PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Atmospheric Chemistry: Response to Human Influence

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ATMOSPHERIC CHEMISTRY: RESPONSE TO HUMAN INFLUENCE

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CONTENTS

Present understanding of global atmospheric chemistry is reviewed. Models are presented and compared with a wide range of atmospheric observations, with emphasis on the stratosphere. In general, excellent agreement is found between the calculated and observed distributions of long lived trace gases. The abundances of many shorter lived species are also satisfactorily reproduced, including NO_2, HNO_3, O, O_3, OH and ClO. Discrepancies between theory and observation are examined and their significance assessed.

The influence of human perturbations due to combustion, agriculture and chlorocarbon releases is discussed with emphasis on O_3. Uncertainties associated with present models are highlighted. Combustion related releases of CO cause a decrease in the abundance of tropospheric OH with consequent increase in the concentrations of CH_4, H_2, CH_3Cl and other halocarbons. CO emissions may become sufficiently large during the next century to induce substantial increases in tropospheric ozone on a global scale. Recombination of nitrogen fixed by agriculture and combustion may lead to an enhanced source of atmospheric N_2O with a related impact on stratospheric NO_x. Chlorocarbon industry provides an important source of stratospheric chlorine, and enhanced levels of stratospheric Cl_x and NO_x may cause a significant reduction in the abundance of atmospheric O_3, by as much as 10% during the next century. Perturbations due to various anthropogenic activities interact in a nonlinear fashion and the influence on atmospheric chemistry is correspondingly complex.

1. Introduction

Atmospheric chemistry has enjoyed a period of remarkable growth over the past decade. Interest has been stimulated mainly by concern that a variety of human influences might lead to detectable change in the abundance of stratospheric ozone.

Advances have occurred in all important areas of the subject. New techniques have been developed for detection of reactive species at exceedingly low concentration. They have been applied in the laboratory to study a wide range of important reactions. Corresponding developments have provided a wealth of new data on the concentration of important atmospheric species including CH_4 (Ehhalt 1974), CO (Seiler 1974; Volz, Ehhalt, Heidt & Pollock 1976), NO (Ridley, Bruin, Schiff & McConnell 1976), NO_2 (Noxon 1975; Noxon, Whipple & Hyde 1977), HNO_3 (Murcray *et al.* 1975) N_2O, (Ehhalt, Heidt, Lueb & Pollock 1975*b*; Schmeltekopf *et al.* 1977), OH (Anderson 1976; Burnett 1976), Cl and ClO (Anderson, Margitan & Stedman 1977), HCl (Farmer, Raper & Norton 1976; Williams, Kosters, Goldman & Murcray 1976; Eyre & Roscoe 1977), and various halomethanes (Lovelock 1974, 1975, 1977; Grimsrud & Rasmussen 1975*a*, *b*; Heidt, Pollock & Lueb 1976).

On the conceptual level it has become clear that the stratosphere cannot be regarded as an isolated compartment. Ozone in the natural environment is removed, at least in part, by catalytic reactions involving NO (Crutzen 1970; Johnston 1971). Nitric oxide is formed in the stratosphere by photochemical decomposition of N_2O (Nicolet & Vergison 1971; McElroy & McConnell 1971; Crutzen 1971) generated by microbial processes at and below the Earth's surface (Bates & Witherspoon 1952; Goody & Walshaw 1953; Bates & Hays 1967). Stratospheric chemistry is coupled, not only to the mesosphere and troposphere, but also, in an important manner to the biosphere.

This paper is concerned primarily with an attempt to assess Man's impact on atmospheric chemistry. The anthropogenic influence is diverse and complex. Combustion of fossil fuels provides important sources of atmospheric CO, CO_2 and H_2 (Keeling 1973; Jaffe 1973; Schmidt 1974). Emissions of CO may produce a significant enhancement of tropospheric ozone with possibly important consequences for air quality on a global scale. An increased burden of tropospheric CO should also lead to reduction in the concentration of tropospheric OH, with an associated increase in the lifetimes and abundances of gases such as CH_4, CH_3Cl and H_2 (Sze 1977; Penner, McElroy & Wofsy 1977). These gases play a significant rôle in stratospheric chemistry. Reaction of chlorine atoms with CH_4 represents the chain terminating step for catalytic chlorine chemistry. In this sense combustion might be expected to lead to an increase in O_3. On the other hand enhanced concentrations of CH_3Cl and other halogenated hydrocarbons have the opposite effect, increasing the supply of reactive chlorine to the stratosphere. Combustion results in both direct (Pierotti & Rasmussen 1976; Weiss & Craig 1976) and indirect (McElroy, Wofsy & Yung 1977) sources of N_2O with corresponding perturbations to the nitrogen catalytic cycle. The nitrogen and chlorine cycles are coupled, resulting in further complications.

Previous attempts to assess human influences on atmospheric chemistry have emphasized effects to be expected from a single perturbation. It was estimated that a fleet of supersonic aircraft as contemplated by the United States in 1970, 500 aircraft flying 8 h per day at 16 km, would result in a global scale reduction to the level of atmospheric O_3 by about 4% (C.I.A.P. 1974). Release of CCl_2F_2 and $CFCl_3$ from aerosol spray cans and refrigeration systems at rates

applicable in 1974, 5×10^5 t (Cl) per year, was predicted to cause a 7% reduction in O_3 at steady state (National Academy of Sciences 1976). Nitrous oxide formed by denitrification of agriculturally related nitrogen could lead to reductions in O_3 as large as 20% by the end of the next century (McElroy 1976; McElroy *et al.* 1977).

The calculations on which these estimates were based employed a number of simplifying assumptions. With two exceptions, a single calculation described by the National Academy of Sciences (1976) and a recent study by Kurzeja (1977), mathematical models used diurnally averaged values to describe solar radiation. They omitted complexities associated with non-linear interactions of perturbations.

It is important that the model used to assess perturbations should provide results consistent with present laboratory and atmospheric constraints. This matter is pursued in §§ 2 and 3. Section 2 discusses present understanding of relevant chemical reactions, attempting to identify reactions of potential importance in the atmosphere for which data are either lacking or ambiguous. Models are compared with atmospheric measurements in § 3 in an effort to develop a consistent chemical scheme. The rationale for selection of specific emission models is described in § 4, while atmospheric implications are investigated in § 5.

2. Chemistry

The chemical processes of importance for the atmosphere have been reviewed extensively in the recent literature. An excellent summary of information available up to mid 1975 is given by Nicolet (1975). We shall concentrate here on subsequent developments, focusing attention on more significant uncertainties. An overview of the important chemistry is presented schematically in figures 1–4.

Reactions important for the mesosphere include

$$H + O_3 \rightarrow OH + O_2, \tag{1}$$

$$O + HO_2 \rightarrow OH + O_2, \tag{2}$$

$$OH + HO_2 \rightarrow H_2O + O_2, \tag{3}$$

and

$$O + OH \rightarrow O_2 + H. \tag{4}$$

The temperature dependence of the rate constant for (1) has been measured recently by Clyne & Monkhouse (1977). They found that the reaction has an activation energy of 4.2 kJ mol^{-1} which results in a relatively slow rate for (1) at altitudes near 70 km. Reactions (2) and (3) have been investigated by Burrows, Harris & Thrush (1977). The rate constant for (3) is smaller than the value reported by Hochanadel, Ghormley & Ogren (1972) by almost a factor of 5. The measurement for (2), 3×10^{-11} cm^3 s^{-1} at 300 K, represents the first experimental determination of a rate constant for this reaction. We adopted a value $9 \times 10^{-11} \exp(-300/T)$ for reaction (4) consistent with measurements by Campbell & Hardy (1977) and Westenberg, deHaas & Roscoe (1970). Rate constants adopted for present purposes are summarized in table 1. We assumed small temperature dependences for reactions (2)–(4). As we shall see, the model described here affords a satisfactory representation of the available mesospheric data.

A new development in stratospheric chemistry concerns the potential importance of $ClNO_3$ (Rowland, Spencer & Molina 1976*a*). Chlorine nitrate is formed by

$$ClO + NO_2 + M \rightarrow ClNO_3 + M, \tag{5}$$

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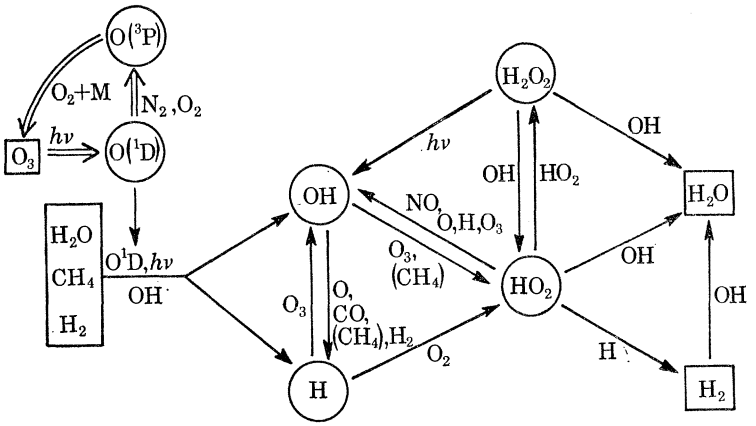

FIGURE 1. The major chemical reactions affecting HO_x(OH, H, HO_2 and H_2O_2) are illustrated schematically.

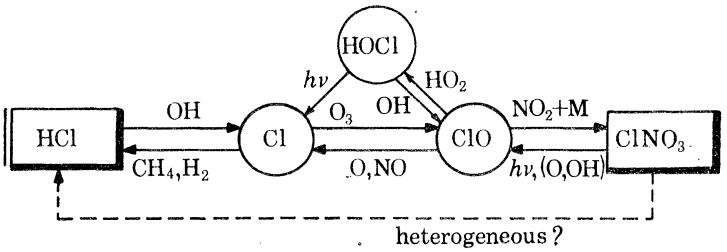

FIGURE 2. The major chemical reactions affecting Cl_x(HCl, Cl, ClO, HOCl and $ClNO_3$) are illustrated schematically. The dashed lines represent possible paths which are not included in the standard chemical model.

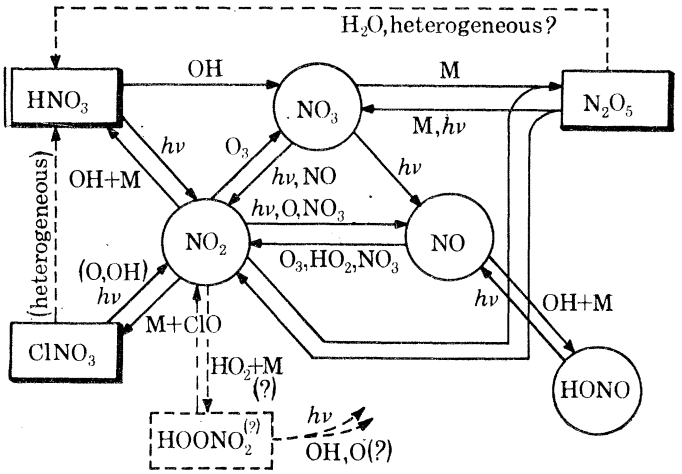

FIGURE 3. The major chemical reactions affecting NO_x(HNO_3, NO_3, NO_2, NO, N_2O_5, HO_2NO_2, HONO, $ClNO_3$) are illustrated schematically.

and removed both by photolysis and by reaction with OH. Products of these reactions are unknown. Smith, Chou & Rowland (1977) believe that the photolytic path may involve initial production of ClONO, by

$$h\nu + ClNO_3 \rightarrow ClONO + O, \tag{6}$$

which should be followed rapidly in the stratosphere (Molina & Molina 1977) either by

$$h\nu + ClONO \rightarrow Cl + NO_2, \tag{7}$$

or by

$$h\nu + ClONO \rightarrow ClO + NO. \tag{8}$$

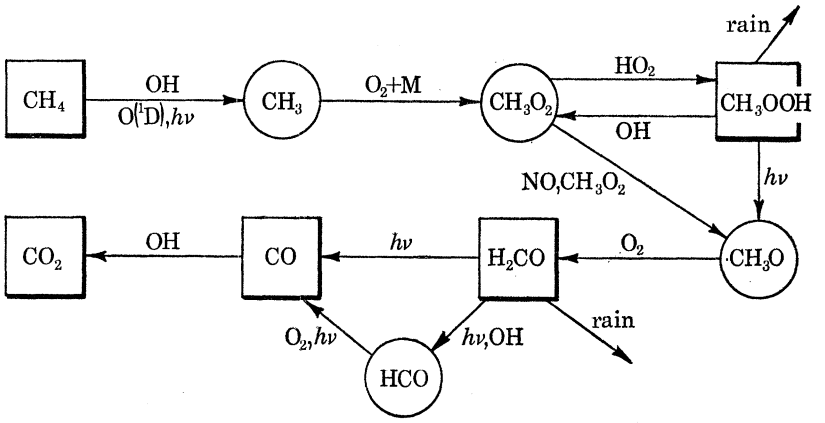

FIGURE 4. The reaction pathway from CH_4 to CO_2 is illustrated schematically.

This scheme involves no net change in the concentration of stratospheric odd oxygen. A similar conclusion holds for photolysis through

$$h\nu + ClNO_3 \rightarrow ClO + NO_2, \tag{9}$$

the path adopted by the National Academy of Sciences (1976). Photolysis of $ClNO_3$ through

$$h\nu + ClNO_3 \rightarrow Cl + NO_3, \tag{10}$$

followed by

$$h\nu + NO_3 \rightarrow NO + O_2 \tag{11}$$

provides a possible catalytic mechanism for removal of odd oxygen. The rate for (11) is approximately 30% of the net rate for removal of NO_3, which proceeds mainly by

$$h\nu + NO_3 \rightarrow NO_2 + O. \tag{12}$$

We shall adopt the reaction path favoured by the National Academy of Sciences (1976). The scheme favored by Smith *et al.* (1977) would give essentially identical results. We shall investigate the possible rôle of (10) and (11), which could have a significant impact at high concentrations of Cl_x (see figure 28).

