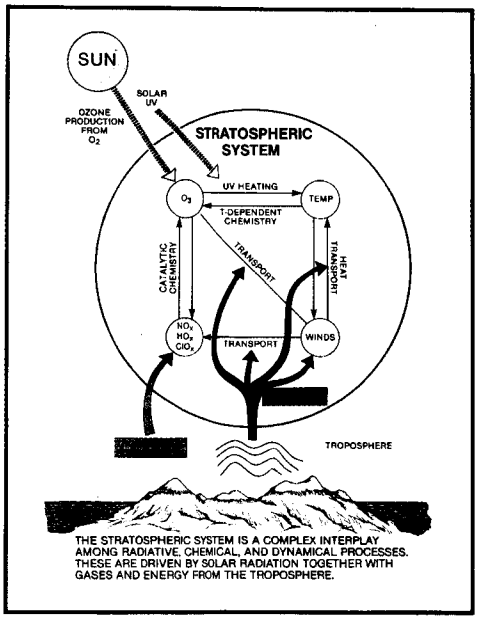
CHAPTER 1

INTRODUCTION AND SCIENCE SUMMARY



THE STRATOSPHERIC SYSTEM IS A COMPLEX INTERPLAY AMONG RADIATIVE, CHEMICAL, AND DYNAMICAL PROCESSES. THESE ARE DRIVEN BY SOLAR RADIATION TOGETHER WITH GASES AND ENERGY FROM THE TROPOSPHERE.

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CHAPTER 1: INTRODUCTION AND SCIENCE SUMMARY

For several decades scientists have sought to understand the complex interplay between the chemical, radiative, and dynamical processes that govern the structure of the Earth's atmosphere. During the last decade or so there has been particular interest in studying the processes which control atmospheric ozone since it has been predicted that man-made pollutants might cause harmful effects to the environment by modifying the total column content and vertical distribution of atmospheric ozone. Until recently most of the emphasis was directed towards understanding the stratosphere where greater than 90% of the ozone resides. However, during the last few years there has been an increasing interest in studying those factors which control ozone in the troposphere.

Changes in the total column content of atmospheric ozone would modify the amount of biologically harmful ultraviolet radiation penetrating to the Earth's surface with potential adverse effects on human health (skin cancer) and on the aquatic and terrestrial ecosytems. Changes in the vertical distribution of atmospheric ozone, along with changes in the atmospheric concentrations of other infrared active gases, could contribute to a change in climate on a regional and global scale by modifying the atmospheric temperature structure.

The ozone issue has evolved from one of the effect of individual pollutants to consideration of a multiplicity of possible pollutants the effects of which must be considered together. The man-made and natural chemicals of interest include the nitrogen oxides (NO_x) from subsonic and supersonic aircraft, nitrous oxide (N_2O) from agricultural and combustion practices, chlorofluorocarbons (CFC's) used as aerosol propellants, foam blowing agents, and refrigerants, brominated compounds used as fire retardants, carbon monoxide (CO) and carbon dioxide (CO_2) from combustion processes, and methane (CH_4) from a variety of sources including natural and agricultural wetlands, tundra, biomass burning, and enteric fermentation in ruminants. It is now clear that these same gases are also important in the climate issue.

It should be noted that there are two distinct aspects of the issue that need to be considered, i.e. understanding those processes that control the atmospheric distribution of ozone today, and those processes that need to be understood in order to be able to predict the atmospheric distribution of ozone in the future. If changes are observed in the distribution of ozone we must be able to understand how periodic and episodic natural phenomena such as solar activity and volcanic eruptions cause ozone to vary in space and time in order to isolate the impact of the changing atmospheric concentrations of gases such as the CFC's, CO_2, CH_4, and N_2O.

Since the scientific community first attempted to understand the chemical, radiative, and dynamical processes which control the temporal and spatial distribution of atmospheric ozone today, and to predict the distribution of ozone in the future, our recognition of the breadth of the issue has steadily increased. Originally the research emphasis was focused on understanding the physical and chemical processes occurring within the stratosphere. Now, however, we recognize that in order to be able to predict the distribution of ozone in the future we cannot be confined to simply understanding stratospheric chemistry, radiation, and dynamics but we also need to understand the processes controlling the chemical composition of the troposphere, the exchange mechanisms for energy, mass and chemical constituents across the tropopause, and the role of biospheric processes in controlling the emissions of gases into the atmosphere. This has made the ozone issue an example of how one problem requires us to bring knowledge from a variety of sources to bear on its solution and how understanding this problem contributes back to other fields such as the trace gas-climate problem and the global cycling of nitrogen and carbon.

INTRODUCTION

Thus to really understand the processes which control atmospheric ozone and to predict perturbations we are drawn into a study of the complete Earth system. This requires us to study the Earth as a single coupled system which involves chemical, physical, and biological processes occurring in the atmosphere, on land, and in the oceans. This is exactly the same situation which exists if we want to understand and have some predictive capability for the climate system. This report mirrors these increasing perceptions of the coupled nature of the system and, while focusing on the stratosphere, gives more consideration to the other aspects of the issue than previous reports on the ozone issue.

In particular the scientific community recognizes, and this report discusses, that:

(a) There is strong coupling in the stratosphere between the chemistry, radiation, and dynamics. This is because atmospheric ozone is a strong absorber of solar radiation, thus strongly influencing the temperature structure and circulation of the stratosphere, which in turn controls the distribution of atmospheric ozone and the trace gases which control ozone.

(b) Since 1930, when Chapman first proposed a simple photochemical scheme involving only odd oxygen species to explain the atmospheric concentration of ozone, our understanding of the photochemistry of the atmosphere has evolved significantly. Scientists have refined this simple scheme by invoking the importance of trace concentrations (ppbv) of HO_x, NO_x, ClO_x, and to a lesser extent BrO_x species in catalytically controlling atmospheric ozone. In addition, we also recognize that the atmospheric concentrations of a number of carbon compounds including CO, CO_2, and CH_4 play a vital role in the photochemistry of ozone. In particular, we recognize that there is strong coupling between the individual members of each chemical family, and that while each of these families individually is important in controlling odd oxygen, there is strong chemical coupling between the different chemical families, thereby modifying their individual roles in controlling ozone.

(c) At different times during the last decade or so scientists have suggested that the atmospheric concentrations of one or more of the source gases of the hydrogen, carbon, nitrogen, chlorine, or bromine chemical families may be changing due to human activities, and in each case have attempted to predict the response of the ozone layer to such individual changes. We now have reliable experimental evidence that the atmospheric concentrations of several of the source gases, i.e. CH_4, N_2O, and the chlorofluorocarbons, are all currently changing at a significant rate and that their impact on atmospheric ozone must be considered collectively and not in isolation.

(d) We need to understand the role of the biosphere in regulating the emissions of gases such as CH_4, CO_2, N_2O, and CH_3Cl to the atmosphere, and we need to know the most probable future industrial release rates of gases such as the CFC's, N_2O, CO, and CO_2 which depend upon economic, social, and political factors.

(e) Because of the fact that neither the chemical composition nor the interplay between meteorology and chemistry can be duplicated exactly in the laboratory, heavy reliance must be placed on theoretical models to describe the present and future behavior of the atmosphere. As a consequence it is necessary to define a careful strategy of investigation involving the proper balance between laboratory studies of fundamental processes, field measurements, and theoretical studies.

(f) While one-dimensional photochemical models have been, and will continue to be, extensively used for assessment purposes we must place more emphasis in the future on the development of two-dimensional and three-dimensional interactive photochemical models. Such multidimensional models allow us to explore the seasonal, latitudinal, and longitudinal behavior of ozone. Also, given that they more realistically represent the real world, they are more amenable to validation using field measurements of atmospheric composition.

(g) The climate problem has broadened in scope from the CO_2-climate problem to the trace gas-climate problem. Changes in the atmospheric concentrations of ozone as well as H_2O, CH_4, N_2O, the CFC's, and other gases will all modify the thermal structure of the atmosphere.

