roughly relative to general circulation models currently in service, and also their derivatives. The MIT CTM, for example, is quite coarse; the horizontal mesh contains only 12×16 , or about 200 rectangles [Golombek and Prinn, 1986]. The original NCAR community climate model (CCMI) was spectral, but corresponded to 40×48 horizontal cells [Pither *et al.*, 1983; Ramanathan *et al.*, 1983; Malone *et al.*, 1986]. At Los Alamos National Laboratory, a CTM enfolding its wind fields has been expanded to incorporate twenty vertical sigma levels, for a total cell number of about 40,000 [Kao *et al.*, 1990 and 1992 a and b]. Resolution of rapid time constant photochemistries will demand the finest resolution possible, and in the not-too-distant future the number of cells in tracer transport coding may near 10^5 . In the duration of the text, this overall round figure will be segregated on an order of magnitude basis into estimates of 100×100 compartments in the horizontal plane, and ten layers in altitude.

The physical coordinates are not the only ones to be considered. Resolution along the time domain must also be dense. The CO_2 doubling yard stick converts to a rough global change time constant of ten to 100 years, while typical time increments in global transport programs are on the order of an hour [Toon *et al.*, 1988; Kao *et al.*, 1990], translating to 10^4 steps per year. For tropospheric chemical purposes, then, a

hypothetical global change grid may be defined which contains $100 \times 100 \times 10 = 10^5$ physical cells, and 10^4 bins per year in time, for several decades. Over a 100-year run, this would constitute 10^{11} cell-steps.

Even if only a single tracer is under scrutiny, simulations conducted on this massive scale are likely to prove taxing to modern supercomputers [Boris and Winsor, 1982; Almasi and Gottlieb, 1989]. Arguably the most successful of the modern machines have been single cpu vector processors, such as the Cray series predating the XMP [Levesque and Williamson, 1989]; we will center on them momentarily in the interest of simplicity, to dramatize our point. Typical clock cycles are on the order of 10 ns for fast electronics, so that for single processors, the maximum attainable performance rating is about 100 megaflops [Metcalf, 1982; Patton, 1989]. Even the simplest models of tracer physics and chemistry require on the order of ten operations per step [Boris and Winsor, 1982; Elliott *et al.*, 1992], or 10^{12} operations on the global change grid. Assuming asymptotic pipelining and chaining behavior, or, in other words, that all cycles lead directly to operations, a single tracer computation might last 10^4 s; several hours.

Ideally, increases in the number of processing units lead proportionally to performance enhancement, with Amdahl's law formalizing one type of exception [Amdahl, 1967 and 1987]. During the late 1980's and into the 90's, vector processors incorporated several cpu's, and massively parallel machines began to appear. The genealogy in Table 1 is emblematic of such developments. On a multiprocessor vector supercomputer -- say, a Cray XMP -- the theoretical performance rises to hundreds of megaflops. Inserting a factor of 2-3 to account for moderately efficient use of parallelism, a one species CTM calculation might be expected to last on the order of an hour. This is consistent with tests from our own group and is still quite expensive [Kao *et al.*, 1991; Elliott *et al.*, 1992]. It must be remembered that even global change studies of photochemistry alone will necessitate replication, sensitivity analyses [Stolarski *et al.*, 1978; Thompson and Stewart, 1991], and intercomparison [Jackman *et al.*, 1989; Lashof and Tirpak, 1990; WMO, 1991]. Transfer of kinetics from tracer transport templates into general circulation or earth system models will add voluminously to the conjoined physics calculations [Brost *et al.*, 1991; Kao *et al.*, 1992 a; EPA, 1992 a]. And we have constructed all our estimates assuming the 10^5 grid size. Some groups are already running GCM calculations for greater than 10^6 cells in anticipation of application on new generations of massively parallel processors [Mahlman and Umscheid, 1987; Farrara, 1992].

Table 1. A family tree for multiple cpu Cray supercomputers. MPP is an acronym for massively parallel processors.

	clock cycle	memory	address range	vector length	cpu's
XMP	8.5 ns	128 Mbyte, ~ 16 Mword	24 bits	64	4
YMP	6.0 ns	1 Gbyte, ~ 128 Mword	32 bits	64	8
C90	4.0 ns	32 Gbyte	32 bits	128	16
MPP					512

E. The Atmospheric Chemical Species

Even in the stratosphere, chemistry is almost purely inorganic; scores of tracers must be included in a complete kinetic model [Crutzen *et al.*, 1978; Garcia and Solomon, 1983; Turco, 1985; Rodriguez *et al.*, 1989; Cicerone *et al.*, 1991; Elliott *et al.*, 1992]. It follows that optimization of photochemical modules is likely to be desirable in global change science, and some preliminary experiences are already dictating that it will be essential [Kaye and Rood, 1989; Kao *et al.*, 1990; Kaye *et al.*, 1991; Rood *et al.*, 1991]. An

abundance of organic molecules compounds the problem geometrically in the troposphere. Air masses below the tropopause are in close contact with surface biological activity, which is tantamount to saying that they contain hydrocarbons. In ecologically rich areas, there may be thousands of NMHC species present [Graedel, 1978; Singh and Zimmerman, 1992], with the total mass of non-methane and non-CO₂ carbon approaching ppm [Thompson, 1992]. Oxidation leads to a propagation of intermediates along carbon chain degradation sequences as hydrogen atoms are removed, oxygens attached, and C-C bonds broken.

As a sample of the complexity hydrocarbon chemistry can generate, Figure 1 portrays just a few of the decomposition pathways open in the troposphere to the simplest asymmetrical alkene, propylene. The graphic is adopted from the work of Falls and Seinfeld [1978], and is specific to OH attack on the double bond. Hydroxyl can insinuate itself at two distinct sites, leading to several types of peroxy hydroxy radical. The situation is even more arcane following ozone addition, another major propylene removal channel (Figure 2). The existence of ringed structures is notable. Breakdown proceeds through some classic forms from organic synthesis -- species such as the molozonides and eriegee intermediates [Falls and Seinfeld, 1978; Finlayson-Pitts and Pitts, 1986].

Figure 1. Oxidation network following hydroxyl radical reaction with the double bond in propylene. After Falls and Seinfeld [1978].

The profusion of tropospheric organics is much more than just a theoretical construct. Many of the individual carbon species can be detected and measured; witness the gas chromatogram in Figure 3 [D. Blake, personal communication, 1991]. It is fairly typical as an analysis of non-urban air, and was obtained from a sample collected in the Canadian arctic, a biologically unspectacular locale. Yet each peak corresponds to a separate stable hydrocarbon, and not all the hydrocarbons in the sample are represented: the column packing material filters for non-oxygenated species and the retention time selection for chain lengths of fewer than seven carbon atoms. Oxidation of all the stable organics in the air aliquot, whether they appear in the spectrum or not, may be expected to generate branching networks such as those in figures 1 and 2.

Figure 2. Oxidation network following ozone reaction with the double bond in propylene. After Falls and Seinfeld [1978].

North Bay, Ontario C₂ - C₇ NMHC

Figure 3. Gas chromatogram of non-oxygenated hydrocarbons in an air sample taken at North Bay, Ontario. Provided by D. Blake, 1991.

The progression of increasing species totals moving from stratosphere through the tropopause and toward the surface is illustrated schematically in Figure 4. Short bars are rough averages for the number of tracers in some low dimensionality models of each region [*e. g.*, Turco, 1985; Isaksen and Hov, 1987; Atherton and Penner, 1990; Donahue and Prinn, 1990; Kanakidou *et al.*, 1991; Cicerone *et al.*, 1991; Elliott *et al.*, 1992]. Long bars are estimates of the actual number in the air, extrapolated from measurements such as Figure 3 [Graedel, 1978; Singh and Zimmerman, 1992]. There may well be room on the global change grid for only a few dozen tracers [Kaye and Rood, 1989; Kao *et al.*, 1990; Kaye *et al.*, 1991; Elliott *et al.*, 1992], while thousands of individual species are extant. This divergence between the intricacy of the chemistry behind global change and the resources we have to deal with it is one of the prime challenges in photochemical modelling today.

Figure 4. A histogram estimating total numbers of chemical species, including organics, found in typical kinetic models of various regions (short bars), and in the air parcels they are meant to simulate (long bars).

III. MATHEMATICAL FRAMEWORK FOR GLOBAL PHOTOCHEMISTRY

A common theme reverberating through the above discussion of the complexity and non-linearity of the kinetic system, the size of the grid, and the number of tracers resulting from organic oxidation is that chemistry calculations must be optimized in a global tropospheric model. All modes of optimization will be rooted in the numerics to at least some degree. The mathematics behind atmospheric photochemical modelling are treated here to provide the reader with a conceptual framework. We will sketch the evolution of atmospheric kinetics integration, or at least one useful version of it; there are many ways to develop the numerical history, and necessary distinctions are not always clear cut. Our particular selection is meant to enhance the presentation of techniques for global scale photochemistry calculations -- for following long lists of tracers on massive meshes. We do not claim that it is the only valid interpretation.

A. Continuity Equations and Differencing Representations

The full set of tracer transport continuity equations for vapor phase constituents interacting in three dimensions has been expressed in a wide variety of forms [e. g., Oran and Boris, 1981; McRae *et al.*, 1982 a and b; Toon *et al.*, 1988; Rood *et al.*, 1989 a and b; Rose and Brasseur, 1989; Langner and Rodhe, 1991]. Several examples from among the published versions are reproduced here. Their precise structure is non-critical because we will soon be zooming in on the photochemical segments.

Many sources begin with subscripted or scalar continuity relations. The textbook Brasseur and Solomon [1984] provides the rather compact equation

$$\partial s_i / \partial t = -\nabla \cdot \Phi(s_i) + p_i(s) - l_i(s) \quad (8)$$

in which s is a species concentration, i denotes an individual type of molecule, bold quantities are vectors, Φ is a flux, and p and l signify kinetic production and loss. McRae *et al.* [1982 a and b] break Φ down into its advective components us_i , where u is the velocity field, u , v , w , and into diffusion terms. The partials with respect to space can also be expressed directly [Brasseur and Solomon, 1984; Toon *et al.*, 1988; Kaye and Rood, 1989], as in

$$\partial s_i / \partial t = -(\partial us_i / \partial x + \partial vs_i / \partial y + \partial ws_i / \partial z) + D + p_i(s) - l_i(s) \quad (9)$$

where D is a generalized diffusion adjustment. Here the vector s could just as easily be replaced by the indexed form s_j , where j may or may not be equivalent to i .

When (8) and (9) are solved with chemistry coupled to transport, standard finite differencing is customary. The spectral techniques which lie at the heart of advection in some GCM calculations [see the series Dickinson and Williamson, 1972; Williamson, 1976; Williamson and Temperton, 1981; Rasch, 1985 a and b; Rasch and Williamson, 1990 and 1991] are rarely introduced into chemical kinetics [Norelli, 1986]. Early endeavors first adopted the method of lines to reduce the partial derivatives and yield ODEs (ordinary differential equations) [Liskovets, 1965; Chang *et al.*, 1973].

$$ds_k / dt = f(s_k), \quad (10)$$

where k now covers species and geography. In vector form,

$$ds/dt = f(s). \quad (11)$$

The systems were often very large. Given the spacing on our hypothetical global change grid and, say, 100 species, the result would be 10^3 , 10^5 and 10^7 ODEs in vertical one, zonal two, or full three dimensions -- the method of lines gives 10^3 , 10^5 or 10^7 independent variables.