Reaction with OH represents a minor path for removal of $ClNO_3$. We assume that the reaction proceeds through

$$OH + ClNO_3 \rightarrow HOCl + NO_3, \tag{13}$$

though an alternate path might involve

$$OH + ClNO_3 \rightarrow HO_2 + ClONO. \tag{14}$$

Reaction (13) could provide a detectable source of HOCl, which may be formed in addition by

$$ClO + HO_2 \rightarrow HOCl + O_2. \tag{15}$$

Reaction (15) followed by

$$HOCl + h\nu \rightarrow OH + Cl \tag{16}$$

and

$$Cl + O_3 \rightarrow ClO + O_2 \tag{17}$$

represents a potentially important sink for O_3 below about 25 km. Cross sections for photolysis of HOCl have been measured by DeMore (1977). The rate constant for (15) is unknown. A value in excess of 10^{-11} cm^3 s^{-1} would imply a major rôle for HOCl in stratospheric chemistry.

TABLE 1*a*

number	reaction	rate expression†	references and notes
1	$O(^1D)+N_2 \rightarrow O(^3P)+N_2$	$2.0\text{–}11 \exp(+107/T)$	Streit *et al.* (1976)
2	$O(^1D)+O_2 \rightarrow O(^3P)+O_2$	$2.9\text{–}11 \exp(+67/T)$	Streit *et al.* (1976)
3*a*	$O(^1D)+N_2O \rightarrow NO+NO$	$5.5\text{–}11$	Davidson *et al.* (1977)
3*b*	$\rightarrow N_2+O_2$	$5.5\text{–}11$	Davidson *et al.* (1977)
4*a*	$O(^1D)+CH_4 \rightarrow OH+CH_3$	$1.3\text{–}10$	Davidson *et al.* (1977)
	$\rightarrow H_2+H_2CO$	$1.3\text{–}11$	Hampson & Garvin (1975)
5	$OH+CH_4 \rightarrow CH_3+H_2O$	$2.36\text{–}12 \exp(-1710/T)$	Davis *et al.* (1974*a*)
6	$OH+CO \rightarrow CO_2+H$	$2.10\text{–}13 f(M) \exp(-115/T)$ $f(M) = 1.0 \; (M < 7.9+17)$ $f(M) = 2.24 \; (M > 1.27+19)$ $f(M) = 0.92+1.02\text{–}19\, M$ $(7.97+17 < M < 1.27+19)$	Greiner (1969); Davis *et al.* (1974*a*); Cox *et al.* (1976); Sie *et al.* (1976); Chan *et al.* (1977); Overend & Paraskevopoulos (1977); Perry *et al.* (1977)
7	$CO+O+M \rightarrow CO_2+M$	$2.2\text{–}36$	Stuhl & Niki (1971), Slanger *et al.* (1972)
8	$O(^1D)+H_2O \rightarrow OH+OH$	$2.3\text{–}10$	Streit *et al.* (1976)
9	$O(^1D)+H_2 \rightarrow OH+H$	$1.0\text{–}10$	Davidson *et al.* (1977)
10	$O+OH \rightarrow O_2+H$	$9.0\text{–}11 \exp(-300/T)$	Westenberg *et al.* (1970), Campbell & Hardy (1977) est. E_a.
11	$H+O_3 \rightarrow OH+O_2$	$9.89\text{–}11 \exp(-516/T)$	Clyne & Monkhouse (1977)
12	$OH+O_3 \rightarrow HO_2+O_2$	$1.3\text{–}12 \exp(-956/T)$	Anderson & Kaufman (1973)
13	$HO_2+O_3 \rightarrow OH+2O_2$	$8.3\text{–}14 \exp(-1250/T)$	$(k_{13}/k_{24})^{\frac{1}{2}}$ from Simonaitis & Heicklen (1973)
14*a*	$O+H_2O_2 \rightarrow O_2+H_2O$	$1.38\text{–}12 \exp(-2175/T)$	Davis *et al.* (1974*b*)
14*b*	$\rightarrow OH+HO_2$	$1.38\text{–}12 \exp(-2175/T)$	Est. branching ratio
15*a*	$H+H_2O_2 \rightarrow H_2+HO_2$	$2.8\text{–}12 \exp(-1900/T)$	Baulch *et al.* (1972)
15*b*	$\rightarrow OH+H_2O$	$5.2\text{–}12 \exp(-1400/T)$	Klemm *et al.* (1975)
16*a*	$H+HO_2 \rightarrow H_2+O_2$	$4.2\text{–}11 \exp(-350/T)$	Baulch *et al.* (1972)
16*b*	$\rightarrow OH+OH$	$4.2\text{–}10 \exp(-950/T)$	Baulch *et al.* (1972)
17	$H+O_2+M \rightarrow HO_2+M$	$1.90\text{–}32 \exp(+350/T)$	Wong & Davis (1974)
18	$OH+OH \rightarrow H_2O+O$	$1.7\text{–}12$	Clyne & Down (1974)
19	$O+HO_2 \rightarrow OH+O_2$	$6.8\text{–}11 \exp(-200/T)$	Burrows *et al.* (1977) est. E_a
20	$OH+H_2 \rightarrow H_2O+H$	$1.8\text{–}11 \exp(-2350/T)$	Smith & Zellner (1974)
21	$O+H_2 \rightarrow OH+H$	$5.3\text{–}11 \exp(-5100/T)$	Westenberg & deHaas (1969)
22	$OH+H_2O_2 \rightarrow HO_2+H_2O$	$8.0\text{–}12 \exp(-670/T)$	Hack *et al.* (1975)
23	$OH+HO_2 \rightarrow H_2O+O_2$	$1.0\text{–}10 \exp(-200/T)$	Burrows *et al.* (1977) est. E_a
24	$HO_2+HO_2 \rightarrow H_2O_2+O_2$	$1.9\text{–}11 \exp(-500/T)$	Paukert & Johnston (1972) Hamilton (1975), est. E_a
25	$N+O_2 \rightarrow NO+O$	$1.1\text{–}14T \exp(-3150/T)$	Baulch *et al.* (1973)
26	$OH+HCl \rightarrow H_2O+Cl$	$2.0\text{–}12 \exp(-313/T)$	Zahniser *et al.* (1974)
27	$Cl+H_2 \rightarrow HCl+H$	$4.7\text{–}11 \exp(-2340/T)$	Watson (1977)
28	$H+HCl \rightarrow Cl+H_2$	$2.3\text{–}11 \exp(-1816/T)$	estimated from the reverse reaction
29	$O+HCl \rightarrow OH+Cl$	$2.5\text{–}12 \exp(-2980/T)$	Brown & Smith (1975)
30	$Cl+O_3 \rightarrow ClO+O_2$	$2.7\text{–}11 \exp(-257/T)$	Watson (1977)
31	$Cl+Cl+M \rightarrow Cl_2+M$	$1.6\text{–}33 \exp(+800/T)$	Widman & DeGraff (1973)
32	$ClO+NO \rightarrow Cl+NO_2$	$1.7\text{–}11$	Clyne & Watson (1974)
33	$ClO+O \rightarrow Cl+O_2$	$1.1\text{–}10 \exp(-220/T)$	Clyne & Nip (1976)
34	$ClO+NO_2+M \rightarrow ClNO_3+M$	$\dfrac{3.33-23T^{-3.34}M}{1+8.7\text{–}9T^{-0.6}M^{0.5}}$	Zahniser *et al.* (1977)
35	$O+ClNO_3 \rightarrow$ products	$3.4\text{–}12 \exp(-840/T)$	Molina *et al.* (1977) products taken to be $ClO+NO_3$
36	$OH+ClNO_3 \rightarrow$ products	$1.2\text{–}12 \exp(-333/T)$	Zahniser *et al.* (1977) products taken to be $HOCl+NO_3$
37	$H+Cl_2 \rightarrow HCl+Cl$	$1.40\text{–}10 \exp(-589/T)$	Bemand & Clyne (1977)
38	$O+Cl_2 \rightarrow ClO+Cl$	$4.15\text{–}12 \exp(-1368/T)$	Watson (1977)
39	$H+ClO \rightarrow OH+Cl$	$1.0\text{–}11$	estimated
40	$Cl+H_2O_2 \rightarrow HCl+HO_2$	$2.0\text{–}11 \exp(-1050/T)$	Watson (1977). est. E_a
41	$Cl+HO_2 \rightarrow HCl+O_2$	$8.1\text{–}11 \exp(-300/T)$	Leu & DeMore (1976) est. E_a
42	$ClO+HO_2 \rightarrow HOCl+O_2$	$2.0\text{–}12$	estimated
43	$OH+HOCl \rightarrow H_2O+ClO$	$8.0\text{–}12 \exp(-670/T)$	estimated
44	$Cl+CH_4 \rightarrow CH_3+HCl$	$8.2\text{–}12 \exp(-1320/T)$	Zahniser *et al.* (1978)
45	$OH+CH_3Cl \rightarrow$ products	$2.18\text{–}12 \exp(-1142/T)$	Watson (1977)

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TABLE 1*a*. (*cont.*)

number	reaction	rate expression†	references and notes
46	$OH + CH_3CCl_3 \rightarrow$ products	3.72–12 exp $(-1627/T)$	Watson *et al.* (1977)
47	$OH + CH_2O \rightarrow HCO + H_2O$	1.4–11	Morris & Niki (1971)
48	$N + NO \rightarrow N_2 + O$	8.2–11 exp $(-410/T)$	Clyne & McDermid (1975)
49	$O + NO_2 \rightarrow NO + O_2$	9.12–12	Davis *et al.* (1973*a*)
50	$O_3 + NO \rightarrow NO_2 + O_2$	1.5–12 exp $(-1330/T)$	Baulch *et al.* (1973)
51	$H + NO_2 \rightarrow OH + NO$	4.81–10 exp $(-405/T)$	Clyne & Monkhouse (1977)
52	$O_3 + NO_2 \rightarrow O_2 + NO_3$	1.34–13 exp $(-2466/T)$	Graham & Johnston (1974)
53	$O + NO + M \rightarrow NO_2 + M$	4.0–33 exp $(+940/T)$	Baulch *et al.* (1973)
54	$O + NO_2 + M \rightarrow NO_3 + M$	1.0–31	Hampson (1973)
55	$NO + NO_3 \rightarrow NO_2 + NO_2$	8.7–12	Harker & Johnston (1973)
56	$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$	2.3–13 exp $(-1600/T)$	Baulch *et al.* (1973)
57	$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$	5.0–12 exp $(-3000/T)$	Schott & Davidson (1958)
58	$N + NO_2 \rightarrow N_2O + O$	1.4–12	Clyne & McDermid (1975)
59	$OH + HNO_3 \rightarrow H_2O + NO_3$	8.9–14	Margitan *et al.* (1975)
60	$HO_2 + NO \rightarrow OH + NO_2$	8.25–11 exp $(-700/T)$	Howard & Evenson (1977) est. E_a
61	$N + O_3 \rightarrow NO + O_2$	5.7–13	Phillips & Schiff (1962)
62	$OH + NO + M \rightarrow HNO_2 + M$	$k_2 = 2.74\text{–}12 \exp(+850/T)$ $k_2/k_3 = 1.12 + 20$ $\left(\frac{1}{k_1}\right)^{\frac{1}{2}} = \left(\frac{1}{k_2}\right)^{\frac{1}{2}} + \left(\frac{1}{k_3 M}\right)^{\frac{1}{2}}$ $k(M = N_2) = 1.5\, k_1(M = Ar)$	fit to data of Atkinson *et al.* (1975)
63	$O + HNO_3 \rightarrow OH + NO_3$	3.0–17	Chapman & Wayne (1974)
64	$H + HNO_3 \rightarrow H_2 + NO_3$	2.0–15	Chapman & Wayne (1974)
65	$O + O_2 + M \rightarrow O_3 + M$	1.05–34 exp $(+510/T)$	Huie *et al.* (1972)
66	$O + O_3 \rightarrow O_2 + O_2$	2.0–11 exp $(-2280/T)$	Davis *et al.* (1973*c*)
67	$O + O + M \rightarrow O_2 + M$	9.59–34 exp $(+480/T)$	fit to data of Campbell & Gray (1973)
68	$NO + NO + O_2 \rightarrow NO_2 + NO_2$	3.30–39 exp $(+530/T)$	Baulch *et al.* (1973)
69	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ $N_2O_5 + M \rightarrow NO_2 + NO_3$		see expression adopted by McConnell & McElroy (1973)
70	$N + OH \rightarrow NO + H$	6.8–11	Campbell & Thrush (1968)
71	$N + O \rightarrow NO + h\nu$	1.0–17	Nicolet (1965)
72	$H + H + M \rightarrow H_2 + M$	8.3–33	Baulch *et al.* (1972)
73	$NO + O \rightarrow NO_2 + h\nu$	4.2–18	Becker *et al.* (1973)
74	$OH + HNO_2 \rightarrow H_2O + NO_2$	6.6–12	Cox *et al.* (1976)
75	$HO_2 + NO_2 \rightarrow HNO_2 + O_2$	3.0–15	Howard (1977)
76*a*	$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	$k_2 = 1.0\text{–}13$ $k_2/k_3 = 5.0 + 17$ $\frac{1}{k} = \frac{1}{k_2} + \frac{1}{k_3 M}$	k_3 from Howard (1977) k_2 estimated
76*b*	$HO_2NO_2 \xrightarrow{M} HO_2 + NO_2$	$1.4 + 14 \exp(-10400/T)$	Graham *et al.* (1977)
77	$OH + HO_2NO_2 \rightarrow H_2O + O_2 + NO_2$	5.0–13	estimated
78	$OH + CH_3OOH \rightarrow CH_3O_2 + H_2O$	5.2–12 exp $(-670/T)$	estimated
79	$CH_3OO + NO \rightarrow CH_3O + NO_2$	5.3–12 exp $(-500/T)$	estimated
80	$CH_3OO + HO_2 \rightarrow CH_3OOH + O_2$	5.3–12 exp $(-500/T)$	estimated
81	$CH_3OO + CH_3OO \rightarrow 2CH_3O + O_2$	2.00–12 exp $(-500/T)$	Hochandel *et al.* (1977) est. E_a
82	$OH + NO_2 + M \rightarrow HNO_3 + M$	$k_2 = 2.77\text{–}11$ $k_3 = 7.14\text{–}32 \exp(1080/T)$ $\left(\frac{1}{k_1}\right)^{\frac{1}{2}} = \left(\frac{1}{k_2}\right)^{\frac{1}{2}} + \left(\frac{1}{k_3 M}\right)^{\frac{1}{2}}$ $k(M = \text{air}) = 0.95\, k_1(M = N_2)$	fit to the data of Anastasi & Smith (1976)
83	soluble gas → precipitation scavenging (units: s^{-1}) (HCl, HNO_3, HNO_2, HO_2NO_2, H_2O_2, H_2CO, CH_3OOH)	2.31–6 $0 < z \leqslant 4$ km 1.16–6 $4 < z \leqslant 6$ km 5.79–6 $6 < z \leqslant 8$ km 2.31–7 $8 < z \leqslant 10$ km 7.72–8 $10 < z \leqslant 14$ km 0 14 km $< z$	see Wofsy (1976)