(h) We need to improve our understanding of tropospheric chemistry because of its vital role in controlling the atmospheric lifetimes of many of the source gases such as CH_4 and CH_3Cl, which influence atmospheric ozone and the radiative balance of the atmosphere. We also recognize that changes in tropospheric ozone will influence the climate system and will affect our interpretation of trends in the total ozone column.

(i) A vital component of any atmospheric research program is the acquisition of well calibrated long-term (multiyear) measurements of atmospheric parameters in order to monitor the state of the atmosphere and to differentiate between the different scales of temporal variability.

(j) Global data sets obtained from satellites are essential to complement data obtained using ground, aircraft, balloon, and rocket based instrumentation. Such data sets are essential to more fully understand the interplay on a global scale between chemical, radiative and dynamical processes, and to validate aspects of the multidimensional models. In addition, such data are needed to check the geographical representativeness of local measurements of large scale phenomena.

Unlike some other more localized environmental issues, e.g. acid deposition, ozone layer modification is a global phenomenon which affects the well-being of every country in the world. Many nations around the world have actively demonstrated their commitment to understand the processes which control atmospheric ozone, and its susceptibility to change because of human activities, by funding research which should reduce the uncertainties that currently exist concerning the magnitude of predicted ozone modification for different atmospheric concentrations of pollutants. In order to achieve this required greater level of understanding, national and international scientific agencies have implemented long range research programs aimed at developing an organized, reliable body of knowledge of upper atmospheric processes while providing, in the near term, assessments of potential effects of human activities on the atmosphere.

Many governments around the world have recognized that the use of chlorofluorocarbons constitutes a potential threat to the stability of the ozone layer, and have taken a series of individual actions to regulate the use of these substances. However, there has been no coordinated international approach to safeguard the ozone layer. It was recognized by several nations that effective protection of the ozone layer requires a coordinated international approach to regulating substances that are thought to modify atmospheric ozone. Consequently, the United Nations Environment Program (UNEP) Governing Council, at its ninth session in 1981, decided to initiate work aimed at the elaboration of a global framework convention for the protection of the ozone layer. It was decided to establish an Ad Hoc Working Group of Legal and Technical Experts nominated by interested governments and intergovernmental organizations. Representatives from about twenty different countries met in Stockholm, Sweden in January 1982 to initiate formal discussions on the desirability of a global framework ozone convention which would (a) harmonize regulatory control

actions on ozone modifying substances at the international level, (b) increase coordination of ozone related research, and (c) increase the exchange of information on all scientific, economic, technical, and legal issues relevant to the ozone issue. After a series of meetings of the Ad Hoc Working Group of Legal and Technical Experts, a Convention for the Protection of the Ozone Layer was adopted by twenty-one nations at a Diplomatic Conference held in Vienna, Austria, in March 1985. Since that time four more nations have signed the convention. At the thirteenth UNEP Governing Council meeting held in May, 1985, a schedule was adopted for the possible completion of a protocol to regulate chlorofluorocarbons. Since the convention specifically states that all measures taken under this convention should be based on relevant scientific and technical considerations, and that nations should collaborate on scientific assessments, the need for a comprehensive evaluation by the international scientific community of all facets of the ozone issue is clear.

Therefore, in order to provide governments around the world with the best scientific information currently available on whether human activities represent a substantial threat to the ozone layer, several scientific agencies agreed to co-sponsor a peer reviewed international assessment of our current state of knowledge. This assessment is much more comprehensive than any previous assessment. It discusses, among other topics, the physical, chemical, and radiative processes which control the spatial and temporal distribution of ozone in the troposphere and stratosphere; the magnitude of natural and industrial sources of substances capable of modifying atmospheric ozone; observations of the composition and structure of the stratosphere; the predicted magnitude of ozone perturbations for a variety of emission scenarios involving a number of substances changing both individually and together; the predicted climate change for similar trace gas scenarios employed to predict ozone perturbations; and the ozone and temperature data used to detect the presence or absence of a long-term trend. Previous assessments have tended to be narrower both in scope and in the degree of international participation.

There has been an increasing level of cooperation and coordination at the international level over the last decade for ozone assessment activities. This is demonstrated by the international participation in this report and the previous World Meteorological Organization (WMO)/National Aeronautics and Space Administration (NASA)/National Oceanic and Atmospheric Administration (NOAA)/Federal Aviation Administration (FAA) report in 1982. There have been at least three types of assessment report relating to the ozone issue produced over the last decade, i.e.

(a) comprehensive national assessment reports such as the series produced biennially by the National Academy of Sciences in the USA, the latest of which is "Causes and Effects of Changes in Stratospheric Ozone: Update 1983," and those issued by the Department of the Environment, United Kingdom, the latest of which is "Chlorofluorocarbons and Their Effect on Stratospheric Ozone (second report)" - Pollution Paper #15, 1979.

(b) international summary reports written by a small select group of scientists at a one-week meeting such as the yearly series issued by the UNEP Coordinating Committee on the Ozone Layer (CCOL), the latest of which is "Environmental Assessment of Ozone Layer Depletion and its Impact as of October 1984," and the one issued in 1981 by the Commission of the European Communities, (CEC), "Evaluation of the Effects of Chlorofluorocarbons on Atmospheric Ozone: Present Status of Research."

(c) comprehensive international reports such as that issued by the WMO in 1982 which had over 100 participants from the international scientific community, "The Stratosphere 1981: Theory and Measurements" WMO Global Ozone Research and Monitoring Project Report #11.

This scientific assessment is being co-sponsored by three US agencies, i.e. the National Aeronautics and Space Administration (NASA), the Federal Aviation Administration (FAA), and the National Oceanic and Atmospheric Administration (NOAA); three international agencies, i.e. the World Meteorological Organization (WMO), the United Nations Environment Program (UNEP), and the Commission of the European Communities (CEC), and Bundesministerium für Forschung und Technologie (BMFT) of the Federal Republic of Germany.

Approximately 150 scientists from Australia, Belgium, Brazil, Canada, the Federal Republic of Germany, France, Italy, Japan, Norway, the United Kingdom, and the United States of America contributed towards this assessment, which was coordinated by NASA.

This assessment builds upon previous national and international assessments, in particular the most recent comprehensive report, "The Stratosphere 1981: Theory and Measurements" WMO Global Ozone Research and Monitoring Project Report #11 which was prepared in 1981 (issued in 1982) and was co-sponsored by the same three U.S. scientific agencies, (NASA, FAA, and NOAA) and by one international scientific agency, WMO. The rationale for the scope of the present assessment report was based on information gained at a scientific workshop, entitled "Current Issues in Our Understanding of the Stratosphere and the Future of the Ozone Layer" which was held in Feldafing, Federal Republic of Germany in June 1984 with international participation, co-sponsored by NASA, FAA, WMO, and BMFT. The assessment activities officially began in the fall of 1984 when leading scientists were selected as chairpersons, and each charged with the responsibility to produce a specific chapter in the assessment report. At a meeting held in November, 1984, the timetable for the assessment was established and key atmospheric scientists who could make valuable contributions were identified and invited to participate in chapter working groups. The participants were chosen for their expertise and represented a cross section of the international scientific community. The assessment was developed through a series of small focused workshops, chapter by chapter, each addressing a specific scientific issue. Considerable care was taken to ensure that those aspects of the issue which involved more than one chapter were carefully coordinated. Over 30 small working meetings were held between November, 1984, and May, 1985, to prepare draft chapters which were then critically peer reviewed at a workshop held at Les Diablerets, Switzerland July 7-14, 1985. The 32 participants who attended the meeting included 19 chapter chairpersons, 8 senior reviewers from the atmospheric scientific community, and 5 sponsoring agency representatives. Based on the reviews, the chapters were then finalized and sent to the printers in November/December 1985.

The following section of the Introduction describes the contents, and major conclusions and recommendations for future research of each chapter of the assessment report.