Most of the finite differencing techniques are subsets of the general multistep [Byrne and Hindmarsh, 1987],

$$s^{t+1} = \sum_{h=0}^{K_1} \alpha_h s^{t-h} + \Delta t \sum_{h=1}^{K_2} \beta_h f(s^{t-h}) \quad (12)$$

where t and $t+1$ are the current and future locations in time, Δt is the step size, and α and β are specific constants. Fundamentally, equation (12) simply states that the time tendency over a new step may be conceived of through the Taylor series approximation and averaging techniques as constructable from estimates of actual values, the time tendency and second derivative at sets of earlier points. Expressed somewhat more succinctly, the vector s^{t+1} can be a weighted string of s and f extending into the past. The α and β are the relevant weighting factors.

Equation (12) can be reduced to the most fundamental of all differencing molecules, the forward (explicit) Euler,

$$s^{t+1} = s^t + \Delta t f(s^t) \quad (13)$$

or to the reverse (implicit) Euler,

$$s^{t+1} = s^t + \Delta t f(s^{t+1}) \quad (14)$$

or even to combinations of them such as the Crank-Nicholson [Crank and Nicholson, 1947; Toon *et al.*, 1988],

$$s^{t+1} = s^t + \Delta t [f(s^{t+1}) + f(s^t)] / 2. \quad (15)$$

The latter is better known for applications to pure transport problems. The multistep also leaves room for an adjustable degree of implicitness [Richtmyer, 1957; Turco and Whitten, 1974], or in other words,

$$s^{t+1} = s^t + \Delta t[\gamma f(s^{t+1}) + (1 - \gamma)f(s^t)] \quad (16)$$

where γ lies between 0 and 1. The generalized backward differentiation formulas (BDFs), of which (14) is a prime example, are another subset of (12) [Byrne and Hindmarsh, 1987].

B. Matrix Iterative Solutions

The term $f(s)$ is necessarily non-linear if photochemistry is included, because of the bimolecular nature of the majority of environmental vapor phase reactions. The chemistries of the atmosphere are driven by solar ultraviolet radiation, which leads to bond breaking, and so to radicals, which are fleeting. Implicit forms of (12) were used initially to stabilize the radicals, and error controls were often instituted, so that the time step was kept small and adjustable. The best known integrator of this type was the Gear code, a multistep BDF [Gear, 1971; Lapidus and Seinfeld, 1971; Chang *et al.*, 1973; Wuebbles and Chang, 1975]. They generally involved iterative matrix inversion to handle the non-linearities. The implicit Euler is taken as a sample of implicit versions of (12) here, though the overall concepts apply to others [Curtiss and Hirschfelder, 1952; Wofsy, 1978]. With g subsuming Δt and s^{t+1} , (14) becomes

$$g(s^{t+1}) = s^t \quad (17)$$

where s^{t+1} are unknown. The most common linearization invokes the Jacobian J , and is another application of the Taylor series. The Jacobian is a multidimensional derivative, a matrix of partials [McRae *et al.*, 1982 a and b], *e. g.*, $J = \partial g / \partial s$. It leads to the multi-dimensional Newton's method or Newton Raphson. The substitution

$$g(s^{t+1}) = g(s^t) + J\Delta s \quad (18)$$

is made into (17), where $\Delta s = s^{t+1} - s^t$. The solution may then be iterated to some desired convergence.

Note that the matrix inversions will be expensive. Packaged linear algebra routines [Dongarra *et al.*, 1979; Dongarra and Sorensen, 1986] usually employ Gauss-Jordan elimination, requiring approximately n^3 operations to solve (18) just once, where n is the number of equations [Oran and Boris, 1981]. In one, two, and three dimensions on our grid, this translates to 10^9 , 10^{15} , and 10^{21} , and in the context of flops estimates from earlier in this report, a step even in one dimension will take exorbitant amounts of time to complete. Although early atmospheric chemical models relied heavily on the Gear code, many groups have since rejected it as too slow [Kasting *et al.*, 1984; Chang *et al.*, 1987]. Certain closely related exponential fitting techniques incorporating the Padé approximation are somewhat more efficient because they allow longer Δt , but still have not found continued applicability in high dimension [Liniger and Willoughby, 1970; Lapidus and Seinfeld, 1971; Thompson and Cicerone, 1982; Cicerone, *et al.*, 1983].

C. Stiffness

Having established the Jacobian as the matrix of partial derivatives, we are now in a position to discuss the motion of "stiffness" in ODEs. The term appears abundantly in the atmospheric chemical literature [*e. g.*, Chang *et al.*, 1973; Turco and Whitten, 1974; McCrae *et al.*, 1982 a and b; Brasseur and Solomon, 1984]. It was coined in 1952 by Curtiss and Hirschfelder. Gear [1971] and Lapidus and Seinfeld [1971] took up the topic in great detail, and Byrne and Hindmarsh [1987] review their work and that of others. One manifestation is a divergence of time constants. In the atmosphere, the short lived radicals which forced implicit techniques upon us must coexist with the major gases. But stiff systems are not only those with a spread in time scales. Many different definitions have been offered for them, and we will attempt to clarify some of the subtleties here.

In the atmosphere, certain species lack sources but possess rapid removal processes and so drop steeply in concentration under some circumstances. The primary examples are radicals at dusk. One of the major reasons for instituting implicit solutions is to preserve stability, or more precisely, positive definiteness, through nightfall. To understand the broadest definitions of "stiffness," imagine at the outset an arbitrary set of ODEs as simply a set of time rates of change for unspecified entities x . If later there is a need to familiarize the problem, they can be identified as chemical species. Assume that the entities are completely decoupled, but for some hypothetical reason we want to integrate them together with a time step dictated by the shortest lived from among them. Some groups of atmospheric species actually behave towards each

other in this way, as in the instances of stable molecules and radicals of different atom type. Now picture another system which happens to be coupled; other atmospheric species track each other -- radicals of varying oxidation state but like atom type. There may be several solution modes for a single species which have different time constants. The latter is one of the less obvious features of stiffness.

The Jacobian eigenvalue problem provides a window on the phenomena. $\mathbf{J}$ may be taken for the time rates of change of $\mathbf{x}$, and put in eigen-problem form:

$$\mathbf{J}\mathbf{x} = \lambda\mathbf{x} \text{ or } [\mathbf{J} - \mathbf{I}\lambda] = \mathbf{0}. \quad (19)$$

Homogeneous linear equations are created; observe that (19) encompasses no constant vector. According to the formal laws of linear algebra, and most particularly, Cramer's rule, solutions other than the null vector $\mathbf{0}$ exist only if the determinant of the matrix $[\mathbf{J} - \mathbf{I}\lambda] = 0$. This yields a polynomial in λ , the eigenvalues. Absolute values of their reciprocals give a spectrum of time constants which correspond to those of individual $\mathbf{x}$ in number and range, but not exact value; some reflect modes, not entities. For the completely decoupled system, the Jacobian is diagonal, and $1/\lambda = \tau$.

Amplification of tutorial calculations first introduced by Gear [1971] are helpful in delineating the roles played by the Jacobian. He outlines one entity-independent example. Stiffness applies but since the variables are uncoupled, they could of course be solved separately. What would Jacobian eigenvalues tell us about such a system?

$$dy/dt = -y, \quad y(0) = 1, \quad (20)$$

$$dz/dt = -1000z, \quad z(0) = 1, \quad (21)$$

$$\mathbf{J} = \begin{bmatrix} -1 & 0 \\ 0 & -1000 \end{bmatrix}. \quad (22)$$

The two λ 's can be solved for directly; $\lambda_1 = -1$ and $\lambda_2 = -1000$. Reciprocals of eigenvalues correspond exactly to time constants in this uncoupled case. As a coupled stiff problem, Gear lists the following,

$$dy/dt = 998y + 1998z, \quad (23)$$

$$dz/dt = -999y - 1999z, \quad (24)$$

with verifiable solutions

$$y = 2e^{-t} - e^{-1000t}, \quad (25)$$

$$z = -e^{-t} + e^{-1000t}. \quad (26)$$

Here the Jacobian is

$$\mathbf{J} = \begin{bmatrix} 998 & 1998 \\ -999 & -1999 \end{bmatrix}. \quad (27)$$

The λ from equation (19) can be derived readily by substitution and a quadratic, and are again -1 and -1000. The $1/\lambda$ are time constants for components of the solutions, not merely for rates of change of the entities.

D. Improvements in Species-segregated Calculations

The need for speed in atmospheric photochemical modelling has driven an evolution of numerics away from the three sources of computational delay we have thus far encountered: the large number of ODEs in the method of lines, matrix inversions, and iteration to convergence for non-linear algebra.

The sheer quantity of variables may be reduced through a procedure known as time or operator splitting. The full continuity equations (8) and (9) transform to

$$\partial s_i / \partial t = -\nabla \cdot \Phi(s_i), \quad (28)$$

and to

$$ds_i/dt = p_i(s_j) - l_i(s_j), \quad (29)$$

which can be thought of in the vector form of equation (11) if f refers to chemistry alone. Both i and j can vary over all constituents. (29)/(11) are now a set of coupled ODEs in the kinetic tracers at each mesh point. Solution over our hypothetical global grid for 100 species requires around grid boxes $\times 100^3 =$ grid boxes $\times 10^6$ operations per iteration. Some groups made this shift directly [McRae *et al.*, 1982 a and b; Rood, 1987; Kaye and Rood, 1989], while others accomplished it in effect by block diagonalizing. The

series of papers by the Lawrence Livermore National Laboratory (LLNL) numericists offers the clearest example of the latter [Byrne and Hindmarsh, 1987; Brown, 1987; Brown and Hindmarsh, 1989; Brown and Saad, 1990; Strout *et al.*, 1991]. Krylov subspace is a critical element in their schemes.

Expressions (28) and (29) dissect full continuity relations into sub-equations pertaining to separate physical processes, which are then solved separately. The same manipulations which lead to them can be performed internally to divide transport into the physical directions, or kinetics into phases. The advantages of decoupling the operators are self-evident; appropriate numerical techniques can be applied independently to different sub-relations, yielding enhancements in speed [McRae *et al.*, 1982 b; Rood, 1987]. Time constants for advection and diffusion within the atmosphere tend to be much longer than those for some chemical reactions, so that transport can be addressed at its own intrinsic efficiency level. Chemistry itself is reduced to an inherently ordinary system, the only independent variable being time.

The cons of splitting are more difficult to assess. Assumptions underlying the approximation are non-physical; forcings which must compete with one another in nature are permitted to act alone on model tracers. McRae *et al.* [1982 b] offer a sophisticated algebraic treatment of the resulting errors and their sources. One important conclusion is that accuracy may be improved if the order in which split equations are solved, or, in other words, the order in which operators are applied is alternated with each new time step. Further details are to be found in Yanenko [1971].