TABLE 1*a*. (*cont.*)

number	photolytic process	references and notes
84	$NO + h\nu \rightarrow N + O$	see table 1*b*
85	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$	Graham & Johnston (1978)
86	$NO_2 + h\nu \rightarrow NO + O$	Hall & Blacet (1952)
87	$HNO_2 + h\nu \rightarrow OH + NO$	Cox & Derwent (1976)
88	$HNO_3 + h\nu \rightarrow OH + NO_2$	Johnston & Graham (1974)
89	$N_2O + h\nu \rightarrow N_2 + O(^1D)$	$\lambda > 1730$ Å Selwyn *et al.* (1977) values at 243 K $\lambda < 1730$ Å Zelikoff *et al.* (1953), Romand & Mayence (1949)
90*a*	$NO_3 + h\nu \xrightarrow{1} NO + O_2$	Graham & Johnston (1978)
90*b*	$\xrightarrow{2} NO_2 + O$	
91	$O_3 + h\nu \rightarrow O_2 + O$	Griggs (1968), Philen *et al.* (1977)
92	$O_2 + h\nu \rightarrow O + O$	$\lambda < 2000$ Å‡ See table 1*b* $\lambda > 2000$ Å Ditchburn & Young (1962)
93	$H_2O + h\nu \rightarrow H + OH$	$\lambda > 1800$ Å Thompson *et al.* (1963) $\lambda < 1800$ Å Watanabe & Zelikoff (1953)
94	$CH_4 + h\nu \rightarrow CH_2 + H_2$	Sun & Weissler (1954), Watanabe *et al.* (1953)
95	$CO_2 + h\nu \rightarrow CO + O$	Shemansky (1972)
96	$H_2O_2 + h\nu \rightarrow OH + OH$	Schumb *et al.* (1955)
97	$CH_3OOH + h\nu \rightarrow CH_3O + OH$	$0.65 \times J_{H_2O_2}$ estimated
98	$HO_2 + h\nu \rightarrow OH + H$	Paukert & Johnston (1972)
99	$H_2CO + h\nu \rightarrow HCO + H$ $\rightarrow H_2 + CO$	Calvert *et al.* (1972)
100	$Cl_2 + h\nu \rightarrow Cl + Cl$	Seery & Britton (1964), Gibson & Bayliss (1933)
101	$HCl + h\nu \rightarrow H + Cl$	Inn (1975)
102	$ClO + h\nu \rightarrow Cl + O$	Johnston *et al.* (1969), Clyne & Coxon (1968)
103	$ClNO_3 + h\nu \rightarrow ClO + NO_2$	Rowland *et al.* (1976*b*)
104	$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$	Chou *et al.* (1977) (230 K)
105	$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$	Chou *et al.* (1977) (230 K)
106	$CCl_4 + h\nu \rightarrow CCl_3 + Cl$	Rowland & Molina (1975)
107	$CH_3Cl + h\nu \rightarrow CH_3 + Cl$	Robbins (1976)
108	$CH_3CCl_3 + h\nu \rightarrow CH_3CCl_2 + Cl$	Chou, Ruiz, Moe & Rowland, private communication in Watson (1977)
109	$HOCl + h\nu \rightarrow OH + Cl$	DeMore *et al.* (1977)
110	$HO_2NO_2 + h\nu \rightarrow OH + NO_3$	$1.5 \times J_{H_2O_2}$ estimate

† Units: $cm^3\ s^{-1}$ for bimolecular reactions; $cm^6\ s^{-1}$ for termolecular reactions. The notation 1.0–11 is intended to be read as 1.0×10^{-11}.

‡ 1 Å = 0.1 nm = 10^{-10} m.

We adopted a somewhat smaller value, basing our choice on laboratory studies of the isoelectronic process

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \quad (18)$$

Assessment of the possible rôles of $ClNO_3$ and HOCl requires an accurate treatment for the diurnal cycle of solar radiation. The important species OH, HO_2, O, NO_2, ClO and $ClNO_3$ exhibit significant and complex diurnal variations, as shown in figure 5. Models based on the assumption of a diurnal mean insolation lead to an underestimate of the net rate for the key reaction

$$ClO + O \rightarrow Cl + O_2. \quad (19)$$

The discrepancy arises in part due to inadequacies of the simple models, which tend to overestimate the daytime concentration of $ClNO_3$. It may be attributed also to difficulties which arise due to covariance of the concentrations for ClO and O. Our model allows for backscatter of solar radiation from the lower atmosphere, as described by Yung (1976). Scattered radiation

is important at longer wavelengths where it leads to a significant increase in the rates for photolysis of $ClNO_3$, HOCl and NO_2 and to an enhanced source for $O(^1D)$.

Another development of note concerns the rate for reaction of NO with HO_2,

$$NO + HO_2 \rightarrow NO_2 + OH. \qquad (20)$$

Howard & Evenson (1977), using laser magnetic resonance to monitor HO_2, find a rate for this reaction at room temperature of 8×10^{-12} cm^3 s^{-1}, significantly larger than indirect measurements reported earlier by Davis, Payne & Stief (1973*b*), Cox & Derwent (1975), Hack, Hoyerman & Wagner (1975) and Simonaitis & Heicklen (1976). The reaction is of considerable

TABLE 1*b*. SCHUMANN–RUNGE BAND PARAMETERS

wavelength interval Å	temp. K	cross sections/cm^2					
1775–1783	190	4.33 (−21)	4.89 (−21)	6.63 (−21)	1.60 (−20)	7.20 (−20)	1.59 (−18)
1783–1793	190	2.10 (−21)	2.32 (−21)	3.02 (−21)	6.30 (−21)	3.46 (−20)	7.52 (−19)
1793–1804	190	5.95 (−22)	9.75 (−22)	2.53 (−21)	7.57 (−21)	7.38 (−20)	7.44 (−19)
1804–1816	190	3.33 (−22)	1.02 (−21)	4.09 (−21)	1.63 (−20)	8.79 (−20)	3.81 (−19)
1816–1825	190	1.09 (−21)	1.16 (−21)	1.45 (−21)	3.32 (−21)	2.00 (−20)	4.04 (−19)
1825–1831	270	1.15 (−21)	1.30 (−21)	1.90 (−21)	4.89 (−21)	2.62 (−20)	4.08 (−19)
1831–1846	270	3.90 (−22)	4.90 (−22)	9.49 (−22)	3.33 (−21)	2.14 (−20)	2.39 (−19)
1846–1863	270	1.29 (−22)	2.18 (−22)	8.28 (−22)	3.46 (−21)	1.94 (−20)	1.06 (−19)
1863–1882	270	6.26 (−23)	7.80 (−23)	2.62 (−22)	1.83 (−21)	1.25 (−20)	6.95 (−20)
1882–1902	270	2.74 (−23)	3.58 (−23)	8.64 (−23)	4.03 (−22)	2.13 (−21)	1.95 (−20)
1902–1925	270	1.95 (−23)	2.44 (−23)	4.89 (−23)	2.87 (−22)	1.95 (−21)	1.36 (−20)
1925–1947	230	1.84 (−23)	1.96 (−23)	2.71 (−23)	8.52 (−23)	6.48 (−22)	3.89 (−21)
1947–1972	230	1.80 (−23)	1.81 (−23)	1.87 (−23)	2.69 (−23)	1.34 (−22)	1.52 (−21)
1972–1985	230	1.80 (−23)	1.80 (−23)	1.82 (−23)	2.40 (−23)	5.71 (−23)	5.70 (−22)
1985–2000	230	1.76 (−23)	1.76 (−23)	1.76 (−23)	1.76 (−23)	1.76 (−23)	3.50 (−23)
2000–2025	230	1.71 (−23)	1.71 (−23)	1.71 (−23)	1.71 (−23)	1.71 (−23)	2.68 (−23)
weight(w_i)		0.05	0.20	0.25	0.25	0.20	0.05

The transmission T in any wavelength interval is given by

$$T(\lambda_1, \lambda_2) = \sum_{i=1}^{6} w_i \exp\left[-(\sigma_i C + Q)/\cos\chi\right],$$

where χ is the solar zenith angle, C is the $\mathbf{O_2}$ vertical column and Q is any additional opacity source. The photodissociation rate J_{O_2} is given by

$$J_{O_2}(\lambda_1, \lambda_2) = F(\lambda_1, \lambda_2) \sum_{i=1}^{6} w_i \sigma_i \exp\left[-(\sigma_i C + Q)/\cos\chi\right],$$

where F is the solar flux incident on the top of the atmosphere. Photolysis of NO in the $\delta(0, 0)$ band is associated with transmission in the wavelength interval 1902–1925 Å and with a mean cross section of 3.67×10^{-18} cm^2. The $\delta(1, 0)$ band lies in the interval 1816–1825 Å and has a mean cross section of 1.96×10^{-17} cm^2. This formulation provides a representation of the opacity distribution functions of Fang *et al.* (1974), and adequately reproduces the observed transmission of O_2 reported by Hudson & Mahle (1972).

importance for the stratosphere. It provides a source for OH and, coupled with photolysis of NO_2, a source also for odd oxygen. The large discrepancy between new and old measurements for (20) raises questions with regard to the validity of rate expressions reported earlier for other reactions involving HO_2, for example,

$$HO_2 + O_3 \rightarrow OH + 2O_2, \qquad (21)$$

and reaction (18). We shall return to this matter later, in § 5.

Several investigators (Simonaitis & Heicklen 1976; Niki, Maker, Savage & Breitenbach 1977; Howard 1977) have raised the possibility that reaction of NO_2 with HO_2 might lead to

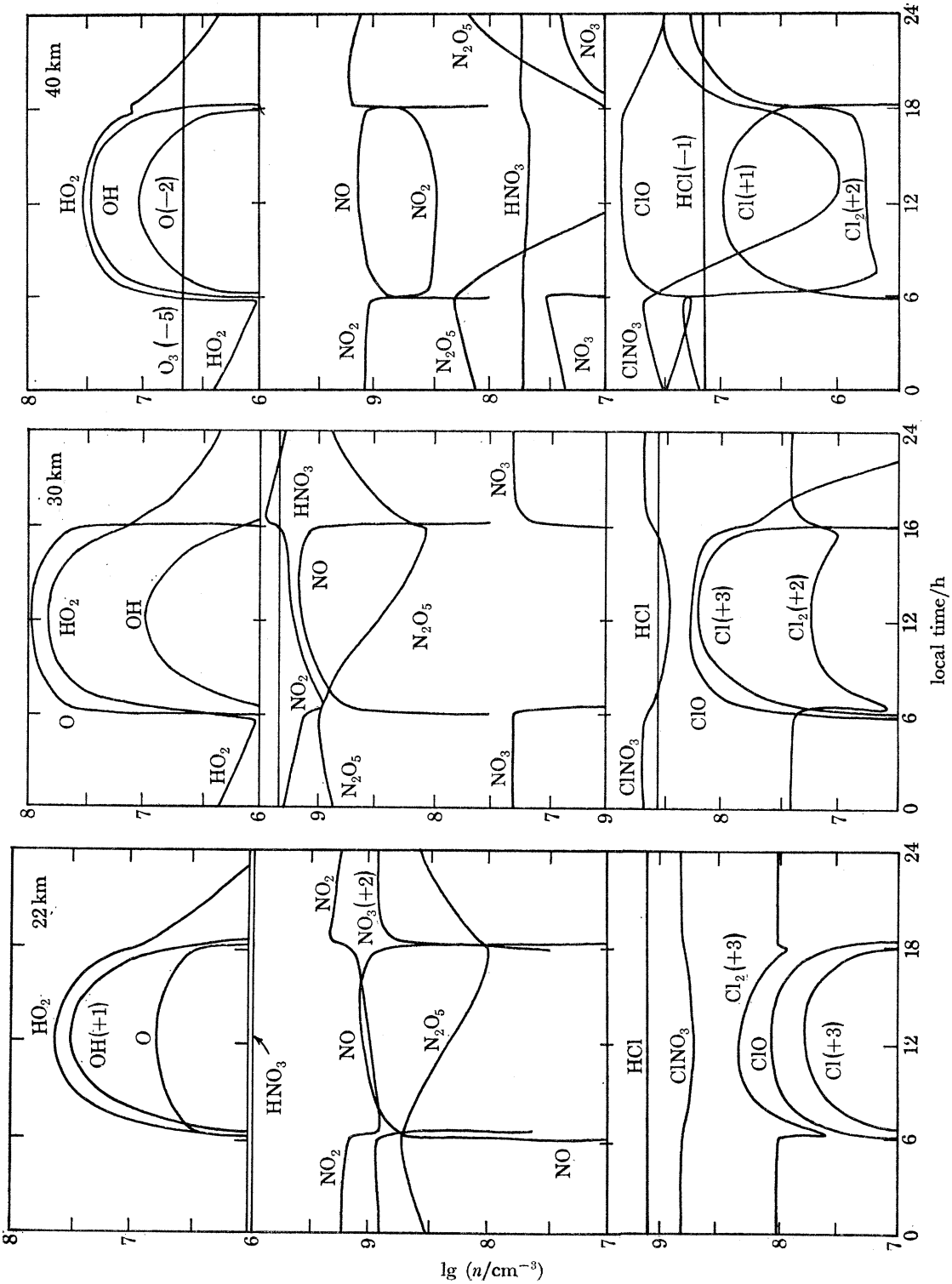

FIGURE 5. The diurnal variations of several species at 22, 30 and 40 km are shown for 30° N latitude and 0° solar declination. The notation (−2) indicates that the number density for that species has been multiplied by 10^{-2}.

formation of pernitric acid, HO_2NO_2. The subsequent chemistry of this compound is unknown. It will be treated here according to the scheme

$$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M, \quad (22)$$

followed by

$$HO_2NO_2 + h\nu \rightarrow OH + NO_3, \quad (23)$$

$$OH + HO_2NO_2 \rightarrow H_2O + O_2 + NO_2, \quad (24)$$

by thermal decomposition (Graham, Winer & Pitts 1977), or by rain out. The rate for (22) has been measured by Howard (1977). Table 1 includes estimates of rates for (23) and (24). Pernitric acid could represent a sink for odd nitrogen in the lower stratosphere and troposphere. It could provide also a source of tropospheric odd oxygen, through (23) followed by (12), and it might be detectable in the atmosphere with current spectroscopic techniques. With our estimated reaction rates, HO_2NO_2 plays only a minor rôle in atmospheric chemistry.