CHAPTER 2: STRATOSPHERIC CHEMISTRY

This Chapter deals with the elementary chemical and photochemical processes involving atmospheric trace gases and is written in two parts. The first part discusses the recent improvements in the data base for the reactions currently identified to be important in describing the chemistry of the major chemical families of trace gases in the stratosphere or unpolluted troposphere, i.e. oxygen, hydrogen, nitrogen, chlorine, bromine, sulfur, halocarbons and hydrocarbons. The second part discusses a number of special issues relating to stratospheric chemistry including:

(a) The importance of ion chemistry; sodium chemistry; heterogeneous chemistry; and reactions between long-lived reservoir species in controlling ozone;

(b) The ability of current reaction rate theory to describe reactions with complex pressure and temperature dependence functions;

(c) Errors and uncertainties in current kinetic and photochemical data, and the prospects for improvement;

(d) Prospects for developing a systematic approach for identifying gaps in the chemical description of the atmosphere.

Major Conclusions and Recommendations

(1) There has been continued steady improvement in the data base for the reaction rate coefficients, product distributions, absorption cross sections, and photodissociation quantum yields of the elementary processes;

(2) No significant new catalytic cycles, or radical or reservoir species have been identified since WMO (1982);

(3) Changes or re-evaluations in accepted rate coefficients for several important reactions, e.g. $O+ClO$, $OH+HCl$, $OH+HNO_3$, and HO_2+NO_2+M have led to refinements in predictions of ozone depletion, and have in general improved agreement between measured and computed vertical profiles for trace gases.

(4) Further laboratory studies of the rates, branching ratios and photodissociation channels of reactions involved in the production of NO_x from N_2O in the stratosphere, are required to reduce the uncertainties in this source term.

(5) Several key reactions involving HO_x species proceed through long lived intermediates, resulting in complex pressure and temperature behavior, e.g. $OH+CO$, HO_2+O_3, HO_2+OH, etc. These reactions need further study to provide better characterization over the full range of atmospheric conditions.

(6) Uncertainties in the data base for BrO_x and coupled BrO_x-ClO_x catalyzed ozone destruction need to be reduced.

(7) A continued effort is required to identify possible missing chemistry or species of significance in the stratosphere, making use of all state-of-the-art experimental and computational techniques.

CHAPTER 3: TROPOSPHERIC TRACE GASES: SOURCES, DISTRIBUTION AND TRENDS

This Chapter discusses the important source gases (CFC's, CH_4, CO, CO_2, N_2O, and NO_x) which are emitted at the Earth's surface. For each of these gases, measurements of their current atmospheric concentrations and trends are discussed, as well as information about their sources and their possible future course.

Major Conclusions and Recommendations

(1) There is now compelling evidence that the composition of the atmosphere is changing on a global scale reflecting in part the metabolism of the biosphere and in part a broad range of human activities. These source gases play important direct and indirect roles in both atmospheric chemistry and climate.

(2) Halocarbons
- The halocarbons are generally of industrial origin except for CH_3Cl.
- The atmospheric concentrations of CFC-11, CFC-12, CH_3CCl_3, and CCl_4 as of late 1985 were about 230 pptv, 400 pptv, 130 pptv and 125 pptv and are observed to be increasing at annual rates of about 5% for CFC's 11 and 12, 7% for CH_3CCl_3 and 1% for CCl_4.
- The Atmospheric Lifetime Experiment (ALE) measurements indicate an increase in the atmospheric concentration of CFC-11 consistent with the Chemical Manufacturers Association (CMA) release estimates, but to explain the observed increase in the atmospheric concentration of CFC-12 requires a substantial additional source. Insufficient information is available about possible releases from the USSR and Eastern Europe. There is consistency between the sources and inventory for CCl_4 and CH_3CCl_3.
- Based on ALE data the atmospheric residence times for CFC-11, CFC-12, CCl_4, and CH_3CCl_3 are calculated to be approximately 75, 110, 50 and 6.5 years, respectively.
- Only a few atmospheric measurements exist, and there is limited information on emission strengths, for the numerous other halocarbons.

(3) Methane (CH_4), Carbon Monoxide (CO) and Carbon Dioxide (CO_2)
- The world-wide average atmospheric concentration of methane as of late 1985 was 1.65 ppmv, and for the last decade or so has been increasing at an annual rate of about 1%. In addition ice-core data indicate that the atmospheric concentration of CH_4 may have steadily increased over the last several hundred years from a value of approximately 0.7 ppmv.
- The important sources of methane include anaerobic environments such as: natural and agricultural wetlands, termites, enteric fermentation in ruminants, and biomass burning.
- The atmospheric concentration of CO is significantly greater in the Northern Hemisphere than the Southern Hemisphere, and there are indications of an annual rate of increase of 1-2%.
- Projections of concentrations of atmospheric methane and carbon monoxide into the future are difficult because the origins of the current increase of CH_4 are unknown, i.e. what fraction of the increase can be attributed to increased source strengths versus decreased atmospheric removal rates.
- The global mean concentration of CO_2 is currently about 344 ppmv and there is clear evidence of an annual rate of increase of about 0.5% predominantly because of the combustion of fossil fuels.
- The atmospheric concentrations of each of the carbon species exhibit seasonal variability which is largest at high latitudes in the Northern Hemisphere and smallest in the Southern Hemisphere. The seasonal variability in CO reaches 50%, CO_2 ranges from 0.5 to 5%, and CH_4 ranges from 2 to 4%.

(4) Nitrous Oxide (N_2O)
- The atmospheric concentration of nitrous oxide as of late 1985 was about 304 ppbv and is increasing at an annual rate of about 0.25%. Because of its long atmospheric lifetime, i.e. $\sim$150 years, this implies that the current strength of the sources is 30% greater than that of the sinks.

Consequently, if the emissions of N_2O continue at their present rates the atmospheric abundance of N_2O would increase to about 400 ppbv. In addition, there is reason to believe that the strengths of the combustion and intensive agricultural sources of N_2O will continue to increase.

(5) Odd Nitrogen (NO_x)
- There are still many disputes over the magnitude of the lightning source of NO_x.
- It is likely that global emission rates of NO_x are increasing and little doubt that concentrations are now higher than preindustrial values. It is not clear to what extent industrial emissions of NO_x affect the remote atmosphere.

(6) Continued development of baseline measurements for CO, CH_4, N_2O, CO_2 and the halocarbons are vital.

(7) Flux measurements of biogenic gases from representative ecosystems, especially for CO_2, CH_4, N_2O, and NO, are needed in conjunction with studies of the underlying biological and geochemical processes which regulate the observed fluxes. In the case of CH_4, isotopic studies promise to elucidate the relative importance of various ecosystems in producing CH_4.

(8) Studies of trace gases in ice cores should elucidate the historical atmospheric concentrations of these gases.

(9) It is essential that the world-wide industrial production figures of all halocarbons be available.

CHAPTER 4: TROPOSPHERIC CHEMISTRY

This Chapter discusses various aspects of the chemistry of the troposphere. Significant emphasis is placed on discussing factors which control the abundance and distribution of OH and O_3. In addition the roles of these species are discussed in some detail, e.g. the role of OH in controlling the atmospheric abundances (lifetimes) of many trace gases which can affect the chemical composition or the radiative balance of the stratosphere and troposphere. The problems of the chemical description of the unpolluted or non-urban troposphere are considered separately from the polluted troposphere and the problem of transport from polluted to relatively unpolluted regions is discussed. Heterogeneous chemistry is highlighted as a poorly understood area which is likely to be important in the troposphere. Finally, there is a discussion of the problems of surface exchange and vertical redistribution.

Major Conclusions and Recommendations

(1) It is encouraging that the values of globally averaged OH calculated in models of the unpolluted troposphere now seem consistent with CH_3CCl_3 lifetime estimates. However, it should be noted that the lack of reliable atmospheric measurements of NO_x and CO contributes significantly to uncertainties in O_3 and OH photochemistry in the unpolluted troposphere.

(2) Many industrial compounds reach the unpolluted troposphere only after residence in the polluted troposphere - e.g., NO_x, CO, and non-methane hydrocarbons.

(3) One major difference between the chemistry of the troposphere and stratosphere is the recognized importance of heterogeneous reactions. However, our present understanding of heterogeneous

reactions is rudimentary. Consequently, theoretical models currently have to use simple parameterizations of processes not yet understood. Calculations indicate that in regions of high aerosol loading, scavenging by the aerosol could represent a significant sink for HNO_3, NO_3, H_2O_2 and possibly HO_2.