The LLNL group also pioneered in formalizing alternatives to matrix inversion for solution of nonlinear ODEs containing chemistry [Byrne and Hindmarsh, 1987; Brown, 1987; Brown and Hindmarsh, 1989; Brown and Saad, 1990; Strout *et al.*, 1991]. Matrix-free iterations are utilized, with mathematically objective techniques for sorting array elements [Brown and Hindmarsh, 1986]. Some chemically intuitive integrators are closely related. The backward Euler traditional within the Harvard chemistry group models [Wofsy, 1978; Logan *et al.*, 1978; Jacob *et al.*, 1989; Jacob and Wofsy, 1990] is now being converted to the kinetically oriented matrix-free solutions in the interest of speed enhancements [Sillman *et al.*, 1990 a and b; Sillman, 1991]. Time can be advanced semi-implicitly; in the fastest such construction,

$$s_i^{t+1} - s_i^t = (p_i(s_j^t) - s_i^t/\tau_i)\Delta t, \quad \tau_i = s_i^t/l_i(s_j^t), \quad (30)$$

species are completely decoupled from one another. For a single dimension [Richtmyer, 1957] or multiple dimensions with integration in alternating directions [Peaceman and Rachford, 1955; Brasseur *et al.*, 1990], discrete solutions to the partials can be tridiagonal [Richtmyer, 1957; Brasseur *et al.*, 1990]. Species are also segregated if (29) is rewritten

$$ds_i/dt = p_i(s_j^t) - s_i/\tau_i. \quad (31)$$

Analytical solution then gives the standard exponential growth and decay [Hessvedt *et al.*, 1978; McRae *et al.*, 1982 a and b]

$$s_i^{t+1} = s_i^t e^{-\Delta t/\tau_i} + p_i(s_j^t)\tau_i(1 - e^{-\Delta t/\tau_i}). \quad (32)$$

The semi-implicit equation (30) can be placed in an instructive algebraic context. Instead of linearizing (14) or (17) through the Jacobian, we say

$$\mathbf{f}(\mathbf{s}) = \mathbf{f}(\mathbf{s}_{j=i}^t, \mathbf{s}_{j=i}^{t+1}), \quad (33)$$

which gives,

$$\mathbf{s}^{t+1} = \mathbf{s}^t + \Delta t \mathbf{f}(\mathbf{s}_{j=i}^t, \mathbf{s}_{j=i}^{t+1}), \quad (34)$$

or essentially,

$$\mathbf{s}^{t+1} = \mathbf{s}^t + \mathbf{p}(\mathbf{s}^t)\Delta t - \mathbf{s}^{t+1}\Delta t/\tau_i. \quad (35)$$

A few simple steps lead to the system

$$\mathbf{I}\mathbf{s}^{t+1} = \mathbf{q} \quad (36)$$

in which the constant vector $\mathbf{q}$ has the form

$$\mathbf{q} = (\mathbf{s}^t + \mathbf{p}(\mathbf{s}^t)\Delta t)/(1 + \Delta t/\tau_i). \quad (37)$$

The algebra resembles that of the Jacobi method, but is positive definite. Iteration is just a matter of successively substituting the vector $\mathbf{s}^{t+1}$ for $\mathbf{s}^t$, or even $\mathbf{s}_i^{t+1}$ for $\mathbf{s}_i^t$ between vector elements [Elliott *et al.*, 1992].

Iteration and time step control are sometimes preserved in matrix-free solutions to limit error propagation, but there has also been a realization that it only makes sense to impose a certain amount of accuracy upon an atmospheric kinetics calculation [Lapidus and Seinfeld, 1971; Lapidus *et al.*, 1974]. Rate and photolysis constants bear huge inherent uncertainties [Demore *et al.*, 1990], and these are reflected in large disparities in model results [Stolarski *et al.*, 1978; Thompson and Stewart, 1991]. Another step taken by some groups in high dimensionality has been to restrict iteration. Calculations by Sillman [1991] and the Isaksen group in Norway [Hesstvedt *et al.*, 1978; Isaksen and Hov, 1987] fall in this category. In the absence of convergence, concentrations are not evaluated at a unified temporal grid point. Kinetic cancellations are lost and so in turn is mass balance [Shimazaki and Laird, 1970; Turco and Whitten, 1974; Rosenbaum, 1976 and 1977; Shimazaki, 1985; Kaye and Rood, 1989]. Any resulting problems are usually detected by calibration against an integrator of known accuracy [Hesstvedt *et al.*, 1978]. It is worth noting that a separate "clade" [Gould, 1983] on any family tree of photochemical numerics consists of elimination of iterations first, with one-step matrix inversions to advance time. The works of Kasting are a case study [Kasting *et al.*, 1984; Kasting and Singh, 1986].

Having developed a collection of matrix-free and non-iterative formulas for solving the tracer transport continuity equations, we have in hand the tools for a brief heuristic analysis of the time splitting procedure. Our development parallels some idealized one-dimensional coupled chemistry/transport experiments reported by Rood [1987], and relies exclusively on mathematics already familiar to the chemical kineticist.

We begin by imagining a string of cells in a one-dimensional, one tracer calculation, then key on occurrences in a single cell from within the column. Material may be input either through grid point internal kinetics or exchange with neighbors, and there are two loss constants, for chemistry and transport. The system can be solved analytically or numerically, and in either the unified or time split mode, so that comparisons can be made between the different answers and their fidelity can also be assessed. We choose single-step implicit techniques, or, the backward Euler, to discretize both physical processes, in order to mimic as readily as possible the stabilizing properties and positive definiteness of common chemical and transport integrators [Turco and Whitten, 1974; Hesstvedt *et al.*, 1978; Isaksen *et al.*, 1978 a and b; Wofsy, 1978; Smolarkiewicz, 1983; Brasseur *et al.*, 1990; Kao *et al.*, 1991; Elliott *et al.*, 1992].

The arguments spring from the scalar, one-dimensional, and purely advective continuity equation obtained by collapsing (9),

$$\partial s / \partial t = -\partial u s / \partial t + p - k s, \quad (38)$$

where k is a first-order chemical decay constant. The method of lines yields the ordinary differentials

$$ds^n / dt = [(us)^{n-1} - (us)^n] / \Delta x + p - k s^n, \quad (39)$$

in which superscript n refers to position. Need for the superscript is obviated by incorporating external input into production p , so that

$$ds / dt = p - (k_1 + k_2) s, \quad (40)$$

which has the analytical solution

$$s^{t+1} = s^t e^{-(k_1 + k_2) \Delta t} + p(1 - e^{-(k_1 + k_2) \Delta t}) / (k_1 + k_2), \quad (41)$$

by analogy with equation (32), with superscripts denoting the temporal grid once more. Subscripts 1 and 2 now refer to first-order decays associated with transport and chemistry, but not necessarily in that order. A complete and dimensionless derivation is arranged by setting $p = 0$, so that only removal is considered. In this scenario, it can be shown that the fractions of material actually lost to 1 and 2 are

$$F_1 = k_1 / (k_1 + k_2), \text{ and} \quad (42)$$

$$F_2 = k_2 / (k_1 + k_2). \quad (43)$$

Quantities (42) and (43) sum to unity, as of course they must. Unified implicit differencing leads to positive definite predictions for the step Δt ;

$$s^{t+1} - s^t = -(k_1 + k_2) \Delta t s^{t+1}, \text{ and} \quad (44)$$

$$s^{t+1} = s^t / (1 + k_1 \Delta t + k_2 \Delta t). \quad (45)$$

Under time splitting, these become [Toon *et al.*, 1988]

$$s^* - s^t = -k_1 \Delta t s^*, \quad (46)$$

$$s^* = s^t / (1 + k_1 \Delta t), \text{ and} \quad (47)$$

$$s^{t+1} - s^* = -k_2 \Delta t s^{t+1}, \quad (48)$$

$$s^{t+1} = s^* / (1 + k_2 \Delta t), \quad (49)$$

with the step spanning the starred intermediate, and ultimately by elimination,

$$s^{t+1} = s^t / (1 + k_1 \Delta t)(1 + k_2 \Delta t). \quad (50)$$

Calculation of relative amounts of the original material s^t diverted along 1 and 2 is again straightforward. In the unified case, the fractions are identical with (42) and (43). We compact the time split result here by noting that the values $k\Delta t$ are really ratios of time constants r .

$$F_1 = (r_1 + r_1 r_2) / (r_1 + r_2 + r_1 r_2) \quad (51)$$

$$F_2 = r_2 / (r_1 + r_2 + r_1 r_2) \quad (52)$$

Summation to unity again serves as verification.

We may now intercompare results of three methods for advancing the concentrations s in time. Values for final concentrations s^{t+1} and diversions F along the two chambers are listed in Table 2 for different combinations of r_1 and r_2 . It is well known that implicit integrators sacrifice accuracy in order to achieve stability, and the tabulated results reflect this for large r . However, secondary effects involving the distribution of losses are also apparent, and would remain in force for more faithful integrations, such as those invoking fractional steps [Yanenko, 1971]. Only when 1 and 2 are slower than the time step ($r_1, r_2 \ll 1.0$) can relative losses be accurately portrayed, because only then do both processes have call on the same amount of material, namely, the full initial complement of the cell. If sub-solutions alter the original concentration substantially, errors arise. The very coarse sampling in the table suggests that there may be some benefits associated with tackling a fast process first consistently when it is coupled to a slow one, in order to prevent over-estimation of the slower path. If 1 and 2 are both fast ($r_1, r_2 \gg 1.0$), large channelling errors are guaranteed, and alternation of operator order leads to fractions near one half because the first caller always takes the bulk of the material. It should be noted that due to space considerations, our table does not include any instances of $r_1 = r_2$. Their symmetry leads necessarily but fortuitously to the correct result $F_{av} = 0.5$, where the average is taken over two time steps with reversed operator order. No significant new information would be gained by adding them to the itemization.

Table 2. Final to initial concentration ratios and fractions of initial material following each of two loss channels for sets of ratios r of time step to time constant, and for analytical (a), implicit but process unified (iu), and implicit but process split (is) solutions. Subscript *av* signifies averages as the order of operator application is alternated over two time steps.

$r_1:$	0.1	10^{-3}	10	0.1	1000	10
$r_2:$	10^{-3}	0.1	0.1	10	10	1000
$s^{t+1}/s^t:$						
a:	0.904	0.904	4.11e-5	4.11e-5	--	--
iu:	0.908	0.908	0.0901	0.0901	9.89e-4	9.89e-4
is:	0.908	0.908	0.0826	0.0826	9.08e-5	9.08e-5
$F_1:$						
a:	0.990	9.90e-3	0.990	9.90e-3	0.990	9.90e-3
iu:	0.990	9.90e-3	0.990	9.90e-3	0.990	9.90e-3
is:	0.990	0.0109	0.991	0.0991	0.999	0.909
$F_2:$						
a:	9.90e-3	0.990	9.90e-3	0.990	9.90e-3	0.990
iu:	9.90e-3	0.990	9.90e-3	0.990	9.90e-3	0.990
is:	9.89e-3	0.989	9.01e-3	0.901	9.08e-4	0.0908
$(F_1)_{av}:$						
a:	0.990	9.90e-3	0.990	9.90e-3	0.990	9.90e-3
iu:	0.990	9.90e-3	0.990	9.90e-3	9.90e-3	9.90e-3
is:	0.9895	0.0104	0.946	0.0541	0.545	0.455
$(F_2)_{av}:$						
a:	9.90e-3	0.990	9.90e-3	0.990	9.90e-3	0.990
iu:	9.90e-3	0.990	9.90e-3	0.990	9.90e-3	0.990
is:	0.0104	0.9895	0.0541	0.946	0.455	0.545

The physical structure of global photochemical models will in general be dictated by the accurate resolution of winds [Toon *et al.*, 1988; Kaye and Rood, 1989; Kao *et al.*, 1990] so that at least one of the two phenomena transport and chemistry will fall in the $r < 1.0$ regime. Application of GCM wind fields in their CTM descendents has been made to a variety of individual species with lifetimes exceeding transport scales [Rood *et al.*, 1987; Prather *et al.*, 1987; Jacob *et al.*, 1987; Spivakovsky *et al.*, 1990]. These simulations should not lead to errors under time splitting [Kao *et al.*, 1991]. In interactive, multi-species calculations, on the other hand, chemistry could be process 1 in an $r_1 > 1.0 > r_2$ situation. Production terms will buffer the solutions to some extent, but will not always be present, as for radical groupings at dusk. At some point, we hope to explore operator splitting in greater depth by encoding the computation of s^{t+1} and F over wide ranges of p and r for equations (41) through (52).