Recent studies of the reaction

$$CO + OH \rightarrow CO_2 + H \quad (25)$$

indicate that the rate for this process may be a function of ambient pressure (Cox, Derwent & Holt 1976; Sie, Simonaitis & Heicklen 1976; Chan, Uselman, Calvert & Shaw 1977; Overend & Paraskevopoulos 1977; Perry, Atkinson & Pitts 1977). The effective rate constant at a pressure of one atmosphere appears to exceed the low pressure value by about a factor of 2, with consequent implications for the budgets of tropospheric CO and OH. The mechanism for reaction of CO with OH at high pressures is not well understood. The laboratory data indicate that the effective reaction rate is a sensitive function of the particular choice of background gas and data to define the behaviour in air are incomplete. Further work is clearly required in order to resolve this issue. The pressure dependent rate expression used here is given in table 1.

3. The present atmosphere

This section addresses the question of whether models based on our understanding of chemistry as discussed above provide results consistent with available atmospheric constraints. Of special relevance in this context are measurements of mesospheric and stratospheric OH by Anderson (1971, 1975, 1976) and Burnett (1976, 1977), measurements of stratospheric Cl and ClO by Anderson *et al.* (1977), measurements of stratospheric HCl by Lazrus, Gandrud & Woodard (1976), Ackerman *et al.* (1976), Raper, Farmer, Toth & Robbins (1977) and Eyre & Roscoe (1977), data on O_3 from a variety of sources (Miller & Stewart 1965; Evans, Hunten, Llewellyn & Jones 1968; Hilsenrath, Serdon & Goodman 1969; Krueger, Heath & Mateer 1973; Hering & Borden 1967; Hering 1975; Watanabe & Tohmatsu 1976), measurements of total column NO_2 densities (Noxon 1975; Noxon *et al.* 1977), and measurements of total column HNO_3 densities by Murcray *et al.* (1975).

Mesospheric OH and O_3 data give indirect information on the concentration of mesospheric H_2O, together with some check on the validity of rate expressions adopted for reactions (1)–(4). The concentration of stratospheric OH reflects assumptions regarding the concentration of stratospheric H_2O, and rates for the HO_2 reactions, (2), (3), (20) and (21). Measurements of stratospheric Cl, ClO and HCl have implications with regard to the total concentration of stratospheric chlorine, and for the validity of the scheme used to treat the chlorine catalytic

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cycle. Column densities of NO_2 and HNO_3 provide global perspective on the distribution of nitrogen oxides.

Concentrations of the long lived gases N_2O, NO_x, CH_4, H_2, Cl_x and chlorocarbons were calculated using the concept of quasi-horizontal mixing surfaces (McElroy, Elkins, Wofsy & Yung 1976) to define latitudinal distributions, in combination with a one-dimensional model to specify average vertical structure. Preferred surfaces for horizontal mixing were identified by using observations of Sr^{90} and C^{14} (List & Telegadas 1969), supplemented in the equatorial region with recent data for N_2O (Schmeltekopf *et al.* 1977; Goldan 1977). The mixing surfaces

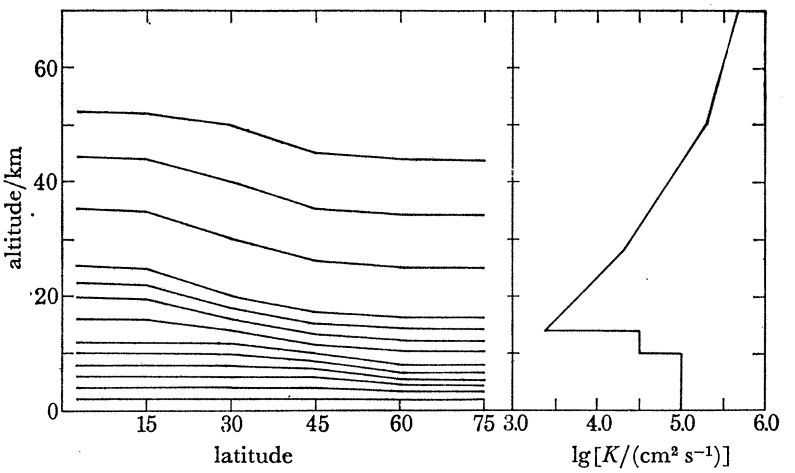

FIGURE 6*a*. The left panel shows preferred surfaces for horizontal mixing. The vertical diffusion coefficient at 30° N latitude is shown on the right.

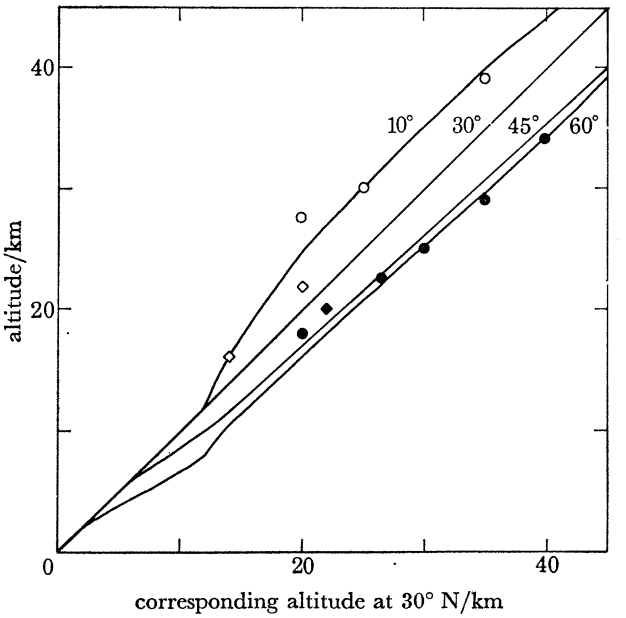

FIGURE 6*b*. An alternative representation of the mixing surfaces in figure 6*a* is given. For each latitude, a given altitude at 30° N (abscissa) is projected onto the corresponding altitude on the ordinate. The symbols show the data used to construct the mixing surfaces; ● (40°–50° N) and ○ (10° N) are from the N_2O measurements of Schmeltekopf *et al.* (1977) and Goldan (1977); ◆ (40°–50° N) and ◇ (10° N) are from C^{14} and Sr^{90} measurements of List & Telegadas (1969).

are shown in figure 6. The one-dimensional model is applied at 30° N latitude where data exist for several important trace species including CH_4. Observations of CH_4 were used to select a set of effective vertical diffusion coefficients as described by Wofsy & McElroy (1973). These coefficients are included in figure 6. They are similar to values used in a variety of recent atmospheric studies (McElroy, Wofsy, Penner & McConnell 1974; Wofsy, McElroy & Sze 1975*a*; Wofsy, McElroy & Yung 1975*b*; Johnston 1976; Hunten 1975; McElroy *et al.* 1977) and agree with results for N_2O reported by Schmeltekopf *et al.* (1977).

TABLE 2. BOUNDARY CONDITIONS (1975)

species	volume mixing ratio (0 km)	species	volume mixing ratio (0 km)
N_2O	3.0–7	$CFCl_3$	1.2–10
NO_x†	5.0–10	CF_2Cl_2	2.0–10
CH_4	1.44–6	CCl_4	1.1–10
CO	1.19–7	CH_3Cl	1.0–9
H_2	5.0–7	CH_3CCl_3	5.0–11
O_3	2.6–8	Cl_x‡	1.0–9

Upper boundary conditions: zero flux at 80 km

† $NO_x = NO + NO_2 + NO_3 + 2 \times N_2O_5 + ClNO_3 + HNO_3 + HONO + HO_2NO_2$.
‡ $Cl_x = HCl + Cl + ClO + ClNO_3 + HOCl + Cl_2$.

The atmosphere contains gases with a wide range of chemical lifetimes. Our selection of long lived gases includes only those species for which the chemical lifetime is very much longer than a day. The concentration, n_i, of these species at 30° N latitude is assumed to satisfy a continuity relation of the form

$$\frac{\partial n_i}{\partial t} + \frac{\partial \phi_i}{\partial z} = \bar{P}_i - \bar{L}_i, \tag{26}$$

where ϕ_i denotes the vertical flux (molecules cm^{-2} s^{-1}) of species i and the symbols $\bar{P}_i$ and $\bar{L}_i$ indicate diurnally averaged values for the production and loss rates of i at altitude z. Equation (26) is solved subject to boundary conditions as summarized in table 2. The chemical terms $\bar{P}_i$ and $\bar{L}_i$ are influenced in general by the complex diurnal variation of other species. The concentrations of short lived species, j, defined to include gases with chemical lifetimes shorter than relevant times for transport, are found by solving local continuity equations

$$dn_j/dt = P_j(\{n_k\}, t) - L_j(\{n_k\}, t). \tag{27}$$

Short lived species include $O(^3P)$, $O(^1D)$, NO, NO_2, NO_3, N_2O_5, HNO_2, HNO_3, HO_2NO_2, $ClNO_3$, HCl, Cl, Cl_2, ClO, HOCl, H, OH, HO_2 and H_2O_2. Averaged production and loss rates for species i were obtained by numerical integration of the instantaneous rates $P_i(t)$ and $L_i(t)$.

The coupled set of equations defined by (27) was treated numerically with an implicit finite difference representation adapted from Richtmeyer (1957),

$$n_j(\Delta t)/\Delta t - [P(\{n_k(\Delta t)\}, \Delta t) - L(\{n_k(\Delta t)\}, \Delta t)] - n_j(0)/\Delta t = 0. \tag{28}$$

This equation must be solved with a precision adequate to ensure conservation of mass to high accuracy over a diurnal cycle. The method adopted here conserves mass to better than 1 part in 10^6. Periodic boundary conditions are imposed by a simple variational technique (see, for example, Wofsy 1978).

Height profiles at various latitudes as calculated for several of the longer lived species are

shown in figures 7 (N_2O), 8 (CH_4, CO) and 9 ($CFCl_3$, CF_2Cl_2, CCl_4, CH_3Cl). Figure 7 includes a comparison of model results with vertical profiles for N_2O as measured at mid-latitudes by Heidt *et al.* (1976), Schmeltekopf *et al.* (1977), and Goldan (1977). A similar comparison with data for CH_4 (Ehhalt 1974; Ehhalt *et al.* 1975*b*; Volz *et al.* 1976) and CO (Volz *et al.* 1976) is given in figure 8. Model results are in satisfactory accord with observational data for all gases with the exception of CF_2Cl_2 and CO. The discrepancy which appears for CF_2Cl_2 at higher altitudes may be attributed to its short lifetime relative to N_2O or CH_4, and is unimportant for present purposes. The agreement lends confidence to the procedures adopted to simulate both vertical and lateral transport, at least for the lower stratosphere. Extension of the data base to higher altitudes is obviously desirable. Results in figures 5 and 7–9 were obtained by using the standard chemical model as defined in table 1.

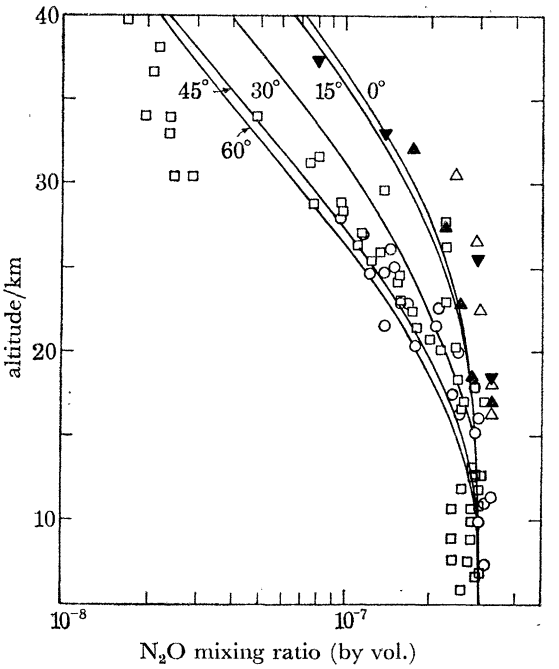

FIGURE 7. Altitude profiles at various latitudes for N_2O. The curves were calculated as discussed in the text for 0° solar declination. The experimental data were taken at 32° N, □ (Heidt *et al.* 1976); 41° N, ○, and 9° N, ▲ (Schmeltekopf *et al.* 1977), △, ▼ (Goldan 1977).

The discrepancy between calculated and observed CO is more difficult to explain. The CO chemical lifetime is fairly short ($2–8 \times 10^6$ s) above 20 km and its abundance in the model is controlled largely by chemical production from CH_4,

$$CH_4 + OH \rightarrow CH_3 + H_2O \rightarrow CO, \tag{29}$$

and loss by reaction (25) (see figure 4). Since (29) and (25) both involve reaction with OH, the CO abundance should be approximately given by

$$[CO] \approx [CH_4]k_{29}/k_{25}. \tag{30}$$

This scheme yields CO abundances too small by at least a factor of 5, as shown in figure 8. An additional source of CO is evidently required. Photolysis of CO_2 would have to be 100 times faster than current estimates in order to be significant and we consider this to be unlikely. A possible source of CO might be reaction of $O(^1D)$ with CO_2,

$$O(^1D) + CO_2 \rightarrow O_2 + CO. \tag{31a}$$

Preston & Cvetanovic (1966) estimated a rate for (31*a*) of approximately 5% of the rate for quenching process,

$$O(^1D) + CO_2 \rightarrow O(^3P) + CO_2, \qquad (31b)$$

although Shortridge & Lin (1975) estimated a much lower value, $k_{31a} < 10^{-14}$ cm^3 s^{-1}. The dashed line in figure 8 demonstrates that a model which includes (31*a*) ($k_{31a} = 1 \times 10^{-11}$ cm^3 s^{-1}) is in agreement with observed CO in the stratosphere. This process would have negligible influence on other species, and would not affect CO in the lower atmosphere. Evidently measurements of the rate for (31*a*) are needed to resolve this question.