(4) Large temporal and spatial variations in the hydrological cycle can lead to large temporal and spatial variations in rainout removal rates and concentrations of species like odd nitrogen.

(5) Vertical redistribution in the troposphere is mainly accomplished by highly intermittent cloud processes that cannot be adequately described in a diffusive model.

(6) Surface deposition is dependent on a combination of the turbulent exchange rate near the surface and the interaction of the particular species with the surface.

(7) To understand the basic chemical cycles in the troposphere, and to predict the tropospheric response to perturbations requires:

- An evaluation of biological sources of chemical substances in the troposphere.
- Determination of the the global distribution of tropospheric trace gases and aerosol particles and assessment of relevant physical properties.
- Testing of photochemical theory through field and laboratory investigations of photochemically driven transformation processes.
- Investigations of wet and dry removal processes for trace gases and aerosol particles.

(8) Methods are now becoming available to measure surface fluxes of chemical species.

(9) Further laboratory studies are needed to determine the kinetics and mechanisms of the oxidation of methyl and other organic radical species under the 'low NO_x' conditions pertaining in the background troposphere.

CHAPTER 5: STRATOSPHERE-TROPOSPHERE EXCHANGE

This Chapter discusses the transport of mass and trace species between the stratosphere and troposphere. Meteorological processes in the tropics which are believed to affect exchange are reviewed; a special section is devoted to cumulonimbus clouds. Detailed aircraft case studies are described, and discussed in the context of the stratospheric water vapor budget. Exchange in the extratropics is considered from the meteorological point of view, and is largely concerned with tropopause folding during upper level frontogenesis. A theoretical outline is briefly presented, followed by a global scale isentropic diagnosis using First GARP Global Experiment (FGGE) data. Past work is reviewed, and recent aircraft studies are considered in some detail. Information about ozone exchange from ground based and satellite studies is also discussed. Results from general circulation models are considered, and analyses from an operational numerical weather prediction model are compared with aircraft data.

Major Conclusions and Recommendations

(1) While considerable progress has been made in aircraft-based studies, both of tropical cumulonimbus and extratropical exchange near polar front jet streams, there remains the need to incorporate

our understanding of these individual cloud-mass and synoptic-scale events into a global framework. In particular, synthesis of the global scale morphology of the cross-tropopause flux of specific molecules will require considerable thought and work, on case studies, satellite data, and global meteorological analyses.

(2) Case studies of exchange processes at subtropical jet streams, particularly above their cores, are required.

(3) Studies of exchange processes at polar front jet streams, particularly where the flow is split, are required, to investigate both the extent of mixing and the possibility of return flow to the stratosphere.

(4) Exchange in cut-off lows needs to be studied further, to establish how much of it is reversible.

(5) Studies near tropopause level should be made in cut-off anticyclones, with a view to establishing the tropopause behavior on radiative time scales.

(6) Investigation of exchange processes in connection with the largest (highest reaching) cumulonimbus storms is required, to establish whether or not they are consistent with the height of the hygropause.

(7) The sources of the water vapor between the tropopause and the hygropause needs to be established, especially in middle and high latitudes. This will afford valuable insight into the role of large scale, quasi-horizontal processes in cross-tropopause fluxes.

CHAPTER 6: DYNAMICAL PROCESSES

The Chapter begins with a description of the structure and circulation of the middle atmosphere and a discussion of the observational techniques on which this picture is based. Our current theoretical understanding of the circulation is presented; particular emphasis is given to the crucial role of eddy motions in the maintenance of the circulation. The present status of general circulation modeling of the region is discussed and the shortcomings of model climatologies are discussed in the light of theoretical knowledge.

The advent of satellite observations of middle atmosphere constituent distributions is having a major impact on our knowledge of these distributions and our understanding of the processes which control them. These new observations are described and our theoretical understanding of global transport processes and their representation in zonally-averaged transport models is discussed.

Major Conclusions and Recommendations

(1) Much of our information on the middle atmosphere circulation is based on satellite observation of temperature alone. Wind and higher-order derived quantities such as potential vorticity are derived from these measurements, together with lower boundary conditions from conventional analyses, using mathematical manipulations such as spatial differentiation which can degrade the signal-to-noise ratio. The availability of direct wind observations from UARS will greatly improve this situation.

(2) The major advantage of satellite measurements is their global coverage and uniformity. One further attribute which needs greater emphasis than it has received in the past is continuity of measure-

ment. This is highly desirable for the establishment of climatologies and absolutely vital for the detection of trends. It is therefore urged that further remote sensing missions be planned to succeed UARS following 1989 and that more emphasis be given to the intercalibration of successive satellite measurements.

(3) Ground-based techniques (radars and lidars) have proven to be very useful for dynamical studies, especially for important small-scale motions such as gravity waves. It is desirable that these facilities operate on a more continuous basis and that observations from different sites be coordinated. Equatorial measurements are needed and networks would be very valuable. Lidars and radars should be co-located.

(4) While general circulation modeling of the middle atmosphere is increasingly proving to be a useful tool in studies of the region, such models continue to have major deficiencies. The most serious of these is their pathology in generating winter high-latitude temperatures far below those observed. Theory suggests that this must be due to an underestimate of eddy transport processes; this could be a result of an inadequate representation of planetary wave activity or of the inability of the models to resolve gravity waves. The role of gravity waves in the actual stratospheric momentum budget requires further study.

(5) Our conceptual picture of stratospheric transport processes has changed dramatically in recent years and the theoretical basis of the parameterization of transport in zonally-averaged models has been made more secure. At the same time, however, the limitations of such models are becoming more apparent. Some of these limitations are obvious, given the highly three-dimensional nature of the wintertime flow (especially during active periods in the Northern Hemisphere). Others, such as the inability of zonally-averaged models to be truly interactive in the sense of predicting climate changes, are perhaps less obvious but equally important. Given the present problems of general circulation modeling and the expense of running such models with chemistry included, however, it is not envisaged that fully three-dimensional assessments will be forthcoming in the near future. Three-dimensional transport modeling may depend on a simplified approach; a new theoretical framework is needed to make this a reality.

CHAPTER 7: RADIATIVE PROCESSES; SOLAR AND TERRESTRIAL

There are two distinct parts to this Chapter. The first deals with solar radiation and its absorption in the stratosphere and mesosphere, and the second deals with terrestrial, or long-wave radiation. The discussion of the solar spectrum is broken up into irradiance from wavelengths shorter than 175 nm which affects the mesosphere and above, and the irradiance for wavelengths longer than this that affects the stratosphere. Tables are given for a reference solar spectrum, and variations of the solar spectral irradiance over the 27-day solar rotation period and the 11-year cycle. Other topics in the solar part of this chapter concern Rayleigh scatter, absorption by molecular oxygen, and ozone. The portion of this chapter dealing with terrestrial radiations deals with the adequacy of spectroscopic data to check our radiation calculations. It also deals with concepts of radiative damping, long-wave radiation in the stratosphere and mesosphere, as well as the distribution of net radiative heating through the atmosphere.

Major Conclusions and Recommendations

(1) Solar spectral irradiance is known to an accuracy of $\pm$10-15% between 175-210 nm, $\pm$10% or better between 210 and 330 nm, and to $\pm$5% or better at longer wavelengths.

(2) The variability in solar irradiance is well determined for the 27-day solar rotation period but not for the 11-year solar cycle.

(3) The accepted values for the molecular oxygen absorption cross-sections at wavelengths relevant to the stratosphere and mesosphere are significantly smaller than those used a few years ago.

(4) An improved determination of cross sections in the Huggins bands would be valuable, especially for ground-based atmospheric ozone measurements.

(5) Improved determination of line shapes, line widths, and their temperature dependencies are needed to better calculate terrestrial heating rates. Present line-by-line calculations are based on idealized values that have not been verified in many cases.

(6) Other uncertainties in calculating terrestrial radiation include the influence of clouds and volcanic aerosols.

(7) The radiative role of trace gases such as N_2O and the CFC's merits further study.

(8) The continued analysis of satellite data sets for ozone, temperature, solar irradiance, and the outgoing terrestrial emission is essential for developing a complete understanding of radiative processes in the Earth's stratosphere and mesosphere.