Perhaps the safest conclusion which can be drawn from Table 2 is that stiff tracers should be observed carefully in any split calculation. Time segregation can be viewed as a necessary evil which is embraced because of its utility and elegance.

E. Families

In parallel with all the individual species photonumerics, family integrations developed. Rapidly interchanging molecules and radicals can be grouped as tracers in and of themselves, with longer collective time constants [Chapman, 1930; Crutzen, 1970]. Families have enabled explicit integration in as high as two dimensions on the global scale [Garcia and Solomon, 1983; Solomon and Garcia, 1983; Crutzen and Gidel, 1983; Gidel *et al.*, 1983]. Forward differencing restores mass balance, and the total number of tracers is reduced while time steps lengthen. There is a small cost associated with family groupings; they must be partitioned before production and loss can be constructed. New continuity equations become appropriate, and some intriguing linear algebraic interpretations follow.

The family method recognizes that rapidly cycling species act in concert as persistent constituents in many photochemical situations, then assumes steady state to repartition [Chapman, 1930; Crutzen, 1971; Turco and Whitten, 1974 and 1977; Brasseur and Solomon, 1984]. A new array of tracers c_n is defined which consists of sums over subsets of s ; $c_n = \sum_j s_{j,n}$, where j,n denotes molecule j within assemblage n . Species containing more than one atom of a type must of course be weighted accordingly [Turco and Whitten, 1974]. For example, Cl_2O_2 may comprise two units of chlorine oxide. Weighting factors will be subverted here to prevent the notation from becoming too cumbersome. Family scale versions of equations presented earlier can then be formulated, with both n and m varying over all groups, as in

$$dc_n/dt = p_n(s_{j,m}) - l_n(s_{j,m}) = f_n(s_{j,m}), \quad (10a), (29a)$$

$$dc/dt = f(s), \quad (11a)$$

$$c^{t+1} = c^t + \Delta t f(s^{t+1}), \quad (14a)$$

$$c_n^{t+1} - c_n^t = (p_n(s_{j,m}^t) - c_n^{t+1}/\tau_n)\Delta t; \quad \tau_n = c_n^t/l_n(s_{j,m}^t), \text{ and} \quad (30a)$$

$$c_n^{t+1} = c_n^t e^{-\Delta t/\tau_n} + p_n(s_{j,m}^t)\tau_n(1 - e^{-\Delta t/\tau_n}). \quad (32a)$$

Analogous statements regarding linearity, solution efficiency, positive definiteness, stability and atom balance remain in force. Identification of appropriate membership j,n can be based on more accurate schemes [Graedel, 1977; Farrow and Graedel, 1977] or on experience [Turco and Whitten, 1977; Solomon and Crutzen, 1981; Garcia and Solomon, 1983] with later confirmation [Solomon, 1981; Chang *et al.*, 1987].

Families have enabled marching at convenient step sizes in a host of detailed one-dimensional photochemical models [*e. g.*, Crutzen, 1971; Turco and Whitten, 1977; Crutzen *et al.*, 1978], and thus far seem to be a method of choice in higher dimensionality as well [*e. g.*, Garcia and Solomon, 1983; Gidel *et al.*, 1983; Kaye and Rood, 1989; Rose and Brasseur, 1989]. Some provisos must be mentioned, however. In three dimensions, some researchers have minimized the tracer number by eliminating source molecules such as N_2O and the chlorofluorocarbons, which do not contribute significantly to chemistry on short time scales [Kaye and Rood, 1989; Rose and Brasseur, 1989]. Additionally, species normally thought of as reservoirs, including ClONO_2 , N_2O_5 , HNO_3 , and HCl , tend to be lumped together into larger, more stable families, in order to promote time step increases [Douglass *et al.*, 1989; Brasseur *et al.*, 1990; Austin,

1991]. Rapidly removed constituents then go untransported [Rose and Brasseur, 1989; Brasseur *et al.*, 1990]. These approximations are to an extent symptoms of the computational stress imposed by massive grids.

Partitioning of assemblages c_n into constituents $s_{j,n}$ can be analyzed in the parlance of certain fundamentals of linear algebra. Topological representations of solutions to linear systems can be constructed and understood in or by analogy with Euclidean 2 and 3 space, which are both readily visualizable.

In the time split mode for our atmospheric chemical systems, the ODEs integrated are from kinetic systems alone. We often use a linearized implicit form such as (14), and this gives us a non-homogeneous algebraic equation set; the constant vector in the general form

$$\mathbf{M}\mathbf{x} = \mathbf{r} \quad (53)$$

is non-zero. For the purposes of the photochemist, the vector $\mathbf{x}$ is a set of concentrations for all species s , so we are operating in n space where n is the total number of constituents. $\mathbf{M}\mathbf{x} = \mathbf{r}$ is a set of equations for objects of dimension $n-1$ in that n space, by analogy with 2 or 3 space, where they would be lines or planes. The shapes are randomly distributed, so that the vector of values which solves them, their intersection, is likely to exist. If the objects were organized in some fashion, intersections might be avoided, but they are not; two lines in 2 space or three planes in 3 space will intersect in a point unless there is some degree of parallelism. Usually in a finite differencing system, parallels do not occur. This means there is probably a unique solution.

We can interpret such geometries in terms of formal definitions for solutions to linear algebra problems found by employing Cramer's rule. The solution vector elements are given by

$$x_i = \det \mathbf{M}_i / \det \mathbf{M} \quad (54)$$

where $\mathbf{M}_i$ has the i th column replaced by $\mathbf{r}$. Usually neither $\det \mathbf{M}$ nor $\det \mathbf{M}_i$ is precisely equal to zero. If $\det \mathbf{M} = 0$, no unique solution exists. The matrix is singular.

In a number of important circumstances in atmospheric chemistry, homogeneous systems are encountered. The first instance met here was the Jacobian eigenvalue problem (19). Note that the constant vector is exactly $\mathbf{0}$. In n space, a homogeneous algebra set also represents n objects of dimension $n-1$, but all are constrained to pass through the origin. The shapes thus already have one point in common. If they have a unique solution, then it is necessarily trivial. Any other solutions must contain the origin. In 2 and 3 space, for example, the two lines may be identical, or three planes may be rotations around a line, and the solution is also a line, through $\mathbf{0}$. In vector notation, this line has the form $\mathbf{p} = \mathbf{0} + \beta \mathbf{p}_0$, where β is a scalar scaling factor, $\mathbf{p}$ is a point in n space on the line, and $\mathbf{p}_0$ is our reference point. In formal solution terms, we can only get non-trivial, or non-unique solutions if $\det \mathbf{M} = 0$ -- if the coefficient matrix is singular. Note also that with Cramer's rule applied, if $\det \mathbf{M}$ is non-zero, $\det \mathbf{M}_i$ must vanish because $\mathbf{r}$ is $\mathbf{0}$. The trivial answer results.

In the eigenvalue problem, $\det \mathbf{M} = 0$ is a polynomial with n solutions for λ . There are n combinations of the $n-1$ -dimensional objects such that they have non-zero solutions. Each of these combinations corresponds to a vector, the eigenvector, and in 3 or 2 space, it defines the line of intersection.

Now finally we move into family chemistry. Here 2 and 3 space serve as more than just analogies, because photochemical ensembles often contain only a few members. Family chemistry usually entails the assumption of photochemical equilibrium, or that $ds_{j,n}/dt = 0$ and $ds_n/dt = 0$. Implicit finite differencing gives a homogeneous set. In our kinetic experience, it must have a non-trivial solution, but according to the above, this is only possible if $\det \mathbf{M} = 0$. By virtue of the cyclic nature of the chemistry, zero determinants are often the case. The odd oxygen family can be cited. Photochemical equilibria for the members ozone and atomic oxygen O³P (ignoring O³D) are

$$\text{O}_3': \quad 0 = k\text{O}_2\text{O} - d\text{O}_3, \quad (55)$$

$$\text{O}: \quad 0 = -k\text{O}_2\text{O} + d\text{O}_3, \quad (56)$$

$$\det \mathbf{M} = k\text{O}_2d - k\text{O}_2d = 0, \quad (57)$$

with kinetic terms comprising the coefficients underlined, and d signifying the photolysis constant. J is a more common choice for the latter, but we wish to avoid nomenclatorial conflicts with the Jacobian. For the hypothetical interchanging collection $s_{1,n} \rightarrow s_{2,n} \rightarrow s_{3,n} \rightarrow s_{1,n}$,

$$s_{1,n}: \quad 0 = -\underline{k}_1 s_{1,n} + \underline{Q} s_{2,n} + \underline{k}_3 s_{3,n}, \quad (58)$$

$$s_{2,n}: \quad 0 = \underline{k}_1 s_{1,n} - \underline{k}_2 s_{2,n} + \underline{Q} s_{3,n}, \quad (59)$$

$$s_{3,n}: \quad 0 = \underline{Q} s_{1,n} + \underline{k}_2 s_{2,n} - \underline{k}_3 s_{3,n}, \quad (60)$$

$$\det M = -\underline{k}_1(-\underline{k}_2 - \underline{k}_3) - 0 + \underline{k}_3(\underline{k}_1 \cdot \underline{k}_2) = 0. \quad (61)$$

In our 2 and 3 spaces, $\det = 0$ indicates that the two lines solving the system are identical, or the three planes are rotations around a line. The concentration relationships we obtain are ratios, as we know from solving such systems analytically, and they can be expressed as a set of concentration values, or values for elements of the concentration vector multiplied by the arbitrary scaling factor, which we determine by mass balance.

Chained kinetics also apply, as in the methane oxidation sequence following the methyl radical;

with parentheses defining a methyl peroxy-oxy assemblage. At photoequilibrium,

$$\text{CH}_3\text{O}_2: \quad 0 = k (\text{CH}_4)(\text{OH}) - k' (\text{NO})(\text{CH}_3\text{O}_2), \quad (63)$$

$$\text{CH}_3\text{O}: \quad 0 = k' (\text{NO})(\text{CH}_3\text{O}_2) - k'' (\text{O}_2)(\text{CH}_3\text{O}), \quad (64)$$

but in fact we only use the second equation to partition because families exclude extra familial P , and because the first does not contain information relating CH_3O_2 to CH_3O . The single equation in two unknowns establishes a line in 2 space, through 0, or, again, just a set of ratios of concentrations.

IV. OPTIMIZATION OF THE CHEMICAL OPERATOR

A. The Integrator

To begin our discussion of techniques for optimizing a photochemical package for the global scale, we center on the kinetic integrator itself. It is the most crucial feature of the program, and it flows most directly from the numerics review. Figure 5 summarizes the evolution of photochemistry solvers as we have traced it. The shaded blocks are elements in the linear algebra problems of equations (11) to (64).