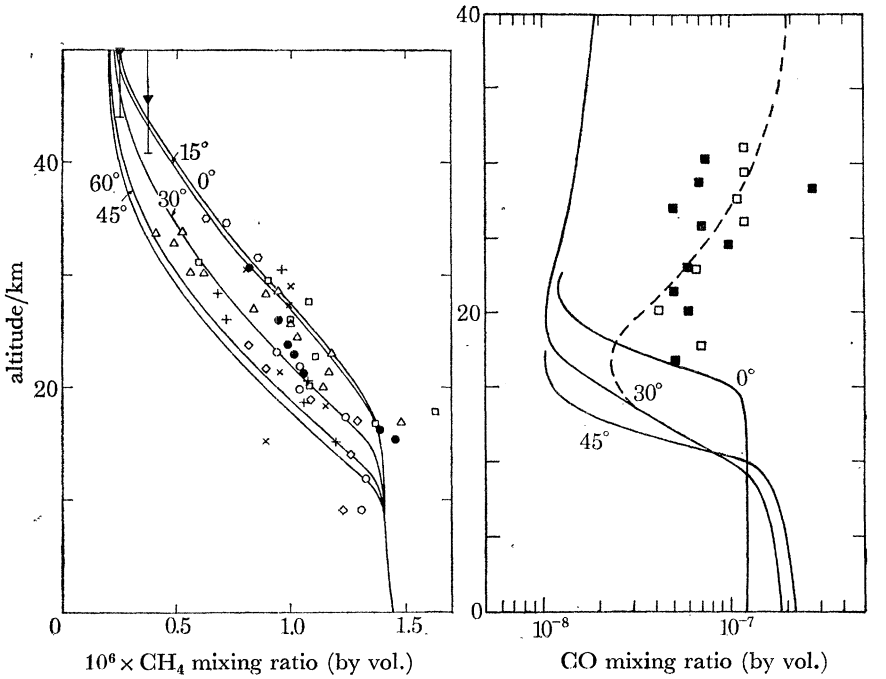

FIGURE 8. Altitude profiles at various latitudes for CH_4 and CO. The CH_4 curves were calculated as discussed in the text. The methane data were taken at 32° N, with the exception of one profile from 32° S (●). The points ▼ are from rocket flights. The different symbols indicate individual profiles, and are from Ehhalt (1974), Ehhalt *et al.* (1975), and Volz *et al.* (1976). The CO profiles in the troposphere were taken from the data of Seiler & Schmidt (1974). In the stratosphere the solid curve results from the standard chemical model, while the dashed curve results from inclusion of the process $O(^1D) + CO_2$ ($k = 1 \times 10^{-11}$ cm^3 s^{-1}) as a source of CO. The CO data were taken at 32° N, □, ■ (Volz *et al.* 1976).

Figures 10 and 11 show profiles as calculated for the concentrations of mesospheric OH and O_3. The lifetime for odd oxygen in the mesosphere is relatively short and O_3 must be treated as a short lived species in this region; see equation (28). The diurnal variations of several species of importance in mesospheric chemistry (H, OH, HO_2, O_3) are shown in figure 12. Concentrations of mesospheric OH and O_3 depend in a direct manner on the abundance of mesospheric H_2O. Our model assumes H_2O abundances as shown in figure 13. The rise in the mixing ratio of H_2O above 20 km reflects conversion of CH_4 to H_2O and CO_2.

The results shown in figures 10 and 11 are in excellent agreement with the available observational data set. Figure 11 includes a model in which the room temperature measurements for reactions (2)–(4) were taken to apply throughout the atmosphere. Both models are in satisfactory accord with Anderson's (1975) observations of OH, and with available measurements of

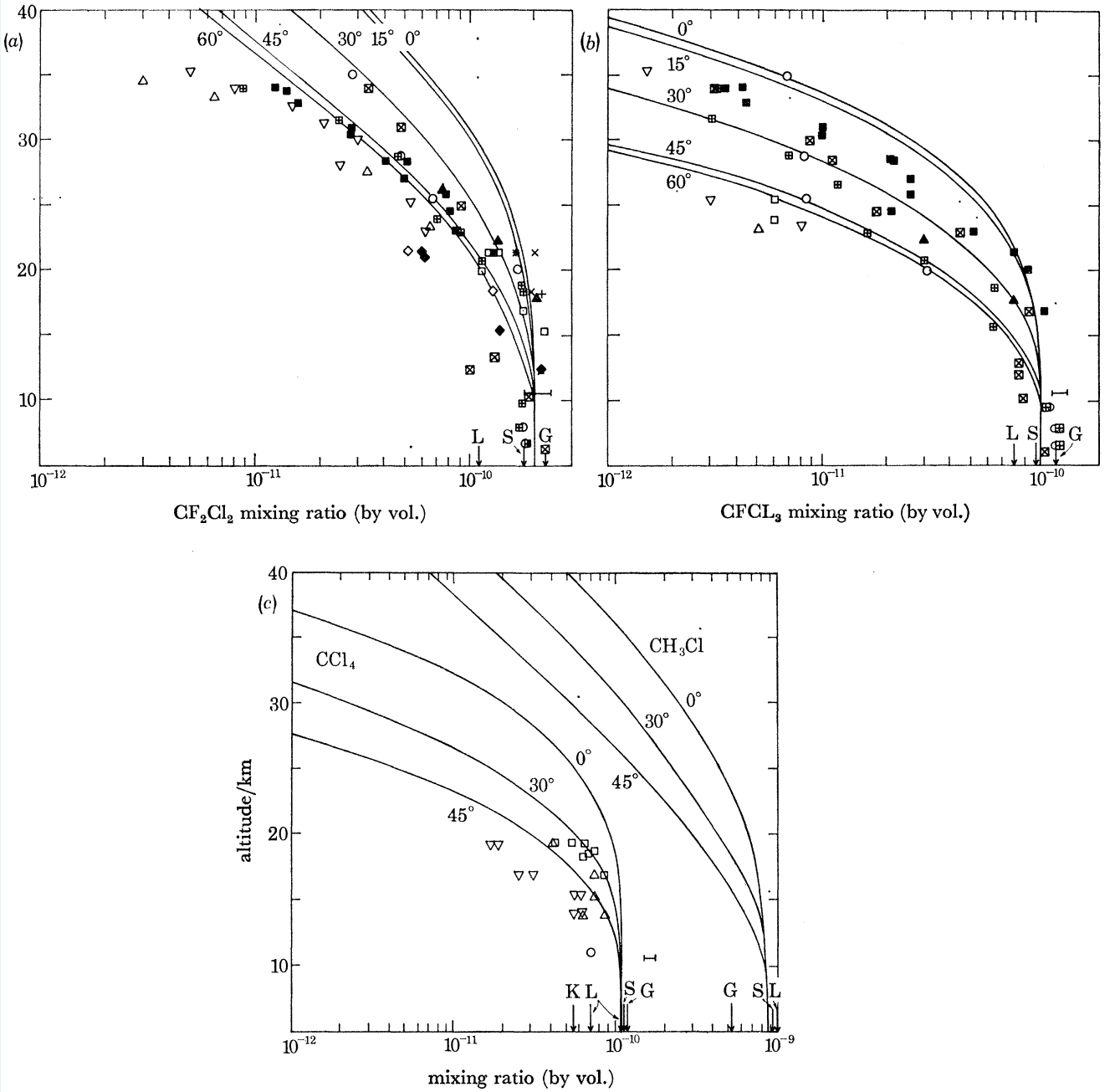

FIGURE 9. Altitude profiles at various latitudes for (*a*) $CFCl_3$, (*b*) CF_2Cl_2, (*c*) CCl_4 and CH_3Cl. The curves were calculated as discussed in the text for 0° solar declination. The experimental data for $CFCl_3$ and CF_2Cl_2 are as follows: ■, ⊠, ⊞ (32° N), ○ (51° N), Heidt *et al.* (1975, 1976); ▲ (41° N), Schmeltekopf *et al.* (1975); ▽, △ (44° N), Fabian *et al.* (1977); × (9° N), + (16° N), □ (30° N), ◇ (60° N), ◆ (75° N), Inn *et al.* (1977*a*); ⊢ Inn *et al.* (1977*b*). The arrows on both panels indicate ground level measurements and are from Lovelock *et al.* (1973, 1974) (L), Grimsrud & Rasmussen (1975*a*, *b*) (G), and Singh *et al.* (1977*a*) (S). The data for CCl_4 are from Krey *et al.* (1977): □ (10°–30° N), △ (30°–45° N), ▽ (45°–60° N), ○ (mean 10–12 km value), K (mean 0–10 km value); and Inn *et al.* (1977*b*) ⊢.

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mesospheric O_3. Day to night differences are adequately reproduced. Watanabe & Tohmatsu (1976) suggest that O_3 may exhibit significant seasonal variations, with winter concentrations at 65 km larger than summer values by a factor of 2.8. It is difficult to account for variations of this magnitude unless we invoke correspondingly large changes in the concentration of mesospheric H_2O. A model with seasonally invariant H_2O would predict a modest winter to summer variation in O_3, about 10%, in the opposite sense to that reported by Watanabe & Tohmatsu (1976).

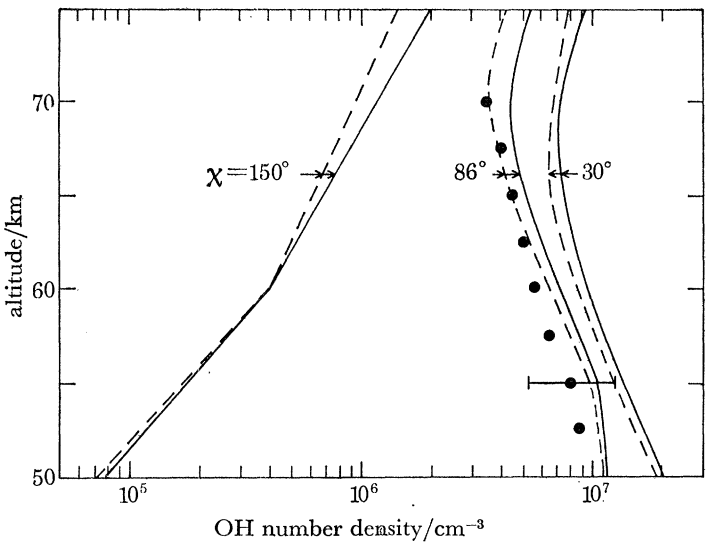

FIGURE 10. Altitude profiles for OH above 50 km. The solid lines were calculated with the standard model, at 30° N latitude and 0° solar declination for solar zenith angles (χ) corresponding to noon, late afternoon and midnight. The dashed lines were calculated with temperature independent rate constants for reactions (2)–(4). The data are from Anderson (1975), taken at 32° N, with $\chi = 86°$. Representative error bars are shown.

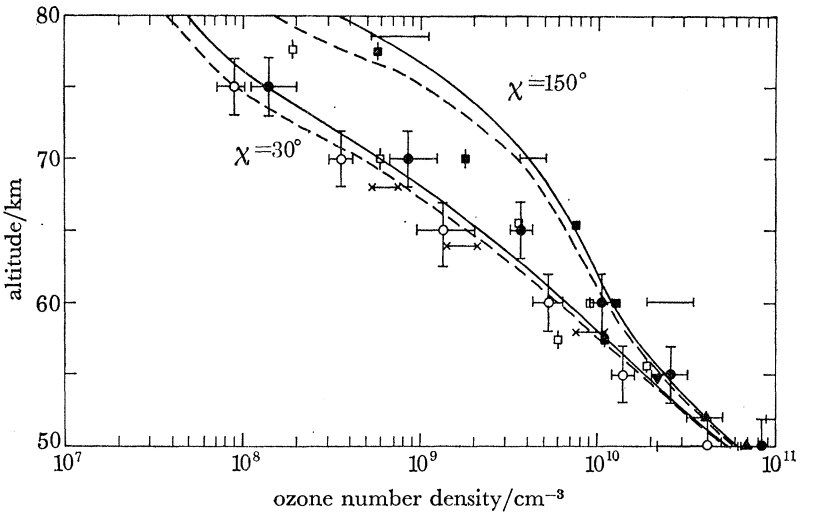

FIGURE 11. Altitude profiles for ozone above 50 km. The solid and dashed lines are for conditions as described in figure 10. The data are as follows: ▼ (sunset, June, 32° N), Johnson, Purcell & Tousey's 1949 distribution, as corrected by Krueger (1969); ▲ (day, September, 38° N), Hilsenrath *et al.* (1969); □ (day), ■ (night, March, 38° N), Hilsenrath (1971); ×—× (sunset, June, 28° S), Miller & Ryder (1973); ⊔ (day), ⊓ (night, February, 31° N), Penfield *et al.* (1976); ○ (summer mean), ● (winter mean, 31° N), Watanabe & Tohmatsu 1976; ⊢ (night, June–July, 6°–12° S), Riegler *et al.* (1977).

Water vapour is known to exhibit significant, factor of 3, variations in the lower stratosphere (Mastenbrook 1971). The measurements of OH (Anderson 1976), Cl and ClO (Anderson *et al.* 1977) between 25 and 40 km may reflect an upward extension of this variability. Model results are compared with stratospheric OH, O, Cl, and ClO measurements in figures 14 and 15, illustrating the dependence of results on the choice of profile for H_2O.