(9) A drift-free record of the ultraviolet solar irradiance covering at least the wavelength range 175-400 nm is needed over one or more entire solar cycles.

CHAPTERS 8, 9, 10, AND 11: OXYGEN, HYDROGEN, NITROGEN AND HALOGENATED SPECIES: OBSERVATIONS AND INTERPRETATION

These Chapters review, and compare to both one-dimensional and two-dimensional model descriptions of the present-day stratosphere, the stratospheric measurements of oxygen, hydrogen, nitrogen, and halogen containing species obtained from ground, aircraft, balloon, rocket, shuttle, and satellite based instruments. There is a brief discussion of each of the *in situ* and remote sensing techniques currently being used to determine the chemical composition of the atmosphere, and a brief discussion of the accuracy and precision of the experimental data. The types of data described include vertical distributions and column contents as a function of season both at a limited number of geographic locations and globally, diurnal variabilities, and long term (multiyear) trends in the column contents. The species described include the source gases of the trace constituents (H_2O, N_2O, CH_4, and the halocarbons), and the active and inactive inorganic species from the oxygen ($O(^3P)$, $O(^1D)$, and O_3), hydrogen (H, OH, HO_2, and H_2O_2), nitrogen (N, NO, NO_2, NO_3, N_2O_5, $ClONO_2$, HNO_3, and HNO_4), chlorine (Cl, ClO, HCl, HOCl, and $ClONO_2$), and fluorine (HF) families.

Major emphasis is placed on describing the satellite data sets which have been analyzed, validated, released, and partially interpreted during the last four years. This includes data obtained by the Limb Infrared Monitor of the Stratosphere (LIMS), the Stratospheric and Mesospheric Sounder (SAMS), and the Solar Backscatter Ultraviolet/Total Ozone Monitoring System (SBUV/TOMS) instruments flown on the Nimbus 7 satellite, the Stratospheric Aerosol and Gas Experiment (SAGE) flown on the Applications Explorer II satellite, and the visible and infrared spectrometers flown on the Solar Mesospheric Explorer satellite.

Major Conclusions and Recommendations

Before discussing specific conclusions which may involve only one particular family of species there are seven conclusions of a more general character.

(1) The most significant recent development in our knowledge of O_x, HO_x, and NO_x in the stratosphere has been the release of several large satellite data sets. They have greatly improved our knowledge of the spatial and temporal distributions of O_3, H_2O, CH_4, N_2O, NO_2, and HNO_3 on a global scale.

(2) There are now some measurements of most key species, including the temporary reservoir species $ClONO_2$, N_2O_5 and HO_2NO_2 predicted to be important in the photochemistry of stratospheric ozone. However, the data base is rather limited in some instances, and while the observed abundances are generally consistent with current theory to within a factor of two or so, the measurements are not adequate for critically testing the photochemical models.

(3) Ground, aircraft, balloon, and rocket-based instrumentation have continued to provide an invaluable data base for vital but limited tests of photochemical theory.

(4) While there has recently been a significant advance in our understanding of the accuracy and precision of atmospheric composition data it is vital to continue the intercomparison of data obtained from different measurement techniques, especially for ClO, OH, HO_2, NO and NO_2.

(5) Several new experimental techniques have recently been developed and demonstrated which will enable us to obtain the type of data needed to test the photochemical models.

(6) We are still data limited, the accuracy and precision of many of the measurements need to be improved, and an improved measurement strategy needs to be formulated in order to more stringently test the photochemical models.

(7) Long term data sets of the vertical distributions of O_x, HO_x, NO_x and ClO_x species are needed both at discrete geographic locations and globally to determine changes in the composition of the stratosphere.

We will now discuss the specific major conclusions in the following order, i.e., oxygen, hydrogen, nitrogen, and halogen species.

CHAPTER 8: OXYGEN SPECIES

(1) Comparison of three distinct satellite measurements (SBUV, LIMS and SAGE), suggests that we can determine ozone in an absolute sense to about 15% (one standard deviation) from 25-30 km and about 6% from 30-55 km.

(2) Comparison of ozone satellite and balloonsonde data suggests that the balloonsondes are systematically lower than SBUV above about 32 km. The cause of this is not currently recognized.

(3) Utilizing SBUV as the basic data source for four year zonal average profiles, the random uncertainties appear to be about 4% (one standard deviation) in mid- and high-latitude winter and about 2% elsewhere.

(4) The observed O_3 abundance above 35 km is underestimated, typically by 30 to 50%, by both one-dimensional and two-dimensional photochemical model calculations. The reason for this discrepancy is not yet clear but could be due to an underestimation of the calculated odd oxygen production rate, an overestimation of the calculated loss rate by HO_x in the mesosphere and/or NO_x in the stratosphere or to missing chemistry.

(5) This significant ozone imbalance in the photochemically controlled region of the middle atmosphere limits the confidence that can be attached to model predictions of future ozone changes in response to long-term increases in the atmospheric concentrations of source gases (e.g. chlorofluorocarbons, nitrous oxide, methane).

(6) Precise determinations of the $[O]/[O_3]$ ratio and of the diurnal variation of O_3 in the upper stratosphere and in the mesosphere are needed.

(7) Stratospheric measurements relating the O_2 cross section determinations by high resolution measurements of the solar irradiance from 180 to 250 nm are required, as are additional laboratory studies of the O_2 absorption cross sections (Schumann-Runge bands and Herzberg continuum) and of the photodissociation rate of O_3 producing $O(^1D)$.

CHAPTER 9: HYDROGEN SPECIES

(1) There has been no major expansion of the profile data base for HO_x (OH, HO_2, and H_2O_2) species since the last assessment.

(2) The only new profile data for OH since the last assessment is lower than most of the earlier data and current model predictions and, while not in serious conflict with model predictions, is insufficient to provide a critical test of theory.

(3) There are over seven years of quasi-continuous column measurements of OH which show a long-term trend, seasonal, diurnal, and spatial variability, and response to volcanic eruptions and a solar eclipse. A large fraction of the OH signal is due to OH in the mesosphere. This data awaits a theoretical interpretation.

(4) HO_2 measurements between 16 and 34 km, and 35 and 60 km have been obtained by *in situ* and ground-based techniques, respectively. The *in situ* HO_2 data between 16 and 34 km is significantly higher than predicted, and suggests a problem with either the measurements or our understanding of HO_x photochemistry.

(5) There has not yet been a single definitive observation of H_2O_2.

(6) From balloon *in situ* data there is clear evidence of a hygropause, a region of minimum H_2O mixing ratios a few km above the tropopause, and small scale vertical structure at northern mid-latitudes.

(7) The LIMS and SAMS H_2O and CH_4 data have clearly demonstrated that air is transported upward and poleward from the tropics, consistent with the Brewer-Dobson hypothesis, and that the total hydrogen budget of the stratosphere, principally $H_2O+2\times CH_4$, is relatively constant with values ranging from 6 to 7 ppmv.

(8) LIMS data has been used to derive global OH fields; (a) using the HNO_3/NO_2 ratio, and (b) by calculating its production and loss with temperature, H_2O, O_3, and HNO_3 data.

(9) Simultaneous measurements of odd hydrogen containing species are required over a full diurnal cycle to provide a more critical test of the photochemical models (OH, HO_2, H_2O_2, H_2O, in conjunction with temperature, solar flux, O, O_3, and NO_x determinations).

CHAPTER 10: NITROGEN SPECIES

(1) While we have a reasonable understanding of the diurnal variability of NO_2, a more rigorous test of theory requires more accurate experimental data.

(2) The observations of HNO_3 at high latitudes in winter, and above 30 km at all latitudes are not in agreement with the theoretical predictions.

(3) The global morphology and variability of N_2O has been measured from satellite, and can be adequately simulated with a two-dimensional photochemical model if the influences of the semiannual oscillation on the zonal mean cross-sections are taken into account.

(4) Using LIMS data the magnitude of the thermospheric source of total odd nitrogen to the stratosphere has been shown to be significant on a local, but not global, scale.