The evolution is also traced in Appendix A, a bibliography including references over and above those in the math framework section. The listing is merely skeletal. The body of knowledge available is vast, definitely running to many hundreds of scientific publications. Full accounting might well reveal thousands of separate papers. We have elected to streamline the search process by adopting a global viewpoint for the entire atmosphere including the stratosphere, since tropospheric work can be thought of as a downward extension. It might eventually prove profitable to repeat our bibliographic strategy springing from the regional smog or acid rain data bases, but we have not stressed the two sources here. We first gathered contributions from a handful of major modelling groups active on the global scale, or potentially so [e. g., Chang *et al.*, 1987; Rose and Brasseur, 1989; Kaye and Rood, 1989; Jacob *et al.*, 1989; Kao *et al.*, 1990; Penner *et al.*, 1991; Sillman, 1991; McKeen *et al.*, 1991; Crutzen and Zimmerman, 1991; Brost *et al.*, 1991], then worked backwards to the ultimate numerical expositions. This led us to a smattering of regional atmospheric investigations with particularly strong explanations of their computational aspects [e. g., McRae *et al.*, 1982 a and b; Carmichael *et al.*, 1986; Chang *et al.*, 1987] and also into the applied mathematics literature on discrete solutions of various types of differential equations [e. g., Crank and Nicholson, 1947; Curtiss and Hirschfelder, 1952; Peaceman and Rachford, 1955; Liskovets, 1965; Liniger and Willoughby, 1970; Gear, 1971; Lapidus and Seinfeld, 1971; Briley and McDonald, 1980; Byrne and Hindmarsh, 1987].

Figure 5. A schematic history of the evolution of integrators in the field of atmospheric chemistry. Squares represent coefficients in the linear algebra problems within the mathematical framework section.

The gathered results are arranged chronologically in the table and within a calendar year, alphabetically. A checklist of computational, philosophical and architectural characteristics is appended and roughly corroborates our story line. A few idiosyncrasies in the footnotes deserve mention. We have marked models dealing with the non-methane hydrocarbons because they are of particular interest in the troposphere. Some references discuss a type of numerics for comparative purposes without ever applying it. Longer symbol lists tend to identify reviews or models with strong review sections.

Based on our computational timing arguments and the trends in Appendix A, several points are clear. First of all, time splitting is likely to be a feature of early global scale photochemical models [McRae *et al.*, 1982 a and b; Rood, 1987; Kaye and Rood, 1989; Kao *et al.*, 1990]. Secondly, the chemical operator must function toward the lower end of the spectrum in Figure 5. Chang *et al.* [1987] concluded, for example, that even in the time split mode, matrix inversion would be prohibitive. Sillman and coworkers [Sillman *et al.*, 1990 a and b; Sillman, 1991] have shown that iterations must be dispensed with whether matrices are involved or not. Atherton and Penner [1991] concur on both points. It will also be advantageous to advance chemistry at near the upper limit time step, defined by the diurnal cycle to be about one hour. Even if diurnal averaging is employed [Isaksen and Hov, 1987], a full daily cycle has to be run around once per week, and so must still be conducted rapidly. Many individual species and several traditional families such as HO_x and $\text{CH}_3\text{O}_2/\text{CH}_3\text{O}$ are unstable at hour increments, so that a conflict necessarily arises between achieving speed, accuracy, and mass balance; implicit integration is demanded, but may be conducted in the spirit of equations (30)-(37). The unity of the concentration vector is then lost [Isaksen and Hov, 1987; Rose and Brasseur, 1989; Brasseur *et al.*, 1990; Sillman, 1991]. Some groups will ignore the conflict [Sillman *et al.*, 1990 a and b; Crutzen and Zimmerman, 1991; Sillman, 1991], while others will attempt to monitor any problems through calibration [Hesstvedt *et al.*, 1978; Isaksen and Hov, 1987].

The authors of the present report have been exploring an alternative option. In several of our models, we have resolved the conflict in part by superimposing mass balance post hoc. The simplest approach would be to integrate over the species semi-implicitly and non-iteratively, then count atoms afterward; since

there are only a few atom types in terrestrial atmospheric models, adjustments can be applied to concentrations through a small linear problem. A more sophisticated technique exploits the lengthened time constants of families and the algebraic properties of their distributions.

Instead of just partitioning at photochemical equilibrium within an assemblage, a family can be distributed into species along a time coordinate. For example, in a hypothetical three-member collection, the time rate of change for species 1 might be expressed in the implicit form

$$s_{1,n}^{t+1} - s_{1,n}^t = (p_{ext} + p s_{2,n}^{t+1} + p s_{3,n}^{t+1} - l s_{1,n}^{t+1}) \Delta t \quad (65)$$

where the subscript *ext* refers to an extra-familial process and *p* and *l* are no longer full production and loss terms, but rather are time constants: *p* for family internal exchange, *l* for loss of the species at hand. Subsuming Δt into matrix coefficients, the family chemistry takes the form

$$(\mathbf{L} - \mathbf{P}_{int} + \mathbf{I}) \mathbf{s}_n^{t+1} = \mathbf{p}_{ext} + \mathbf{s}_n^t, \quad (66)$$

in which **L** and **I** are diagonal, **P** is dense, and *int* identifies internal production.

The family partitioning has now been rendered non-homogeneous, so that a definite result can be obtained for the constituents. The concentrations s_n^{t+1} can be sent through a family version of the forward Euler to restore mass balance, and in our experience, they have a highly stabilizing effect upon it. We have tested these numerics extensively with the inorganic chemistry of the stratosphere as our laboratory. For one-half to two-hour time steps applying the forward filter, negative concentrations almost never arise, even at sunset [Cicerone *et al.*, 1991 and 1992; Elliott *et al.*, 1992]. Bimolecular terms can be linearized to preserve positive definiteness and minimize compromises to atom balance within the family by adopting the conservative substitution

$$k s_{j,n} s_{j',n} = k (s_{j,n}^{t+1} s_{j',n}^t + s_{j,n}^t s_{j',n}^{t+1}) / 2, \quad (67)$$

when the time tendency is for a species $i \neq j, j'$, and the implicit form when *i* is involved in a removal reaction;

$$-k s_{j,n} s_{i,n} = -k s_{j,n}^t s_{i,n}^{t+1}. \quad (68)$$

The species levels must occasionally be summed and normalized to *c*, and calibration is still required, but satisfactory accuracy levels are preserved. Figure 6 gives a sample of fidelity comparisons conducted in the mid-latitude stratosphere. We have recently succeeded in running fully detailed inorganic photochemistry on the global scale in the stratosphere of the Los Alamos GCM using (65)-(68). Figure 7 shows results for the hydroxyl radical at two-hour time steps, on the eighth day of a forty-day simulation.

Figure 6. Comparison of concentrations in a one-hour time step family integration with implicit partitioning and a forward Euler filter, and an individual species calculation at one-second step size. For several members of a ClO_x family at 20 km, 45°N latitude, from a five-day box model run.

Figure 7. Zonally averaged hydroxyl radical concentrations within the stratosphere of the Los Alamos National Laboratory GCM.

B. Parallelism

As a secondary form of optimization, the integrator selected from a menu such as Figure 5 must itself be "integrated" into the tracer transport code at hand, and onto the transport grid. This returns us to the consideration of the multi-processing capabilities of modern supercomputers.

Our calculation of asymptotic performances for simulations on the global change grid assumed that the parallelism was fully realized on some generic machine. This goal may in fact be attainable in part, but only through the design of clever and carefully tailored coding. We have already outlined a hypothetical chemical geographic grid of extent $100 \times 100 \times 10$; modelling of multiple interacting constituents may be viewed as the addition of yet another dimension, and several options exist for pushing chemical calculations through the resulting four-dimensional space at each temporal grid point. We now ask which combinations of dimension best facilitate parallelism.

Let us again turn to the workhorse genre of single cpu vector supercomputers to lay groundwork. In the Cray series, the one processor is partitioned into an instruction unit and several mathematical/logical units [Levesque and Williamson, 1989]. The latter may be thought of as multiple subprocessors. Efficiency is largely maintained through the constructs of pipelining (p) -- enhancing the ratio of instructions, which are expensive, to operations by conducting many per, and chaining (c) -- overlapping of operations. Critical to both are short term memory systems known as registers, to which segments of variable arrays may be promoted for *p* or *c*. Arrays treated in this fashion are designated vectors, and a

vector is simply a list of individual values, or scalars. The size of the registers determines a vector length. On Cray machines, it has tended to be 2^6 , or 64 (Table 1). Crudely speaking, the machine can strip mine short loops, 64 indices at a time [Metcalf, 1982]. Competitive benchmarking for the scalar and vector modes suggests that performance enhancements for specific program segments generally fall between 10-100, as would be expected [Levesque and Williamson, 1989]. Within Cray vector machines, additional cpu's are also partitioned, and to zeroth order, they may be conceived of as working concurrently in the vector or scalar modes on differing stretches of coding, so that maximal performance rises while vector enhancements are similar. As a rule of thumb for the Cray family of machines, then, the theoretical performance can be approached if loops with index ranges greater than the vector length can be prioritized, or more specifically, can be placed innermost.

The simplest chemical integrator within our mathematical framework is the semi-implicit species independent set of equations (34)-(37). Solutions segregate naturally into just a few steps: rates must be calculated first, then production and loss terms, and finally, changes in species concentration. Although analogous manipulations would apply to a family method, we adopt the pure semi-implicit version here as a context in which to explore application of vectorization principles to the photochemical operator. An earlier treatment of the topic by Boris and Winsor [1982] contains some similarities.

The construction of photochemical rates requires looping over all reactions and all locations, with calls to local, initial species concentrations. The major vector inhibitor in most FORTRAN compilers is recursion [Boris and Winsor, 1982; Levesque and Williamson, 1989], but rate calculations involve none, so that vectorization can be arranged along any of the relevant indices. Both the number of reactions and the number of geographical grid points are likely to exceed the vector length, but the grid by a larger margin, because the several physical directions can be sequenced if desired as a single array; there is no inter-cellular chemical coupling. We conclude that during calculation of rates on vector supercomputers, it may be most advantageous to set reaction identity on an outer loop, and then run over large sections of the mesh performing the rate constant/concentration product. This result is chemically somewhat counter-intuitive. The first instinct of most photochemists would likely be to complete the operation set within a particular location. The geographic strategy is portrayed schematically in Figure 8, with the longest loops in the horizontal.

Production and loss terms must be fabricated through loops over the reactions, species, and again, the locations. The reaction index is necessarily recursive, because it constitutes a functional or array-to-scalar type variable reduction [Levesque and Williamson, 1989]. Furthermore, in first-generation global tropospheric photochemical models, the number of species may be much less than vector lengths. The physical grid is therefore again the inner dimension of choice. The actual species concentration integration must also be looped over species and location, with the same result.

Because of their partitioned architecture, the one-cpu Cray machines fall into the category single instruction stream multiple data stream (SIMD) [Flynn, 1966; Jordan, 1982], and later models come under the heading multiple instruction stream multiple data stream (MIMD). Our brief analysis indicates that some advantage may be taken of their diverse parallel processing capabilities by placing the physical dimensions inside chemical looping, and by training the grid indices. The arguments made here should also extend to more massively parallel computers such as the TM Connection Machine or the prototype Cray MPP. Setting aside fundamentals such as Amdahl's law and sorting overhead, their effectiveness is limited either by the number of processors, which may be many hundreds, or by loop length. On the physical grid, the index range can be competitive. The inherently intracellular nature of the chemical operator in fact renders it an ideal vehicle for the many-processor approach.