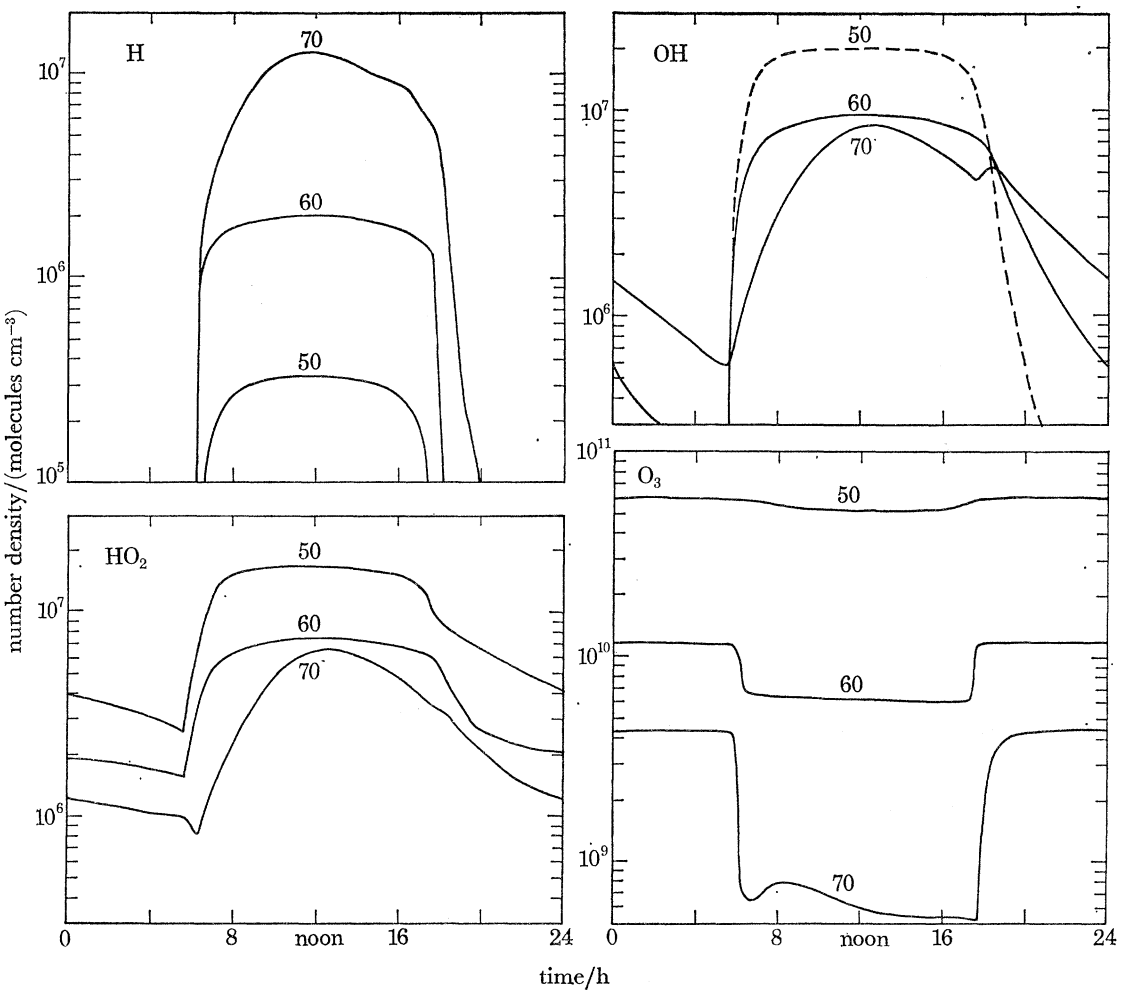

FIGURE 12. The diurnal variations of H, OH, HO_2 and O_3 at 50, 60 and 70 km are shown for 30° N latitude and 0° solar declination. The standard water profile given in figure 13 was used in these calculations.

It would appear that the high values for the concentrations of Cl and ClO cannot be attributed solely to variations in the water vapour mixing ratio, unless the mixing ratios for H_2O are much larger than 10^{-5}. On the other hand the low values for Cl and ClO are consistent with H_2O mixing ratios in the range reported by Mastenbrook (1971). Part of the ClO variability might be attributed to temporal changes in the concentration of total chlorine. We may note in this context that several precursors for stratospheric chlorine, in particular $CFCl_3$, CF_2Cl_2, CCl_4 and CH_3CCl_3, are distributed quite inhomogeneously in the lower atmosphere with abundances in the northern hemisphere typically twice those for the southern hemisphere (Lovelock, Maggs & Wade 1973; Lovelock 1977; Rasmussen, Pierotti, Krasnec & Halter 1976; Inn, Tyson & Arvesen 1977*b*). Changes in the ClO abundance may also result from variations

in the concentration of upper atmospheric CH_4, which could arise due to fluctuations in H_2O. A high concentration of H_2O favours a large source for OH, with a consequent reduction in CH_4. Both influences act to enhance the abundance of Cl and ClO relative to HCl, as illustrated in figures 15 and 17. A more comprehensive test of the chemical model would require simultaneous measurements of OH, Cl, ClO, HO_2, H_2O, O_3, HCl, $ClNO_3$, and CH_4.

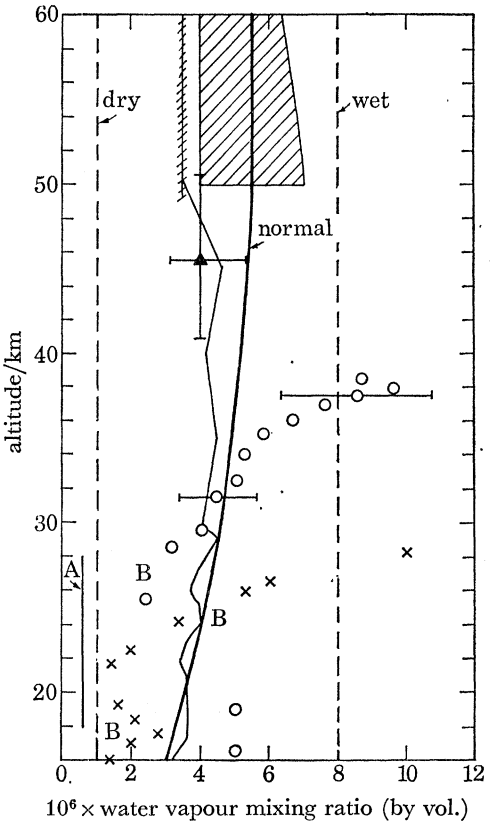

FIGURE 13. Altitude profiles for water. The heavy line shows the profile adopted in the standard model; the wet and dry models (dashed lines) used a water mixing ratio of 8 and 1 parts in 10^6 (by vol.) respectively, as indicated. The profiles were assumed to be constant above 60 km. Also shown is the mean mid-latitude northern hemispheric profile from the recent review by Harries (1976) (light line) and the data of Chaloner *et al.* (1975) (○); Burkert *et al.* (1974) (×); Ehhalt *et al.* (1975*a*) (▲); Murcray *et al.* (1974) (A, from Fairbanks, Alaska; B from Holloman, N. M.); Waters *et al.* (1977) (shaded region); and Rogers *et al.* (1977) (////).

Measurements of HCl provide important information with regard to the rôle of $ClNO_3$ in stratospheric chemistry and may be used to place constraints on the total abundance of stratospheric chlorine. Figure 16 shows a comparison of computed concentrations for acidic chlorine, taken as $HCl + ClNO_3 + HOCl$, with measurements by Lazrus *et al.* (1976). Figure 17 shows model results for the seasonal dependence of HCl concentrations, illustrating the sensitivity of the model to choice of H_2O profile. The model results show little seasonal variation for $ClNO_3$, shown in figure 18. The structure in the HCl profile below 30 km reflects the importance of $ClNO_3$, with largest concentrations of this gas predicted to occur near 20 km. A direct comparison with observation is difficult, given the apparent scatter of the data, and given the possibility of significant temporal variations in H_2O as discussed above. The observations are consistent with the postulate the $ClNO_3$ should play a significant rôle in stratospheric chemistry

(Rowland *et al.* 1976*a*). Major uncertainties remain however and clearly point to the need for a careful observational search for $ClNO_3$. Results presented here are in accord with a recent observational upper limit to the concentration of $ClNO_3$ set by Murcray *et al.* (1977).

Figures 19 and 20 show a comparison as a function of latitude of predicted and observed column densities for stratospheric NO_2 and HNO_3. The height integrated concentrations of these compounds are relatively insensitive to the more uncertain aspects of the model. The

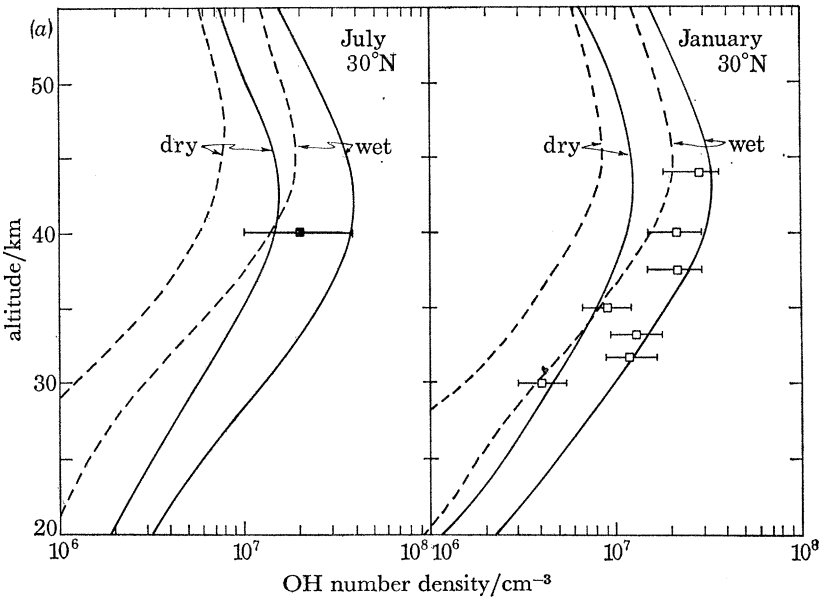

FIGURE 14*a*. Altitude profiles are shown for OH at 30° N in summer and winter, for wet (H_2O = 1 part in 10^6) and dry (H_2O = 8 parts in 10^6) conditions. The solid curves show values at noon, and the dashed curves are for late afternoon (χ = 80°). The data points are from Anderson (1976) for χ = 80°.

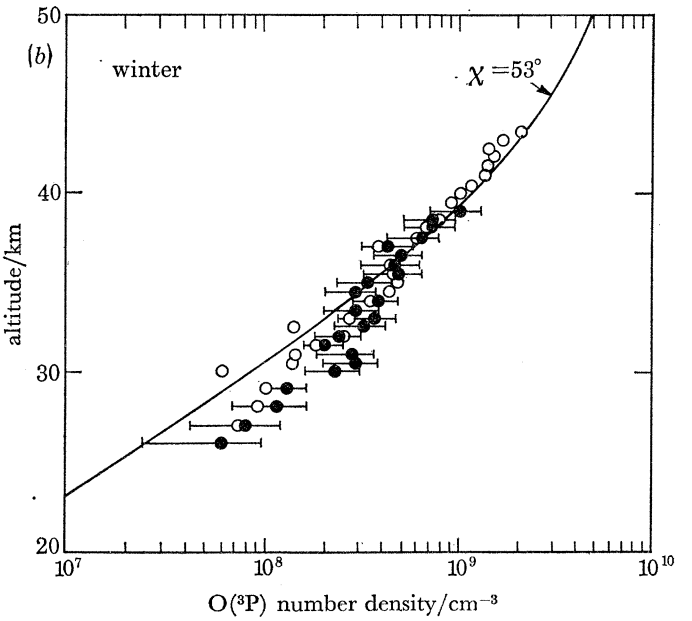

FIGURE 14*b*. The altitude profile of O is shown for 30° N latitude in winter with a solar zenith angle of 53°. The standard water profile from figure 13 is used. The data are from Anderson (1975): ●, November, χ = 56°; ○, February, χ = 51°.

good agreement of theory with observation exhibited by the figures indicates that the total abundance of odd nitrogen is well predicted by the model, and that the model satisfactorily accounts for the apportionment of NO_x among its more abundant constituents. It lends confidence to the validity of procedures adopted to treat lateral transport (see also Wofsy 1978).

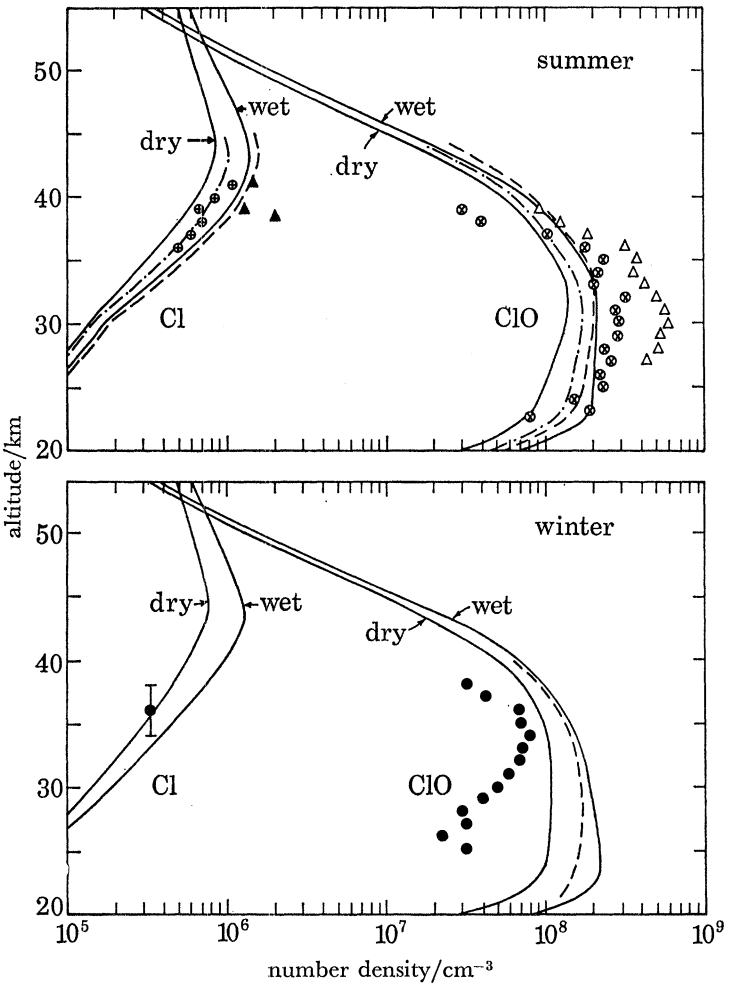

FIGURE 15. Altitude profiles are shown for Cl and ClO at 30° N in summer and winter for wet and dry conditions (solid lines) at noon. The broken lines were calculated by using the standard water profile but employed high (–·–·) and low (– – –) values for methane consistent with the range of the data shown in figure 8. The data points are from Anderson *et al.* (1977) and were taken at 32° N in December (●, $\chi = 50°$), July (⊗, ⊕, $\chi = 16°$), and October (△, ▲, $\chi = 35°$).