(5) Total budgets for odd nitrogen have been derived from satellite measurements (LIMS) of HNO_3 and nighttime NO_2. These are generally consistent with those derived from balloon observations, and predicted by two-dimensional photochemical models near 40 km. However, there are serious discrepancies between observations and two-dimensional photochemical models at lower altitudes.

(6) We now have a basic understanding of the dynamical and photochemical processes responsible for regional phenomenon such as the NO_2 Noxon Cliff.

(7) Global OH fields have been derived using LIMS NO_2 and HNO_3 data. However, given that we do not fully understand the quality of LIMS HNO_3 data above 35 km, and the HNO_3 profile above 30 km is not understood, care must be exercised in using the derived OH fields.

(8) N_2O_5, HNO_4, and $ClONO_2$ have been positively identified from ATMOS spectra.

(9) Simultaneous measurements of nitrogen containing species over a full diurnal cycle are required to critically test the photochemical models. These ratio measurements should be taken in conjunction with appropriate measurements of O_x, HO_x, and ClO_x species.

CHAPTER 11: HALOGENATED SPECIES

(1) While there has not been a significant expansion of the ClO profile data base the measured and model predicted ClO profiles now agree to within a factor of 2 between 28 and 38 km.

(2) The observed diurnal variation of ClO is in reasonable agreement with model predictions, but does show a somewhat slower morning rise than expected.

(3) The existing data base is inadequate to establish seasonal and latitudinal variations, or long-term increases in ClO predicted by theoretical models.

(4) Evidence of the presence of $ClONO_2$ has improved, with balloon-based observations being made in a second spectral region. In addition, $ClONO_2$ has been observed in the ATMOS spectra.

(5) The expected increase with time in stratospheric HCl has not been observed. It has presumably been masked by significant short-term variability in both tropospheric and stratospheric HCl.

(6) The measured and predicted increase with time in stratospheric HF are compatible.

(7) There is now general agreement between calculated and observed vertical profiles for the halogen source species.

(8) Simultaneous measurements of chlorine-containing species are required to provide a satisfactory test of the photochemical models (Cl, HCl, ClO, and $ClONO_2$, preferably coupled to temperature, solar flux, O_3, H_2O, CH_4 and NO_x determinations).

CHAPTER 12: ASSESSMENT MODELS

This Chapter considers the various types of models of the stratosphere which have been used to make predictions concerning the stratospheric composition and possible response to perturbations. One-dimensional models, although limited in many respects, have been our traditional tools. Recent important advances in the treatment of two-dimensional transport have opened the way for a new generation of assessment models with all the photochemical detail of the one-dimensional models but with a more physically-based transport.

Major Conclusions and Recommendations

(1) One-Dimensional Models

- One-dimensional models will continue to play a major role in assessment activities, particularly in the development of new photochemical schemes.

- A comparison of one-dimensional models shows a large range of calculated odd-nitrogen in the middle and upper stratosphere ranging from 13-20 ppbv. An important source of these differences is the treatment of radiation penetration in the Schumann-Runge bands, and more work appears necessary here. However, models with similar radiation schemes still show significant differences in odd nitrogen, and other causes are evidently also important.

(2) Two-Dimensional Models

- There have been significant theoretical advances in the treatment of transport in two-dimensional models.

- There is a good understanding of the cancellation between mean and eddy transport. A net transport circulation can be defined which is closely related to the residual and diabatic circulations.

- The limitations of the treatment of eddy transport in terms of K-theory, and the physical basis for this approach, are better understood.

- Important estimates of the size of the eddy coefficients have come from theoretical, GCM and data studies. These studies suggest the use of somewhat smaller k coefficients than hitherto, in combination with the transport circulation. However, more work is urgently needed in this area, bearing in mind, for example, the known limitations of GCM's and the problem of unresolved scales of motion in satellite data analyses.

- There has been important work on the dependence of the k coefficients (in one-dimensional as well as two-dimensional models) on photochemical lifetimes.

- Two-dimensional models can include some of the important photochemical-radiative-dynamical feedbacks.

- The goal of a completely self-consistent two-dimensional model is denied by our inability to model the eddies in a completely interactive fashion.

(3) Two-Dimensional Model Results

- With the above advances there are now two major classifications of two-dimensional models.

  - (1) Traditional Eulerian (with generally large eddy coefficients)

  - (2) Models with modified Eulerian — residual or diabatic — circulations (and generally smaller eddy coefficients).

- Whichever approach is employed, the eddies remain important. It is the establishment of the correct balance between mean and eddy transport which is crucial. The residual circulation models with small diffusion, in general, predict greater latitudinal structure than the other models. However, equally large differences are sometimes found between models of similar types as between modified and traditional Eulerian models.

- As with one-dimensional models, significant differences in the predicted odd-nitrogen values are found. Tropospheric removal and transport in the equatorial lower stratosphere are believed to play major roles in producing these differences. The equatorial lower stratosphere, where the radiative balance is the small difference of small terms, is identified as an extremely important area for future study.

- As with one-dimensional models, two-dimensional models generally underestimate ozone in the upper stratosphere.

(4) Three-Dimensional Models

- There have been some significant efforts to incorporate detailed chemistry schemes into three-dimensional models.

(5) Models for Assessment

- There is no indication at present that results from two-dimensional models should invalidate in a gross sense assessment studies with one-dimensional models.

- Two-dimensional models provide a much broader predictive capability than one-dimensional models. They can predict important latitudinal and seasonal effects which the one-dimensional models generally cannot. Two-dimensional models thus add significantly to our assessment capability.

- The inability of one-dimensional and two-dimensional models to reproduce upper stratospheric ozone and the significant differences sometimes found between models, for example in calculated odd-nitrogen, undermines our confidence in long term assessment. Priority must be given to resolving these problems.

(6) Testing Models

- Our confidence in models (especially for assessment purposes) depends on satisfactorily 'validating' these models against available data. This is too often an extremely subjective exercise.

- A hierarchy of tests for comparison of models and data could include:
  (a) Identification of predicted species
  (b) Comparison of altitude profiles, latitudinal and seasonal variations.
  (c) Isolation of processes (e.g. chemistry from dynamics by ratio measurements, diurnal variations, correlations).
  (d) Study of natural perturbations (Volcanic eruptions, solar proton events, sudden warmings, etc.)
  (e) Study of chemistry along air parcel trajectories.

CHAPTER 13: MODEL PREDICTIONS

This Chapter presents a series of model calculations detailing the present best estimates of the response of atmospheric composition to a variety of potential perturbations. The computations emphasize the coupled nature of the perturbations. The choice of scenarios involving changes in concentrations of CFC's, N_2O, CH_4 and CO_2 reflect the findings that all of their concentrations are currently increasing and that the perturbations are strongly coupled.

Major Conclusions and Recommendations

(1) Continued release of chlorofluorocarbons 11 and 12 at the 1980 rate would reduce the ozone vertical column by about 5-8% according to one-dimensional photochemical models and by a global average of about 9% according to two-dimensional models, with reductions of $\sim$4% in the tropics, $\sim$9% in temperate zones and $\sim$14% in polar regions.

(2) A major finding of recent years is that two-dimensional models predict large seasonal and latitudinal variations in chlorine-induced ozone column reductions.

(3) All models with all scenarios predict that continued release of CFC's 11 and 12 at the 1980 rate will reduce local ozone at 40 km by $\sim$40% or more.

(4) One dimensional models predict that the magnitude and even the sign of the ozone column changes due to increasing CFC's depend on the future trends of CO_2, CH_4, and N_2O. For example, at about 80% of the present CFC release rate, coupled with a doubling of CH_4 and an increase in N_2O by a factor of 1.2, one-dimensional models predict an ozone decrease of about 3% at steady state while two-dimensional models predict an ozone decrease of 4%. If a simultaneous doubling of CO_2 is also considered, one-dimensional models predict ozone column changes between +0.1 and −3.5%.

(5) If the release rate of CFC's should become twice the present level or if stratospheric Cl_x reaches 15 ppbv, the one-dimensional models predict that there will be a 3% to 12% reduction of the ozone column, assuming that the annual rates of increase in the atmospheric concentrations of CO_2, N_2O, and CH_4 continue at their present rate.