Figure 8. A schematic, massive three-dimensional tracer transport grid. One way to exploit parallelism on supercomputers is to run along large sections, repetitively performing some small segment of a chemical kinetics calculation.

To this point in the text, we have justified our emphasis on speed in photochemistry models by comparison of computational and wall clock times. With reference material on machine architecture now at hand, we are in a position to amplify; it is possible to demonstrate that chemical modules may be rate-limiting relative to the routines which will be their companions in global change calculations. Some of the fastest advection schemes in common use are based on tridiagonal algebraic systems [Chock and Dunker, 1983; Thompson, 1984; Chock, 1985; Rood, 1987; Prather *et al.*, 1987]. The Los Alamos National Laboratory and NASA Ames tracer transport algorithms, for example, are finite-element chapeaux in the horizontal [Toon *et al.*, 1987; Kao *et al.*, 1991], with the alternating directions time split [Peaceman and Rachford, 1955; Brasseur *et al.*, 1990]. On the order of n operations are required to obtain the solution of the advective continuity equations in each column, where n is the number of cells in length. Just as the chemical operator is location-independent, advection in the alternating mode is intracolumnar only. It should therefore be feasible in a transport module to group like tridiagonal solution elements and build innermost loops over two of the three dimensions. This gives loop index ranges of at least 1000 in our hypothetical global change grid, sufficient to exploit normal vector lengths and/or large processor sets.

Since both chemistry and advection should parallelize, their relative computational intensities can be assessed crudely by counting mathematical operations. Both must be looped over geography: chemistry once and transport three times. Both must be looped over the tracers to integrate, requiring several operations in either case. To this stage, the two are competitive, but we have already shown that processing of kinetic data set requires preliminary passes over not just cells and constituents but also over the chemical reactions, even for the least sophisticated numerics. In this scenario, the potential for a photochemical package to limit calculation rates is clear. More refined treatments of parallelism in atmospheric tracer transport problems may be found in Boris and Winsor [1982] or Almasi and Gottlieb [1989].

C. Reaction Set Selection and Automation

Yet other secondary optimizations involve processing of the kinetic data set before calculation begins. The inorganic chemistry of the stratosphere is relatively well understood, but uncertainties and new reactions are continually being uncovered [e. g., Solomon, 1988; Jones *et al.*, 1989]. We have claimed that thousands of organic molecules must be considered in modelling tropospheric chemistry. There will also be thousands of reactions relating them. Clearly, a great deal of streamlining is needed before a photochemist can even write his program.

Several types of trick have been developed for reducing the magnitude of the data set. Smog chemists lump functional groups as a matter of course. For example, in the Falls and Seinfeld mechanism [1978], peroxide radicals in all branching networks of the form of Figure 1 or 2 would be treated as a single tracer RO_2 . The trees from 1 and 2 are reprised in Figure 9 to illustrate; a conceptual band is drawn across the networks, linking common structures. The only species added to such a scheme are the stable organic precursors, so that a relatively few hydrocarbons can comprise a complete list. The price of the reductionism is high, however; extensive calibration of generalized rate constants and branching ratios is required to fit more accurate models or smog chamber experiments. This is true for single pollutants, say O_3 in an urban air shed, or H_2O_2 or H_2SO_4 in acid rain. Quantitative predictions may be possible, but for limited circumstances only. In the global troposphere, NO_x and organic concentrations vary widely, so that the calibration task would be enormous.

Figure 9.
The branching hydrocarbon oxidation networks of figures 1 and 2 repeated and schematic connections drawn between oxidized intermediates of like structure.

There are some subtle variations on the smog lumping theme worth mentioning. McRae and Seinfeld [1983] presented a scheme with some similarities to Falls and Seinfeld [1978]. The carbon bond mechanisms, however, are distinct. Beginning with Whitten *et al.* [1980], it was recognized that organics could be artificially dissected into their constituent parts. For example, the alkene propylene focused upon in figures 1 and 2 might be input as one unit of paraffin, or saturated hydrocarbon, and one unit of olefin, or double bond. The carbon bond scheme has been refined and expanded in the series culminating in Gery *et al.* [1989]. The RADM program has adopted a hybrid mechanism for organics [Stockwell, 1986; Chang *et al.*, 1987; Stockwell *et al.*, 1990]. Two useful reviews/intercomparisons of smog chemical reaction sets have appeared in the last few years [Hough, 1988; Dodge, 1989].

Families offer an alternative to smog chemical lumping as a means to condense organic decompositions. Species are again collected, but in secular equilibria along a single oxidation branch, as displayed in Figure 10. The number of species within each tree is cut dramatically but a full network must be added with each precursor. As a consequence, groups adopting family schemes may be forced to choose representative hydrocarbons as surrogates for classes of compounds. There is ample precedent for the maneuver [Thompson and Cicerone, 1986; Isaksen and Hov, 1987; Chatfield and Delany, 1990; Pickering *et al.*, 1990, 1991 a and b]. Propane propene and isoprene are often selected for the alkanes, alkenes and terpenes, respectively. Detail is abandoned among the stable organics, but calibration problems are reduced, and general mechanistic relationships are preserved. Mechanism may be the most interesting facet of initial global tropospheric chemical models. Only when the myriad feedback loops connecting HO_x , NO_x , ozone and the NMHCs begin to be elucidated can one hope to predict changes in greenhouse gas photochemistry quantitatively. It will be critical first to understand how the changes might occur.

Figure 10.
The branching hydrocarbon oxidation networks of figures 1 and 2 repeated and schematic family linkages drawn around short-lived groups of intermediates.

Once the reaction scheme is decided upon, the kineticist can start to program -- but pitfalls must be avoided here too. Hard wiring of some preliminary chemical data set can leave one painted into a corner. Because of the intricacy of tropospheric chemistry, experimentation with combinations of species, families and reactions is to be expected. Ideally, a photochemistry routine reads lists of constituents and processes, then assembles solutions to the continuity equations automatically.

We have made considerable progress in this area in our group. It is of course likely that other chemistry set-up routines are in existence, but we will review the philosophies behind ours here as a guide. The computer is provided with complete lists of chemical kinetic species, reactions and family definitions as data input. The set-up program reads first the list of species, and creates an array of character data identifiers for them; methane might be indicated CH₄, and peroxy acetyl nitrate as PAN. Next, the list of reactions is read, and smaller arrays of product and reactant identifiers constructed for each reaction. Likewise, arrays of family members are created, and one option is naturally for the list of species and families to be identical, or, in other words, for integration to be performed in the species segregated mode.

The routine now focuses upon one family, and scans the reaction list for processes producing it or destroying it. The reactions are each associated with a numerical tag, and for the family at hand, arrays of production and loss reaction tags ensue. The integrator itself can now sum reaction rates over these arrays, and calculate new, time-advanced concentrations in (13) or its family equivalent. Implicit computations merely require the deduction of a loss constant as in (30) or (30a).

Although we are currently tracking the coefficients in the matrices of (66) largely through manual editing, they lend themselves readily to construction through the same sorts of character data and reaction number arrays [Elliott *et al.*, 1992]. A high priority within our group is automation of the linear algebra underlying family partitioning.

V. SUMMARY AND CONCLUSION

We have argued here that there will be a growing need for chemistry modules to fit into models relating to global change. Because they have appeared first in the stratosphere and because the chemistry of the troposphere is so much more complex, we have focused here on potential lower atmospheric versions. On a sheer numbers basis, the species which influence greenhouse gases in the troposphere are largely organic and total in the thousands, so that chemistry packages addressing them will have to make use of a battery of refinements to operate on what we have defined here as the global change grid: GCM resolutions of 100,000 or more cells blanketing the earth, and runs extending out decades. At least initially, chemical integrations must be matrix-free, non-iterative and must invoke long time steps. They must be directed along the grid in clever ways to take advantage of parallel processing; basically, long physical dimensions can be placed on inner loops, but subtleties remain to be investigated. Only a few dozen tracers will function on the global grid, so the full chemical data set has to be streamlined. Smog-like lumping and family surrogate techniques are possibilities. Streamlining will probably require experimentation which will be facilitated by automation of the setup of solutions.

Some of the tradeoffs involved in the above options are collected in brief in Table 3. We will not make any attempt here to proffer recommendations. As in the two-dimensional case, calls for replication, sensitivity tests and model intercomparison will be heard [Jackman *et al.*, 1989; Lashof and Tirpak, 1990; WMO, 1989 and 1991; Thompson, 1992]. There will undoubtedly be room for many chemical models of the global scale troposphere, and it is likely that different groups will employ different permutations of the Table 3 techniques. This is in fact desirable in several ways: it will lead to natural variation among models and, to draw on a biological analogy, a healthy, adaptable population. Also, the selection of model design will probably vary with the questions asked. For example, it seems safe to assume that although early efforts may be of the surrogate mechanism type so that modellers can follow hydrogen atoms and O-O bond splitting precisely as hydrocarbons decompose as confidence in understanding of mechanism grows, the challenge of calibrating lumped schemes will seem less formidable. Ambient measurements will then permit checking against real data, so that the ability of lumped reaction sets to incorporate large numbers of species will be exploited. They may even achieve eventually the type of quantitative predictive ability already realized in the urban pollution context.

Table 3. Relative advantages of some techniques designed to permit tropospheric chemistry to proceed on the global change grid.

<u>Mode of optimization</u>	<u>pros</u>	<u>cons</u>
the integrator:		
restrict iteration	speed	loss of accuracy mass balance
families	speed	programming effort
vectorization	parallelism	programming effort
the data set:		
lumping	increases number of species	loss of mechanistic detail, heavy calibration requirement
surrogates	preserves mechanistic detail	decreases number of species
automation	permits experimentation	programming effort

Some obvious omissions from our report deserve discussion at this point; we have devoted ourselves almost wholly to the homogeneous phase here, and for good reason. As in other atmosphere contexts such as stratosphere [Solomon, 1988; Brune *et al.*, 1991], it is the best understood phase. Moreover, it dominates the chemistry under many critical circumstances and so will be the first phase modeled. Tropospheric heterogeneous chemistry involves dissolution into cloud droplets and the ensuing aqueous phase kinetics [Graedel and Weschler, 1981; Graedel and Goldberg, 1983; Graedel *et al.*, 1986; Lelieveld and Crutzen, 1990 and 1991]. It will entail subgrid scale components in keeping with cloud patterns and so will constitute a later step in model development. Lelieveld and Crutzen have recently coupled cloud surface area estimates to aqueous models in order to estimate effects on the gas phase [1990 and 1991]. Their work points the way toward subgrid scale heterogeneous parameterizations.