Noxon *et al.* (1977) report very low column abundances for stratospheric NO_2 poleward of 50° N, during winter. The calculations exhibit a significantly smaller decrease of NO_2 in this region. This discrepancy could be resolved in large part by a slight temperature dependence in the photolysis rate of HNO_3, which is the dominant NO_x species at these latitudes.

Figure 21 shows a comparison of observed and calculated profiles for O_3 below 50 km. The gas is treated in this height range as a long lived chemical species by using the one-dimensional diffusion model, equation (26). We did not use mixing surfaces to simulate horizontal transport since chemical lifetimes are too short to permit use of this model above 22 km.

Ozone is formed in the troposphere by

$$NO + HO_2 \rightarrow NO_2 + OH, \quad (20)$$

followed by

$$CO + OH \rightarrow CO_2 + H, \quad (25)$$

$$H + O_2 + M \rightarrow HO_2 + M, \quad (32)$$

$$NO_2 + h\nu \rightarrow NO + O, \quad (33)$$

and

$$O + O_2 + M \rightarrow O_3 + M, \quad (34)$$

equivalent to

$$h\nu + (NO) + CO + 2O_2 \rightarrow (NO) + CO_2 + O_3. \quad (35)$$

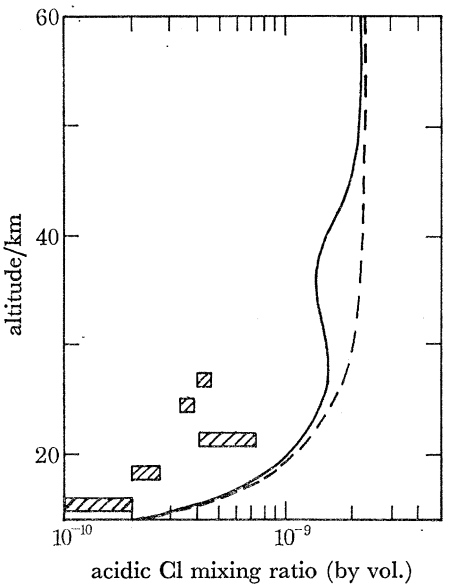

FIGURE 16. Altitude profiles are shown for acidic chlorine taken as $HCl + HOCl + ClNO_3$ (——) and total chlorine (– – –) for 30° N latitude and 0° solar declination, at noon, and compared with the data of Lazrus *et al.* (1976).

Anthropogenic CO leads therefore to some net increase in the abundance of tropospheric O_3. Ozone may be formed also as a by-product of CH_4 oxidation (Levy 1971; Chameides & Walker 1973), by

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2, \quad (36)$$

followed by (33) and (34). The rate for (36) is unknown, however, and we are unable therefore to offer any quantitative assessment of its importance.

The recent measurement of a fast rate for (20) establishes a central rôle for nitrogen oxides in the chemistry of tropospheric O_3. Indeed the ozone source strength for the lower troposphere is large enough to cause difficulties in our attempt to define a balanced chemical system. The time constant for O_3 below 5 km is about 10 days. The production due to (35) and (36) could be balanced by heterogeneous processes either in the atmosphere or at the surface. A quantitative discussion of this possibility is difficult however. Photolysis,

$$h\nu + O_3 \rightarrow O(^1D) + O_2 \quad (37)$$

followed by

$$O(^1D) + H_2O \rightarrow OH + OH, \quad (38)$$

and reaction with HO_2, equation (21), represent the most important gas phase sinks for O_3 in the troposphere.

Figure 21 shows profiles in which we omit the possibility of heterogeneous loss processes for O_3 in the atmosphere, using Simonaitis & Heicklen's (1973) value for the rate constant of reaction (21). The agreement of model with observation is satisfactory at heights above the

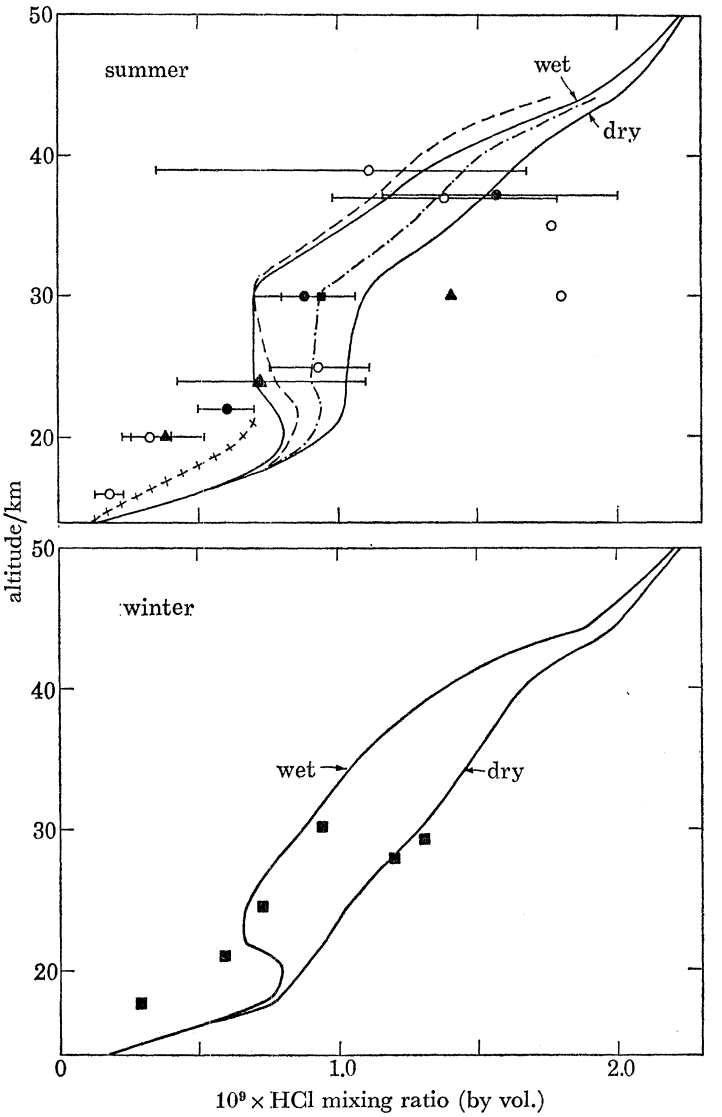

FIGURE 17. Altitude profiles are shown for HCl at 30° N, at noon, in summer and winter for wet and dry conditions (solid lines). The broken lines were calculated with the standard water profile and high (–·–·–) and low (– – –) values for methane, consistent with the range of the data shown in figure 8. The data are from Ackerman *et al.* (1976) (▲, October); Farmer *et al.* (1976) (+ + +, average profile); Williams *et al.* (1976) (■, December); Eyre & Roscoe (1977) (○, March); and Raper *et al.* (1977) (●, May and September) Representative error bars are included.

O_3 maximum. A comparison with observational data at 30° N (Hering 1975; Watanabe & Tohmatsu 1976) suggests that important discrepancies arise below 26 km.

The model is characterized by a peak broader in altitude than that exhibited by the data. The vertical column density of O_3 in the model has a value 10.2×10^{18} cm^{-2}, which may be compared with the observed value of 7.5×10^{18} cm^{-2}. The discrepancy might reflect

inadequacies of the chemical model. On the other hand, it should be noted that the difficulty arises in a region of the atmosphere where transport should play an important rôle for O_3.

As noted earlier, use of one-dimensional vertical diffusion models is somewhat suspect for O_3. Most of the global abundance of atmospheric O_3 is supplied by transport from a source region confined to a relatively narrow altitude region at low latitudes. A major fraction of the vertical column of O_3 at higher latitudes must lie in the dynamical régime, as may be inferred

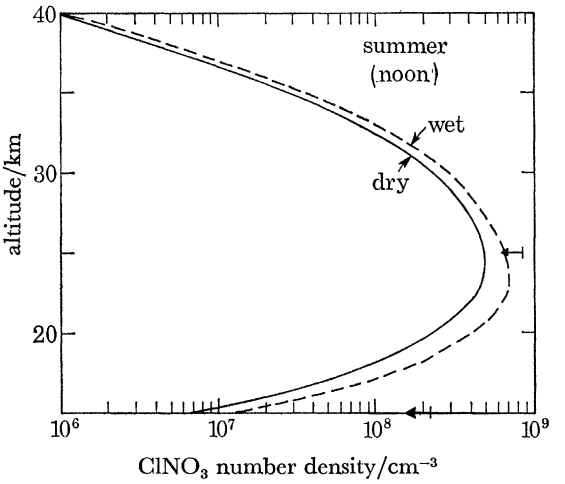

FIGURE 18. Altitude profiles are shown for $ClNO_3$ at 30° N at noon in summer for wet and dry conditions. The arrow symbols show the upper limit of Murcray *et al.* (1977).

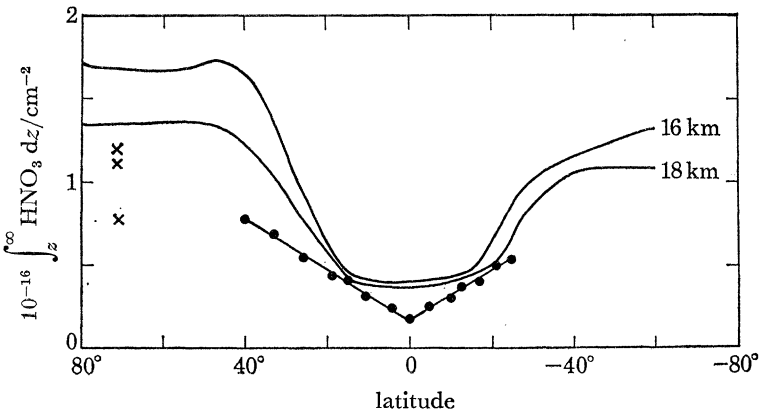

FIGURE 19. The column abundance of HNO_3 is shown as a function of latitude at 20° solar declination. The column integral is started at altitudes of 16 and 18 km. The data are from Murcray *et al.* (1975) and were taken from an aircraft flying at 18 km in January (●), and from balloon flights in September (×).

from the latitudinal distributions of total O_3 shown in figure 22. The calculated distribution results from a model which allows only for vertical transport of ozone. Evidently, the observed latitudinal variations require transport of ozone from the tropics into the higher latitudes.

In light of this discussion, it is perhaps not surprising that one-dimensional models should fail to reproduce the global mean abundance of O_3. The disagreement however emphasizes the difficulty associated with use of one-dimensional models for the assessment of human influence on O_3. One might hope that one-dimensional models should give a reasonable estimate for the magnitude of any particular perturbation to O_3, even though the model might fail to reproduce

details of the vertical distribution. As an alternate approach one might follow the procedures described by McElroy *et al.* (1974) and seek to define a suitable scaling factor with which to model the influence of perturbations in the dynamical zone. Neither procedure is totally satisfactory. A definitive assessment requires a fully integrated chemical–dynamical model for the lower atmosphere.

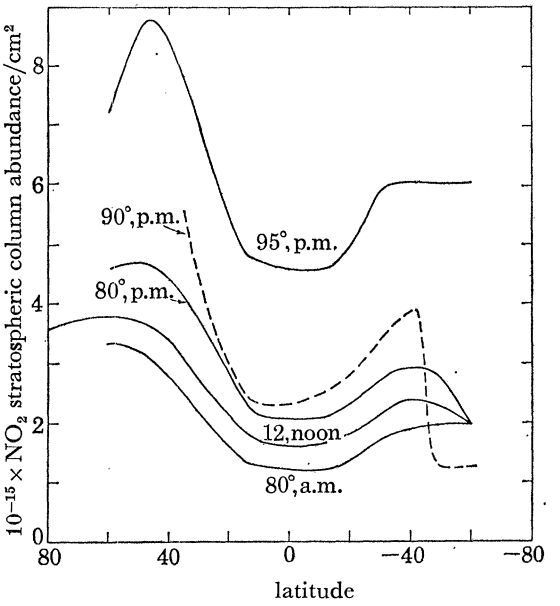

FIGURE 20. The column abundance of NO_2 is shown as a function of latitude at 20° solar declination for several solar zenith angles. The dashed line shows the twilight data of Noxon *et al.* (1977).

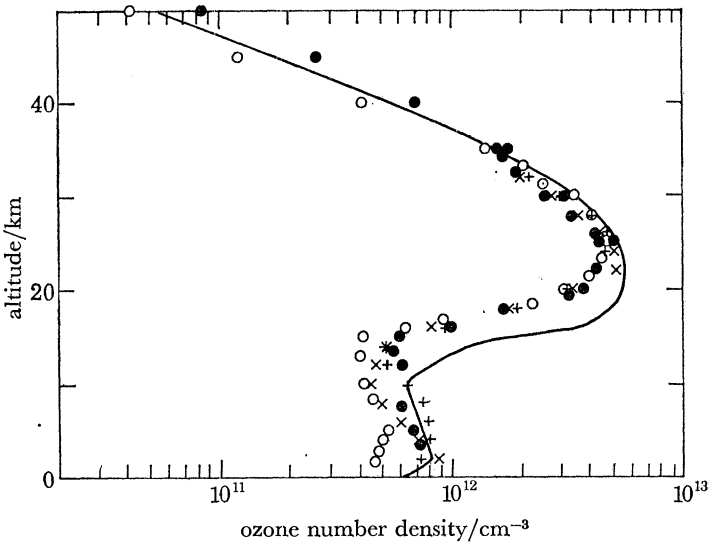

FIGURE 21. The altitude profile for ozone calculated with the standard one-dimensional diffusion model described in the text is shown. The data at 30° N are from Watanabe & Tohmatsu (1976) (○, summer mean, ● winter mean); and Hering (1975) (× summer mean, + winter mean).