(6) One-dimensional models predict that the total ozone column is increased by CO, CO_2, and CH_4, and decreased by CFC's, N_2O and stratospheric aircraft. These individual perturbations do not have an additive effect on ozone.

(7) Time dependent scenarios were performed using one-dimensional models assuming CO_2, CH_4, and N_2O annual growth rates of 0.5%, 1% and 0.25%, respectively, in conjunction with CFC growth rates of 0%, 1.5% and 3% per year. The ozone column effects are relatively small ($<3\%$ over the next 70 years) for CFC increases of $\leq 1.5\%$ per year, but with a CFC growth rate of 3% per year the predicted ozone depletion is 10% after 70 years and still rapidly increasing.

(8) Over the range 1 to 15 ppbv of stratospheric chlorine, one-dimensional models are strongly nonlinear in terms of ozone-column change as a function of added Cl_x, in contrast to the two-dimensional models which are nearly linear over this range of Cl_x. The onset of the nonlinearity occurs in the regime where the Cl_x and NO_y mixing ratios become comparable.

(9) Monte Carlo calculations over the full range of the assessed uncertainties of photochemical parameters were performed with two one-dimensional models. One calculation considered only CFC perturbations. For the release of CFC's at the 1980 rate an ozone column depletion of $-(5.7\pm5.4)\%$ was calculated (1σ uncertainty range). In the second calculation an ozone column depletion of $-(7.7\pm5.8)\%$ was calculated for an increase of 14 ppbv of Cl_x in conjunction with a doubling of CH_4 and a 20% increase in N_2O. In each case the ozone depletion distribution was unsymmetrical with a long tail toward large perturbations.

(10) The past and future changes of the trace species, CH_4, N_2O, and CO_2, involve the biosphere and its great complexity. As the stratospheric models mature, the largest uncertainty in making future predictions of ozone concentrations will probably be the uncertainty in formulating the scenarios for future changes in CH_4, N_2O, and CO_2.

(11) It is vital to continue the development of two-dimensional models for assessment purposes. These must include the effects of temperature feedback.

(12) The new Monte Carlo method that screens the results against atmospheric observations should be emphasized.

CHAPTER 14: OZONE AND TEMPERATURE TRENDS

This Chapter contains a discussion of the evidence for statistically significant trends in ozone and temperature. In particular, the evidence for a trend in the total ozone and in ozone profiles is examined. Temperature data in the troposphere and in the lower stratosphere are also examined from the viewpoint of looking for trends.

Major Conclusions and Recommendations

(1) Global trend estimates of total ozone determined from the Dobson spectrophotometer network indicate little overall support for a statistically significant trend during the 14-year period 1970-1983.

(2) Recent evidence has been presented that indicates a considerable decrease in Antarctic total ozone during the spring period since about 1968. This is presently the subject of further analysis.

(3) Trend estimates from 13 ozone balloonsondes indicate statistically significant positive trends in the lower troposphere and negative trends in the lower stratosphere. The interpretation of these results, however, is clouded by uncertainties in instrument behavior and lack of a global station network.

(4) Ozone trend estimates from 13 Umkehr stations indicate statistically significant negative trends from 1970 to 1980 in the middle stratosphere that are in substantive agreement with results from one-dimensional numerical models. The observational results are sensitive to the inclusion of a term to account for stratospheric aerosol impact on the measurements and the spatial distribution of the sites, but do not appear sensitive to the inclusion of a 10.7 cm flux variation (an indicator for solar flux variation).

(5) Examination of the NOAA SBUV-2 satellite measurement program indicates that if the system operates as designed, it is capable of global ozone trend detection in the middle to upper stratosphere, as well as total ozone, to within about 1.5% over a period of one decade at the 95% confidence level.

(6) As with other long-term measurement programs however, it is necessary to examine continually the SBUV-2 instrument performance and satellite measurements and compare them with independent data.

(7) We note, moreover, that the SBUV-2 data are inherently total ozone and ozone profiles between 25 and 55 km. If ozone trends can be determined unambiguously from the Earth's surface to the overlap region with the SBUV-2 profiles, a high-quality measurement program would exist.

(8) Two independent analyses of lower stratospheric temperatures during the period 1965-1979 are suggestive of a downward temperature trend. Inconsistencies between the two analyses, however, preclude firm conclusions.

(9) The large cooling in rocketsonde temperatures reported for the early 1970's appears now to be due to a change in the rocketsonde temperature measurement system. Taking this into account, statistically significant negative trends are observed in June rocketsonde data at 40-45 km from 1973-1983 that are in substantive agreement with results from one-dimensional numerical models. These preliminary results will have to be examined further with a more complete data set.

(10) Examination of the NOAA TOVS stratospheric satellite temperature measurement program indicates that it is essential that the instrument-to-instrument consistency be verified by a high quality, independent data system. Such a system does not exist.

(11) Resolve the causes of the ozone measurement biases between SBUV, LIMS and SAGE and thereby, reduce the absolute error estimates.

(12) Determine the impact of implementation of the Bass and Paur (1984) ozone absorption coefficients on the ground-based measurements and compare the results with the satellite observations.

(13) Continue development of the ground-based ozone profile measurement program with particular emphasis on the following:

(a) determination of the aerosol impact on Umkehr measurements from El Chichon.
(b) development of the high altitude ($\approx$40 km) balloon sampling system with specific attention to the adjustment procedure to match the Dobson total ozone measurements.
(c) development of a lidar system capable of routine ozone measurements in the troposphere and stratosphere, especially above 40 km.

(14) Develop a long-term satellite and ground-based temperature measurement program sufficient to measure a mid-stratospheric temperature trend to a 95% confidence level of 1.5K/decade.

(15) Update the accuracy (as opposed to precision) estimates of the meteorological rocketsondes and satellite observations.

(16) Determine the satellite ozone and temperature temporal and spatial sampling requirements with estimates of resolution, accuracy and precision necessary to verify chemical, dynamical and radiation theory.

CHAPTER 15: TRACE GAS EFFECTS ON CLIMATE

This Chapter examines our understanding of how increasing concentrations of radiatively active trace gases might lead to changes in the Earth's climate. The nature of the radiative forcing of the climate system from changes in trace gas concentration is discussed. The roles of the various types of climate models are discussed, and the predictions of resulting climate perturbations resulting from individual increases in atmospheric trace gas concentrations are presented from such models. The role of the oceans in delaying these climate changes is discussed. Finally, the effects of simultaneous increases in trace gas concentrations on the climate are estimated.

Major Conclusions and Recommendations

(1) The problem concerning the greenhouse effects of human activities has broadened in scope from the CO_2-climate problem to the trace gas-climate problem.

(2) Non-CO_2 greenhouse gases in the atmosphere are now adding to the greenhouse effect by an amount comparable to the effect of CO_2. This is a fundamental change from the situation during the period of 1850-1960.

(3) The rate of increase of the total greenhouse forcing is now 3-10 times greater than the mean rate for the period 1850-1960.

(4) The cumulative effect of the increase in all trace gases for the period from 1850-1980 is a predicted equilibrium warming in the range of 0.7 to 2 K. The three-fold range in the estimated equilibrium warming arises from the currently perceived uncertainty in the sensitivity of climate models. The contribution of the non-CO_2 trace gases to the cumulative equilibrium surface warming is about 30%. Time dependent calculations with a simplified one dimensional diffusive ocean model suggest that a surface warming of about 0.4-0.8 K (of the 0.7 to 2 K) should have occurred during 1850 to 1980. The estimated surface warming is not inconsistent with the value of 0.5 to 0.6 K that can be inferred from observed surface-air temperature records.

(5) If the growth rates of trace gas concentrations (or their emission rates) that were observed during the decade of the 1970's continue unabated for the next several decades, non-CO_2 trace gases can have as much impact as CO_2 on future trends of surface and atmospheric temperatures. For the various trace gas scenarios considered in this study, the equilibrium surface warming for the period 1980 to 2030 range from 0.8 to 4.1 K. This wide range in the projected warming is due to the range in the assumed scenarios as well as due to the earlier mentioned uncertainty in climate sensitivity of current models.