Itemization of some of the specific calculations which could eventually be tackled in a global tropospheric chemical model is also in order before closing here. Crutzen and Zimmermann [1991] have already shown that an idealized reaction scheme with just methane oxidation from among the organics can be used to investigate remote ozone chemistry. They have studied O_3 distributions before and after industrial era effects on CH_4 and CO distributions. But this had also been done in low dimensionality [*e. g.*, Isaksen and Hov, 1987], and CH_4 and CO are both long enough lived that their chemistry can be thought of at least to zeroth order as linear. We have demonstrated here that in the vicinity of biological activity, the short-lived O_3 precursors NO_x and NMHC decay rapidly along a latitude circle so that their interactions can only be modeled with zonal resolution. Projects relating to their effects on the photochemical greenhouse gases abound, and a few may be mentioned here as motivation for continued work; Crutzen, for example, has pointed out that as third world nations industrialize, NO_x emissions will encroach on the huge hydrocarbon releases associated with tropical forests [1988]. Presently, only 10% of NMHC is oxidized at nitrogen oxide levels sufficient for ozone production. The potential exists to turn the rain forests into smog chemical regimes and to drastically raise the extent of internal ozone production within the troposphere. Internal production currently accounts for only about 50% of all lower-atmosphere ozone, with the bulk of the remainder transported across the tropopause from the stratosphere [Crutzen, 1988]. As a second example, it may be noted that subsonic aircraft release NO_x into the free troposphere, and could move large sections of it above the organic titration points [Crutzen, 1988]. The effect has been modeled thoroughly in one dimension [Liu *et al.*, 1980; Johnston *et al.*, 1989] and later in two [Derwent *et al.*, 1982; Johnson *et al.*, 1992], but is again inherently zonal because flight corridors have longitudinal dependence [Thompson, 1992; personal communication with M. Prather, 1992].

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APPENDIX A: BIBLIOGRAPHY

Table A. A coarse sampling of chemical numerics discussed and applied in the global atmospheric and related literatures.

Legend			
A	= automation	M	= matrix inversion
B	= mass balance	N	= non-iterative
0,1,2,3D	= dimension, 0, 1, ...	NMHC	= non-methane hydrocarbons
E	= exponential	Pa	= parameterized chemistry
Fa	= families	Po	= positive definiteness
Fr	= matrix free	S	= time splitting
G	= global	St	= stiffness
I	= iteration	V	= vectorization
L	= method of lines	1,2,3,...	= number of chemical species

Year/Author(s)	Model Features	Year/Author(s)	Model Features
30 Chapman	Fa	76 Edelson	M, I, 0D, St, A
47 Crank Nicholson	L, Fr, N, B, 1D	76 Liu <i>et al.</i>	Fa, 1D
51 O'Brien <i>et al.</i>	L, Fr, N, B, 2D	76 Matloff	M, I
52 Curtiss Hirschfelder	M, I, St	76 Rosenbaum	B
55 Peaceman Rachford	L, S, Fr, N, B, 2D	77 Farrow Graedel	M, I, Fa, 0D
57 Richtmyer	I, 1D, 1	77 Gelinas Cox	M, I, 0D, A
60 Wachspress	1D, 1	77 Graedel	M, I, Fa
65 Bellman Kalaba	M, I	77 Liu	Fa, 1D
65 Liskovets	L	77 Oran Young	S, Fr, N
67 Emanuel	Fa, B	77 Reinhardt	S
68 Keller	M, I	77 Ridler <i>et al.</i>	B, A
68 Lomax	M, I, Fr, N	77 Ridler	M, I
69 Ames	M, I, Fr, N	77 Rosenbaum	B
69 Gear	M, I, 0D	77 Turco Whitten	Fr, N, B, Fa, 1D, G
70 Crutzen	Fa	77 Warner	Fr, N, St
70 Liniger Willoughby	M, I, E, St	77 Winslow	M, I
70 Shimazaki Laird	I, Fr, N, B	77 Young Boris	Fr, N
70 Strobel <i>et al.</i>	I, L, 1D, 2	78 Brasseur	Fr, N, Fa, 2D, G
71 Crutzen	Fa, 1D	78 Crutzen <i>et al.</i>	Fa, 1D
71 Gear	M, I, E, Fr, N, St	78 Crutzen Solomon	M, I, Fr, N, B, Fa, 1D
71 Lapidus Seinfeld	M, I, E, Fr, N, St	78 Engquist <i>et al.</i>	M, I
71 Strobel	I, L, 1D	78 Hesstvedt <i>et al.</i>	M, I, Fr, N, B, 0D, Po
72 Gelinas	St	78 Isaksen Hesstvedt Hov	M, I, Fr, N, B, 0D, Po
72 Shimazaki	I, Fr, N, B	78 Isaksen Hov Hesstvedt	M, I, Fr, N, B, 0D, Po
73 Chang <i>et al.</i>	M, I, L, 1D, G, St	78 Johnston Podolske	Fa
73 Edelson	Fa, B	78 Kreskovsky Shamr...	M, I, 2D
73 Whitten <i>et al.</i>	Fr, N, B, Fa, 1D, G	78 Logan <i>et al.</i>	M, I, 2D
73 Young Boris	Fr, N	78 Mahlman Moxim	3D, 1
74 Crutzen <i>et al.</i>	Fa, 1D	78 Miller <i>et al.</i>	M, I, 1D, St
74 Farrow Edelson	M, I, Fa, St	78 Penner Chang	M, I, L, 1D
74 Gear Watanabe	M, I, St	78 Wofsy	M, I, S, B, 2D, Po
74 Liu Donahue	Fa, 1D	79 Graedel	M, I, 0D
74 McElroy <i>et al.</i>	Fa, 1D	79 Iserles	M, I, E
74 Turco Whitten	M, I, Fr, N, B, Fa, 0D, Po, St	79 Levy <i>et al.</i>	3D, 1
74 Whitten Turco, A	Fr, N, B, Fa, 1D	79 Miller <i>et al.</i>	M, I, 1D, St
74 Whitten Turco, B	Fr, N, B, Fa, 1D, G	79 Shampure Gear	St
74 Wofsy McElroy	M, I, Fa, 1D	79 Turco <i>et al.</i> , A & B	Fr, N, B, Fa, 1D, G, St
75 Byrne Hindmarsh	M, I	80 Briley McDonald	M, S, Fa
75 Cunnold <i>et al.</i>	3D, 1	80 Kasting Donahue	Fa, 2D
75 Ogawa Shimazaki	Fa	80 Liu <i>et al.</i> , A & B	Fa
75 Turco Whitten	Fr, N, B, Fa, 1D, G	80 Mahlman	3D, 1
75 Whitten <i>et al.</i> , A & B	Fr, N, B, Fa, 1D, G	80 Miller <i>et al.</i>	M, I, 2D
75 Wofsy McElroy Sze	M, I, Fa, 1D	80 Saad	M, I, Fr, N
75 Wofsy McElroy Yung	M, I, Fa, 1D	81 Brasseur Simon	Fa, 2D
75 Wuebbles Chang	M, I, L, 1D, G, St	81 Kansa	M, I
76 Crutzen	Fa, 1D	81 Logan <i>et al.</i>	M, I, S, B, 2D, Po
76 Dickinson Gelinas	M, I, 0D, St	81 Miller Filkin <i>et al.</i>	M, I, 2D
		81 Miller Steed <i>et al.</i>	M, I, 2D, St

Table A. (continued)

Year/Author(s)	Model Features	Year/Author(s)	Model Features
81 Oran Boris	M, I, S, Fr, N, B, Fa, Po, St	88 Brasseur Hitchman	S, Fr, N, Fa, 2D, G, Po
81 Saad	M, I, Fr, N	88 Brost <i>et al.</i>	L, S, Fr, N, Fa, 3D
81 Solomon	M, I, Fr, N, B, Fa, 2D, G, St	88 Brost	L, S, Fr, N, Fa, 3D
81 Solomon Crutzen	Fa, 1D	88 Bruhl Crutzen	Fa, 1D
81 Solomon <i>et al.</i>	Fa, 1D	88 Liu <i>et al.</i>	0D, NMHC
81 Turco <i>et al.</i>	Fr, N, B, Fa, 1D, G	88 Liu Trainer	0D, NMHC
82 Boris Winsor	V	88 Toon <i>et al.</i>	S, Fr, N, 3D
82 Kasting	M, I, L, 1D	88 Zimmermann <i>et al.</i>	3D, G, 1
82 McRae <i>et al.</i> , A	S	89 Atherton	M, I, 0D
82 McRae <i>et al.</i> , B	M, I, S, B	89 Brasseur <i>et al.</i>	S, Fr, N, Fa, 3D, G, Po
82 Thompson Cicerone	M, I, E, 1D	89 Brost <i>et al.</i>	L, S, Fr, N, Fa, 3D
82 Zinn <i>et al.</i>	M, I, 2D	89 Brost Chatfield	L, S, Fr, N, Fa, 3D
83 Cicerone <i>et al.</i>	M, I, E, 1D	89 Brown <i>et al.</i>	M, I, Fr, N
83 Crutzen <i>et al.</i>	Fr, N, Fa, 2D, G	89 Brown Hindmarsh	M, I, Fr, N
83 Garcia Solomon	Fr, N, Fa, 2D, G	89 Douglass <i>et al.</i>	S, Fa, 2D
83 Gear Saad	M, I, Fr, N	89 Jacob <i>et al.</i>	3D, Pa
83 Gidel <i>et al.</i>	Fr, N, Fa, 2D, G	89 Jones <i>et al.</i>	Fr, N, B, Fa, 0D
83 Rogers Pyle	Fr, N, Fa, 2D, G	89 Kaye <i>et al.</i>	3D, 1
83 Solomon Garcia	Fr, N, Fa, 2D, G	89 Kaye Rood	S, Fr, N, B, Fa, 3D, G
83 Wuebbles	M, I, L, 1D	89 Kinnison <i>et al.</i>	M, I, 2D
83 Wuebbles <i>et al.</i>	M, I, L, 1D	89 Ko <i>et al.</i>	M, I, 2D
84 Chatfield Crutzen	Fa, 2D, G	89 McElroy Sala..., A & B	M, I, S, B, 2D, Po
84 Kasting <i>et al.</i>	M, I, L, 1D	89 Rood <i>et al.</i> , A	3D, 1
84 Ko <i>et al.</i>	M, I, 2D	89 Rood <i>et al.</i> , B	L, S, Fr, N, B, Fa, 3D
84 Kurzeja <i>et al.</i>	3D, 1	89 Rood Kaye	3D, V
84 Prather <i>et al.</i>	M, I, S, B, 2D, Po	89 Rose Brasseur	Fa, 3D
84 Zimmermann	3D, G, 1	89 Turner <i>et al.</i>	Fa, 3D
85 Brasseur Rose	Fa, 3D	89 Wuebbles Kinnison	M, I, 2D
85 Kasting	M, I, L, 1D	89 Zimmermann <i>et al.</i>	3D, G, 1
85 Kasting <i>et al.</i>	M, I, L, 1D	90 Atherton Penner	M, I, 0D
85 Keating <i>et al.</i>	Fa, 1D	90 Brasseur <i>et al.</i>	S, Fr, N, Fa, 2D, G, Po
85 Shimazaki	M, I, L, Fr, N, B, Fa, Po, St	90 Cariolle <i>et al.</i>	3D, G, 1
85 Stordal <i>et al.</i>	L, S, Fr, N, 2D, G	90 Donahue Prinn	Fr, N, 0D, Po
86 Brown Hindmarsh	M, I, Fr, N	90 Jacob Wofsy	M, I, B, Po, 1D, NMHC
86 Cariolle Deque	S, 3D, 1	90 Kao <i>et al.</i>	S, Fr, N, B, Fa, 3D, G
86 Carmichael <i>et al.</i>	S, 3D	90 Rood <i>et al.</i>	S, 3D, 1
86 Dunker	Pa	90 Sillman <i>et al.</i> , A & B	M, I, L, S, Fr, N, 3D, NMHC
86 Golombek Prinn	3D, 1	90 Smith Brasseur	S, Fr, N, Fa, 3D, G, Po
86 Kouker Brasseur	3D, 1	90 Spivakovsky <i>et al.</i>	3D, 1, Pa
86 Kasting Singh	M, I, L, 1D	90 Zinn Sutherland	M, I, 2D
86 Jacob	M, I, 0D	91 Austin	Fa, 2D
86 Mahlman <i>et al.</i>	3D, 1	91 Brost <i>et al.</i>	3D, 1
86 Malone <i>et al.</i>	3D, 1	91 Erickson <i>et al.</i>	S, 3D, G, 5
86 McElroy <i>et al.</i>	M, I, 0D	91 Feichter <i>et al.</i>	3D, 1
87 Brasseur <i>et al.</i>	Fa, 1D	91 Granier Brasseur	S, Fr, N, Fa, 3D, G, Po
87 Brown	M, I, Fr, N	91 Kanakidou <i>et al.</i>	S, Fr, N, Fa, 2D, G, NMHC
87 Byrne Hindmarsh	M, I, Fr, N	91 Kaye <i>et al.</i>	S, Fr, N, B, Fa, 3D, G
87 Chang <i>et al.</i>	M, I, L, S, Fr, N, Fa, 3D, Po, NMHC, St	91 Langner Rodhe	3D
87 Jacob <i>et al.</i>	3D, 1	91 Mc Keen <i>et al.</i> , A & B	Fr, N, 3D, NMHC
87 Liu <i>et al.</i>	Fa, 0D, NMHC	91 Penner <i>et al.</i>	3D, 1
87 Marsden <i>et al.</i>	Pa	91 Rood <i>et al.</i>	3D, 1
87 Prather <i>et al.</i>	3D, 1	91 Sillman	Fr, N, 3D
87 Rood <i>et al.</i>	S, 3D, 1	91 Smolarkiewicz Rasch	P
87 Rood	S	91 Strout <i>et al.</i>	M, I, Fr, N, V
87 Toon <i>et al.</i>	M, I, L, 1D	91 Trainer <i>et al.</i>	1D, NMHC
87 Trainer <i>et al.</i>	S, 1D, NMHC	92 Elliott <i>et al.</i>	M, I, E, L, S, Fr, N, B, Fa, 0D, Po, V
88 Atherton Penner	M, I, 0D	92 Jacobson Turco	M, I, L, S, Fr, N, B, Fa, 3D, Po, V, NMHC