(6) Thus for the 180 year period from 1850 to 2030, our assessment suggests a trace gas induced cumulative equilibrium surface warming in the range of 1.5 to 6.1 K. Because of the huge thermal inertia of the world oceans, only about 40 to 50% of the above equilibrium warming will be realized by the year 2030. Consequently, if the current rate of increase in trace gas concentrations continue unabated for the next several decades, the climate system would be increasingly in a state of disequilibrium with the radiative forcing by the trace gases.

(7) The important non-CO_2 greenhouse gases are $CFCl_3$, CF_2Cl_2, CH_4, N_2O, O_3 and stratospheric H_2O. On time scales longer than a century, radiatively active gases with lifetimes of the order of 100-500 years (e.g., CF_3Cl, CF_4, CF_2ClCF_2Cl, CF_3CF_2Cl, $CBrF_3$) may also become important in determining climate change if their growth rates continue to increase indefinitely.

(8) CFC's, through their indirect chemical effects on O_3, have a potentially large stratospheric cooling effect, as large as that due to CO_2 increase. For a given scenario for increase in trace gases (including CO_2), the computed stratospheric cooling is significantly larger (by factors ranging from 2 to 10 depending on the altitude) than the computed surface warming.

(9) In addition to the direct radiative effect, many of the trace gases have indirect effects on climate. For example, addition of gases such as CH_4, CO and NO_x can alter tropospheric O_3, which is a radiatively active gas. Within the troposphere, the indirect climate effects can be as large as the direct effects. On the other hand, within the stratosphere, temperature changes are largely determined by indirect effects of CFC's. Stratospheric H_2O will increase due to the oxidation of the increasing concentrations of CH_4, and can be influenced by the trace gases through their effect on tropical tropopause temperatures. Furthermore, increases in tropospheric H_2O, through the temperature-H_2O feedback, can perturb tropospheric chemistry and alter the concentration of CH_4 and O_3.

(10) The fundamental issue that needs to be addressed within the context of the trace gas-climate problem is the relative importance of transport, chemistry and the indirect effects of trace gases in governing the long-term trends of tropospheric and stratospheric O_3, CH_4 and stratospheric H_2O. A credible and successful attack on this problem must include model as well as *in situ* observational studies. The specifics of such studies are identified in this assessment.

(11) Cloud feedback continues to be the major source of uncertainty in the surface temperature sensitivity of climate models. At present, even the sign of this feedback is not known.

(12) The next crucial issue concerns accurate determination of decadal trends in radiative forcings, trace gases, planetary albedo (to determine effects of aerosols and cloud feedback) and surface-troposphere-stratosphere temperatures. The observational challenges are formidable and must be overcome for a scientifically credible interpretation of the human impacts on climate.

APPENDIX A: CHEMICAL KINETICS DATA BASE

This Appendix contains tables of evaluated data for chemical rate constants and equilibrium constants. The first table gives rate constants for second order reactions. The reactions are grouped into the classes: O, $O(^1D)$, HO_x, NO_x, hydrocarbon reactions, ClO_x, BrO_x, FO_x, SO_x, and metal reactions. The second table gives rate constants for three-body reactions in the form of values for the low pressure limit and for the high pressure limit. There is also a table of equilibrium constants for those systems in which unstable products may be formed in association reactions. The values given are those recommended by the NASA Panel for Data Evaluation in the Panel's complete report which was published by the Jet Propulsion Laboratory, Pasadena, CA as JPL Publication 85-37.

APPENDIX B: SPECTROSCOPIC DATABASE: INFRARED TO MICROWAVE

Accurate modeling of radiative transfer in the atmosphere is very dependent on the accuracy to which the spectroscopic parameters of the optically active atmospheric gases are known. The primary objective of this Appendix is to review the status of the presently available database of spectroscopic parameters (line positions, intensities, pressure-broadened halfwidths, etc.) in the infrared to microwave spectral region for molecules of interest for remote sensing and climate studies in the terrestrial atmosphere. In addition, this review contains detailed discussions of quantitative high-resolution atmospheric spectroscopy, laboratory spectroscopy (including reviews of current capabilities and efforts in progress), and spectroscopic data accuracy requirements for space-based remote sensing of the atmosphere.

Major Conclusions and Recommendations

(1) The three major computer-accessible compilations of spectroscopic line parameters (AFGL, GEISA, and JPL) contain among them data on over 400,000 transitions for 42 molecular species, covering the spectral range from 0 cm^{-1} to 18,000 cm^{-1}. For the parameters presently contained in the compilations approximately 80% of the line positions, 50% of the intensities, and only 5% of the air-broadened halfwidths may be considered to be of sufficient accuracy for most atmospheric remote sensing applications. In addition, spectroscopic parameters are totally missing from the compilations for a number of species of atmospheric interest (e.g. N_2O_5 and HNO_4).

(2) With the present capabilities for laboratory spectroscopy and analysis, line positions can be routinely determined with high absolute accuracy. However, absolute line or band intensities and pressure-broadened halfwidths can be measured with accuracies no better than 5%. This level of accuracy is insufficient to meet some of the requirements for future space-based atmospheric sensors.

(3) The two major requirements for further work in laboratory spectroscopy for atmospheric measurements and climate modeling are:
   (a) Line Positions and Intensities: Spectral parameters are needed for several infrared bands of major and trace constituents where data are either totally missing from the present compilations or are of very poor quality. These problems are generally more severe at wavelengths shorter than 3 μm, although improvements are needed for certain species in all spectral regions.
   (b) Line Widths: Improved knowledge of air-broadened halfwidths and their temperature dependence is needed for nearly all of the optically active atmospheric species. Self-broadened and nitrogen-broadened halfwidths are also needed for special applications such as gas correlation radiometry.

(4) Other requirements, in order of their relative importance, include laboratory and theoretical studies of deviations from the Lorentz line shape, accurate integrated intensities and band model representations for unresolved bands, more accurate absorption coefficients for the important pressure induced bands of oxygen and nitrogen, improved models for the temperature and pressure dependence of the water vapor continuum, improved parameters for transitions involved in non-LTE radiative transfer in the upper atmosphere, and quantification of other effects such as pressure induced line shifts which are presently considered to be insignificant for atmospheric spectroscopy.

APPENDIX C: INSTRUMENT INTERCOMPARISONS AND ASSESSMENTS

This Appendix summarizes what has been learned regarding the reliability with which the concentrations of stratospheric trace species can be measured with current techniques and instruments. During the last several years, there have been a number of field campaigns that have focused on the assessment of this reliability by direct intercomparison of results for a given species obtained by a variety of different methods applied simultaneously under representative atmospheric conditions. These formal and rigorous intercomparisons have revealed both strengths and shortcomings.

Major Conclusions and Recommendations

(1) Stratospheric ozone can likely be measured with a $\pm 4\%$ relative uncertainty at altitudes up to about 40 km with state-of-the-art balloon-borne *in situ* UV absorption photometers.

(2) The monitoring-type electrochemical ozonesondes appear to have, on the average, an overall uncertainty of $\pm 10\%$ and a precision of 5% at stratospheric altitudes below 25-30 km, given consistent preparation of the sondes.

(3) The data from the frostpoint and fluorescence water vapor instruments have a systematic difference of about 0.75 ppmv (20%), the origin of which remains unknown.

(4) Such intercomparisons are vital to real progress in assessing the reliability of stratospheric observations and must be a component of experimental research in this field.

(5) There are numerous unresolved differences among the results of balloon-borne long path techniques for several species, e.g. NO_2.

APPENDIX D: OZONE AND TEMPERATURE MONTHLY MEANS

This Appendix is provided because global monthly mean charts of ozone and temperature have become available, covering for the first time the height range 30 to 0.1-mbar, (approximately 24 to 64 km).

For both hemispheres these charts are given for the four mid-season months, and for the pressure levels 30, 10, 1, and 0.1 mbar, (0.4 mbar for ozone). Charts with total ozone are provided separately. This set of charts shows clearly the very close coupling between the temperatures and the ozone distribution and demonstrates the influence of the large-scale planetary waves, giving rise to very large longitudinal variations.

A discussion on the regular and interannual variability of temperature and ozone is followed by a description of the mean state.