APPENDIX B: EQUATIONS

	section
(1) $dO_3/dt = k(OH)(NMHC)$	(II. C.)
(2) $dO_3/dt = f[(NO_x)^n(NMHC)^m]$	(II. C.)
(3) $p = a(NO_x)(NMHC)$	(II. C.)
(4) $(p_h + p_l)/2 = a[(NO_{xh})(NMHC_h) + (NO_{xl})(NMHC_l)]/2$	(II. C.)
(5) $p_{av} = a(NO_{xav})(NMHC_{av})$	(II. C.)
(6) $= a[(NO_{xh} + NO_{xl})/2](NMHC_h + NMHC_l)/2$	(II. C.)
(7) $= a[(NO_{xh})(NMHC_h) + (NO_{xl})(NMHC_l) + (NO_{xh})(NMHC_l) + (NO_{xl})(NMHC_h)]/4$	(II. C.)
(8) $\partial s_i/\partial t = -\nabla \cdot \Phi(s_i) + p_i(s) - l_i(s)$	(III. A.)
(9) $\partial s_i/\partial t = -(\partial u s_i/\partial x + \partial v s_i/\partial y + \partial w s_i/\partial z) + D + p_i(s) - l_i(s)$	(III. A.)
(10) $ds_k/dt = f(s_k)$	(III. A.)
(11) $ds/dt = f(s)$	(III. A.)
(12) $s^{t+1} = \sum_{h=0}^{K_1} \alpha_h s^{t-h} + \Delta t \sum_{h=1}^{K_2} \beta_h f(s^{t-h})$	(III. A.)
(13) $s^{t+1} = s^t + \Delta t f(s^t)$	(III. A.)
(14) $s^{t+1} = s^t + \Delta t f(s^{t+1})$	(III. A.)
(15) $s^{t+1} = s^t + \Delta t [f(s^{t+1}) + f(s^t)]/2$	(III. A.)
(16) $s^{t+1} = s^t + \Delta t [\gamma f(s^{t+1}) + (1 - \gamma)f(s^t)]$	(III. A.)
(17) $g(s^{t+1}) = s^t$	(III. B.)
(18) $g(s^{t+1}) = g(s^t) + J\Delta s$	(III. B.)
(19) $Jx = \lambda x$ or $[J - I\lambda] = 0$	(III. C.)
(20) $dy/dt = -y, \quad y(0) = 1$	(III. C.)
(21) $dz/dt = -1000z, \quad z(0) = 1$	(III. C.)
(22) $J = \begin{bmatrix} -1 & 0 \\ 0 & -1000 \end{bmatrix}$	(III. C.)
(23) $dy/dt = 998y + 1998z$	(III. C.)
(24) $dz/dt = -999y - 1999z$	(III. C.)
(25) $y = 2e^{-t} - e^{-1000t}$	(III. C.)

EQUATIONS (continued)

section

- (26) $z = -e^{-t} + e^{-1000t}$ (III. C.)
- (27) $J = \begin{bmatrix} 998 & 1998 \\ -999 & -1999 \end{bmatrix}$ (III. C.)
- (28) $\partial s_i / \partial t = -\nabla \cdot \Phi(s_i)$ (III. D.)
- (29) $ds_j/dt = p_i(s_j) - l_i(s_j)$ (III. D.)
- (30) $s_i^{t+1} - s_i^t = (p_i(s_j^t) - s_i^{t+1}/\tau_i)\Delta t, \quad \tau_i = s_i^t/l_i(s_j^t)$ (III. D.)
- (31) $ds_i/dt = p_i(s_j^t) - s_i/\tau_i$ (III. D.)
- (32) $s_i^{t+1} = s_i^t e^{-\Delta t/\tau_i} + p_i(s_j^t)\tau_i(1 - e^{-\Delta t/\tau_i})$ (III. D.)
- (33) $f(s) = f(s_{j\pi i}^t, s^{t+1}_{j=i})$ (III. D.)
- (34) $s^{t+1} = s^t + \Delta t f(s_{j\pi i}^t, s^{t+1}_{j=i})$ (III. D.)
- (35) $s^{t+1} = s^t + p(s^t)\Delta t - s^{t+1}\Delta t/\tau_i$ (III. D.)
- (36) $Is^{t+1} = q$ (III. D.)
- (37) $q = (s^t + p(s^t)\Delta t)/(1 + \Delta t/\tau_i)$ (III. D.)
- (38) $\partial s/\partial t = -\partial us/\partial t + p - ks$ (III. D.)
- (39) $ds^n/dt = [(us)^{n-1} - (us)^n]/\Delta x + p - ks^n$ (III. D.)
- (40) $ds/dt = p - (k_1 + k_2)s$ (III. D.)
- (41) $s^{t+1} = s^t e^{-(k_1 + k_2)\Delta t} + p(1 - e^{-(k_1 + k_2)\Delta t})/(k_1 + k_2)$ (III. D.)
- (42) $F_1 = k_1/(k_1 + k_2)$ (III. D.)
- (43) $F_2 = k_2/(k_1 + k_2)$ (III. D.)
- (44) $s^{t+1} - s^t = -(k_1 + k_2)\Delta t s^{t+1}$ (III. D.)
- (45) $s^{t+1} = s^t/(1 + k_1\Delta t + k_2\Delta t)$ (III. D.)
- (46) $s^* - s^t = -k_1\Delta t s^*$ (III. D.)
- (47) $s^* = s^t/(1 + k_1\Delta t)$ (III. D.)
- (48) $s^{t+1} - s^* = -k_2\Delta t s^{t+1}$ (III. D.)
- (49) $s^{t+1} = s^*/(1 + k_2\Delta t)$ (III. D.)
- (50) $s^{t+1} = s^t/(1 + k_1\Delta t)(1 + k_2\Delta t)$ (III. D.)

EQUATIONS (continued)

	section
(51) $F_1 = (r_1 + r_1 r_2)/(r_1 + r_2 + r_1 r_2)$	(III. D.)
(52) $F_2 = r_2/(r_1 + r_2 + r_1 r_2)$	(III. D.)
(10a),(29a) $dc_n/dt = p_n(s_{j,m}) - l_n(s_{j,m}) = f_n(s_{j,m})$	(III. E.)
(11a) $dc/dt = f(s)$	(III. E.)
(14a) $c^{t+1} = c^t + \Delta t f(s^{t+1})$	(III. E.)
(30a) $c_n^{t+1} - c_n^t = (p_n(s_{j,m}^t) - c_n^t/\tau_n)\Delta t; \tau_n = c_n^t/l_n(s_{j,m}^t)$	(III. E.)
(32a) $c_n^{t+1} = c_n^t e^{-\Delta t/\tau_n} + p_n(s_{j,m}^t)\tau_n(1 - e^{-\Delta t/\tau_n})$	(III. E.)
(53) $Mx = r$	(III. E.)
(54) $x_i = \det M_i / \det M$	(III. E.)
(55) $O_3: 0 = kQ_2O - dO_3$	(III. E.)
(56) $O: 0 = -kQ_2O + dO_3$	(III. E.)
(57) $\det M = kO_2d - kO_2d = 0$	(III. E.)
(58) $s_{1,n}: 0 = -k_1s_{1,n} + Qs_{2,n} + k_3s_{3,n}$	(III. E.)
(59) $s_{2,n}: 0 = k_1s_{1,n} - k_2s_{2,n} + Qs_{3,n}$	(III. E.)
(60) $s_{3,n}: 0 = Qs_{1,n} + k_2s_{2,n} - k_3s_{3,n}$	(III. E.)
(61) $\det M = -k_1(-k_2 \cdot -k_3) - 0 + k_3(k_1 \cdot k_2) = 0$	(III. E.)
(62) $CH_3O_2 (+ NO) \rightarrow CH_3O (+ O_2) \rightarrow CH_2O$	(III. E.)
(63) $CH_3O_2: 0 = k(CH_4)(OH - k'(NO)(CH_3O_2)$	(III. E.)
(64) $CH_3O: 0 = k'(NO)(CH_3O_2) - k''(O_2)(CH_3O)$	(III. E.)
(65) $s_{1,n}^{t+1} - s_{1,n}^t = (p_{ext} + ps_{2,n}^{t+1} + ps_{3,n}^{t+1} - ls_{1,n}^{t+1})\Delta t$	(IV. A.)
(66) $(L - P_{int} + I)s_n^{t+1} = p_{ext} + s_n^t$	(IV. A.)
(67) $ks_{j,n}s_{j',n} = k(s_{j,n}^{t+1}s_{j',n}^t + s_{j,n}^ts_{j',n}^{t+1})/2$	(IV. A.)
(68) $-ks_{j,n}s_{i,n} = -ks_{j,n}^ts_{i,n}^{t+1}$	(IV. A.)

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9/21/93

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