4. Perturbations

Our interest here is directed towards human activities which might be expected to lead to significant changes in the global atmospheric environment. We shall emphasize perturbations which might affect the global distribution of atmospheric O_3.

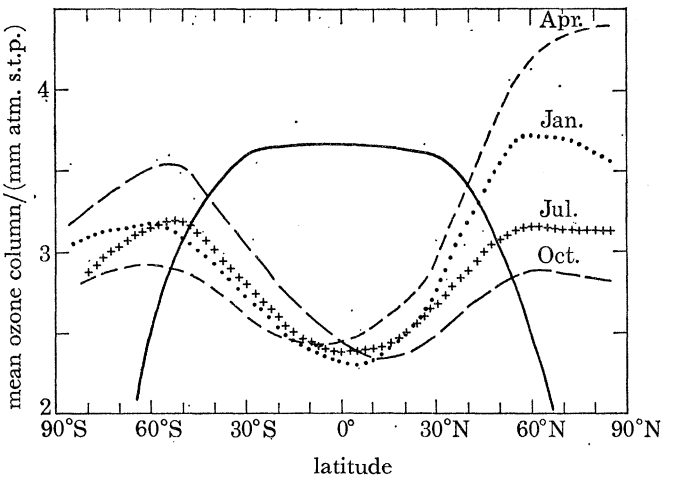

Figure 22. The column density of ozone is shown as a function of latitude. The solid line is the calculated ozone column abundance. The computation employs latitudinal transport of long lived species and vertical diffusion of ozone but ignores the effects of latitudinal transport of ozone. The broken lines show the observed mean ozone column as a function of season (Gebhart *et al.* 1970).

These perturbations fall into two general classes: those which are considered essential to modern society, and those which may be regarded as largely discretionary. Among the essential perturbations, we shall focus mainly on combustion and agriculture. More discretionary human influences include the use of certain halocarbons as working fluids in refrigeration systems, as propellants in aerosol cans, and as solvents and cleaning fluids.

Combustion of fossil fuels provides important direct sources of atmospheric CO_2, CO, H_2, NO_x and N_2O. Biological activity plays a major rôle in regulating the concentrations of these gases in the natural atmospheric environment.

Respiration and decay release CO_2 at rates which can replace the present concentrations of the gas in the atmosphere on a time scale of less than 20 years (see, for example, McElroy 1976; Bolin 1977). Combustion provides a source strength for CO_2 equal to approximately 10% of that from respiration and decay (Keeling 1973; Delwiche & Likens 1977).

Methane, formed as a by-product of microbial fermentation, is the primary natural precursor for atmospheric CO and H_2. Carbon monoxide is produced (see figure 4) by

$$h\nu + H_2CO \rightarrow H_2 + CO \tag{39}$$

and by

$$HCO + O_2 \rightarrow CO + HO_2. \tag{40}$$

Reaction (39) is the primary natural source for H_2, giving a global source strength of magnitude 3.5×10^7 t per year. The source strength for CO has magnitude 1.7×10^{11} molecules $cm^{-2}\ s^{-1}$, 5.5×10^8 t C per year. These inputs may be compared to current estimates for combustion related sources of H_2 and CO of magnitude 2×10^7 t per year and 3×10^8 t C per year respectively (Jaffe 1973; Schmidt 1974; Seiler 1974; Seiler & Schmidt 1974; Penner *et al.* 1977). The

methane-related source strengths for CO and H_2 were estimated by using the pressure dependent rate expression for reaction (25). They are lower therefore than earlier estimates based on a pressure independent value for this coefficient. The revised estimate for the source of CO from CH_4 oxidation, and associated implications for tropospheric OH, introduce some difficulty in attempts to balance the budget for northern hemisphere CO. Either the rate constant for (25) must be less than values assumed here, or there must be sources for CO in the northern hemisphere larger than values usually associated with combustion, by about a factor of 3. Oxidation of terpenes or other hydrocarbon emissions from the terrestrial biosphere could provide an important natural source of CO (cf. Wofsy, McConnell & McElroy 1972). For example, the hemiterpene, isoprene, is a major component of volatile emissions from many species of land plants (Sanadze 1963; Rasmussen 1970). Isoprene is likely to react rapidly with OH radicals (cf. Atkinson, Perry & Pitts 1977), and the ultimate yield of CO could be between 40% and 60%, based on olefin oxidation pathways which we might expect to apply in the atmosphere (Demerjian, Kerr & Calvert 1974; Niki, Maker, Savage & Breitenbach 1978). If global emission rates for isoprene were comparable to those found by Sanadze (1963) and Rasmussen & Jones (1973) under laboratory conditions, photooxidation of isoprene could provide a source for CO comparable to or larger than anthropogenic emissions.

Combustion provides a direct source of fixed nitrogen, NO_x, of magnitude 2.3×10^7 t N per year at the present time. Fixation of nitrogen for fertilizer contributes an additional source of magnitude 4.2×10^7 t N per year. These anthropogenic inputs may be compared to estimates for biological fixation which range from about $1–2 \times 10^8$ t N per year (Burns & Hardy 1975; Soderlund & Svensson 1976; McElroy 1976; Sweeney, Lui & Kaplan 1977; Delwiche & Likens 1977). Both the combustion and fertilizer sources of fixed nitrogen are growing at a steady rate, as illustrated in figure 23, and it is difficult to avoid the conclusion that anthropogenic effects must play a dominant rôle in global nitrogen fixation in the near future.

Our estimates for the combustion source of fixed nitrogen before 1970 use data for the United States published by the U.S. Environmental Protection Agency (Cavender, Kircher & Hoffman 1973). These data were scaled by a factor of approximately 2.7 in order to obtain an estimate of global emissions. The scale factor reflects consumption patterns for various fossil fuels as given by Hamilton (1977). We assumed a growth rate for combustion of fossil fuels equal to 3.6% per year between 1970 and 2000, consistent with projections by the Organization for Economic Co-operation and Development (1976) (see also The National Energy Plan (1977)). The growth rate was taken equal to 2.4% per year between 2000 and 2050, and was lowered to 1% per year for the period 2050 to 2100 (see model C in figure 23). A second model for combustion nitrogen, model D in figure 23, anticipates stringent regulation of NO_x and CO emissions.

We shall explore two models for future use of nitrogenous fertilizers. The models are similar to those used by McElroy *et al.* (1977). Both models assume a relatively stable world population after the turn of the century. Model A allows for grain production equivalent to 4×10^2 kg per person per year for a population assumed to grow to 6.5×10^9 by the year 2000. Model B assumes grain production per person close to current values, 2.5×10^2 kg per person per year, with a similar demographic projection.

Combustion is known to provide a direct source for N_2O as well as NO_x (Pierotti & Rasmussen 1976; Weiss & Craig 1976). Weiss & Craig (1976) report measurements of N_2O and CO_2 emanating from the power plants in California. They find ratios N_2O to CO_2 of 2.05×10^{-4}

for coal and fuel oil plants respectively. Their data, combined with Keeling's (1973) discussion of CO_2 emissions, were used to construct the direct release model for N_2O given in figure 23 (model E). Figure 24 shows the release patterns for CO, CO_2 and H_2. We used Seiler's (1974) estimate for CO release and CO to H_2 emission ratios given by Schmidt (1974).

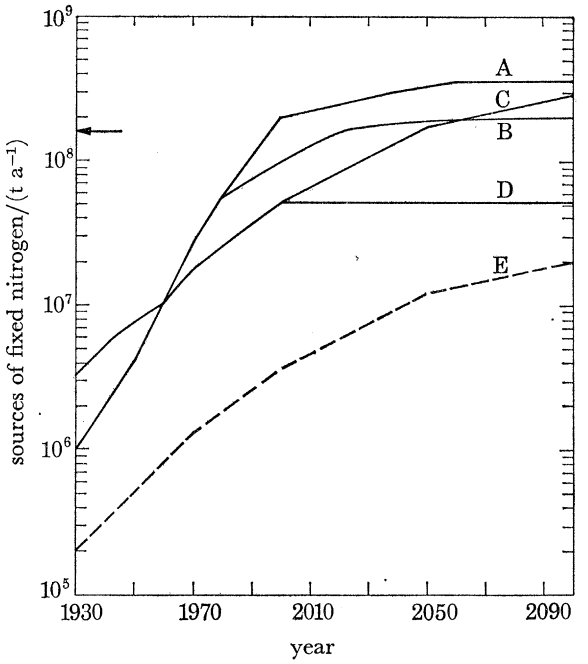

FIGURE 23.

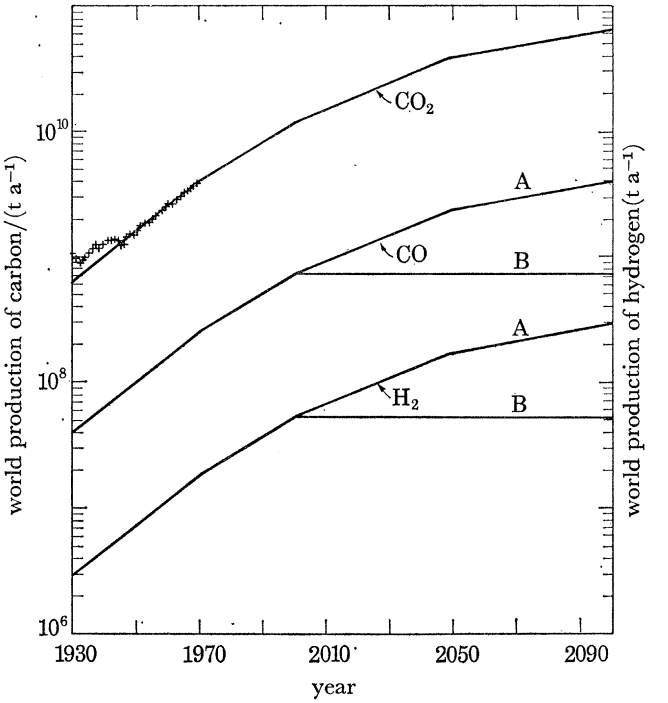

FIGURE 24.

FIGURE 23. Projections for anthropogenic nitrogen fixation. A and B show the nitrogen fixed in the manufacture of fertilizer, C and D show NO_x from combustion of fossil fuels, and E shows the direct production of N_2O in combustion. The arrow indicates the biological fixation rate. The models are discussed further in the text.

FIGURE 24. Projections for CO_2, CO and H_2 emissions from fossil fuel use. Model A assumes a growth rate of 3.6% per year, 1970–2000, reduced to 2.4% per year, 2000–2050, and 1% per year, 2050–2100. Model B assumes constant release of CO and H_2 after 2000, anticipating regulation of emissions. The historical data for CO_2 are from Keeling (1973).

Catalytic converters on automobiles (Pierotti & Rasmussen 1976; Weiss & Craig 1976) are known to provide additional direct sources of N_2O. The automotive source is currently small, much less than 1×10^6 t N per year. We chose to omit this source in light of uncertainties in future development and use of catalytic converters.

The anthropogenic sources of fixed nitrogen shown in figure 23 undergo a complex series of transformations resulting ultimately in recombination of fixed N, with release of both N_2O and N_2. On sufficiently long time scales release of nitrogen as N_2O and N_2 should balance the net global source of fixed N.

An estimate for the anthropogenically related source of N_2O in any given year requires a relatively complete understanding of the global nitrogen cycle. Discussions of this cycle emphasizing Man's impact are given by McElroy (1976) and McElroy *et al.* (1977). The N_2O source strength may be calculated by using the concept of a well defined delay pattern for recombination of fixed N, along with an estimate for the fraction of recombination events resulting in emission of N_2O rather than N_2. The release patterns adopted here are illustrated in figure 25.

The fraction of recombination events leading to release of N_2O in the present system may be estimated if we assume a balance between natural fixation and recombination, and use estimates for the lifetime of atmospheric N_2O to evaluate the current source strength of the gas. We shall adopt for this purpose a natural fixation rate of 1.6×10^8 t N per year, consistent with the range of values quoted above, and we shall assume the same yield of N_2O from recombination of anthropogenic and natural nitrogen.

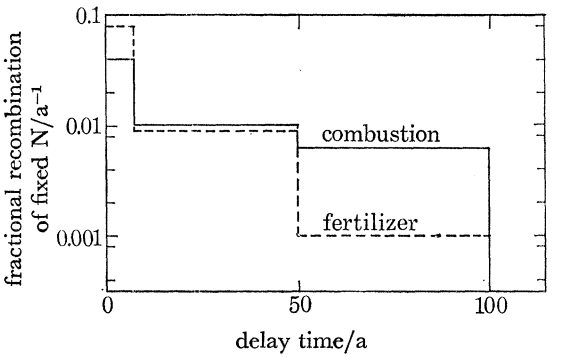

FIGURE 25. The fraction of anthropogenic nitrogen recombined annually is shown as a function of the time elapsed since release of the nitrogen to the environment. The average delay time for recombination is assumed to be considerably larger for combustion nitrogen than for fertilizer.

The uncertainty in the lifetime of atmospheric N_2O is more serious than the ambiguity associated with the fixation rate, with values in the literature ranging from 1.8 a (Hahn & Junge 1977) to an upper limit of about 140 a imposed by stratospheric photolysis. Lifetimes less than about 10 a would appear to require sources for N_2O in addition to denitrification. A source due to nitrification would not obviate the difficulty since the sum of the sources from nitrification and denitrification must be balanced by fixation. Lightening discharges offer a further possibility (Griffing 1977; Zipf & Dubin 1976), though quantitative estimates (Griffing 1977) for the associated source strength suggest that it should be small, less than 2×10^6 t N per year. We shall investigate models with two values for the N_2O lifetime, a low value of 20 a, only slightly larger than the range 4–12 a recommended by Hahn & Junge (1977), and a high value of 140 a, which would apply if stratospheric photolysis were the major sink. Corresponding release rates for N_2O are given in figure 26.

With our choice of fixation rate, the yield of N_2O relative to N_2 in recombination of fixed N is either 6% or 40% for the long and short lifetimes respectively. A yield of 6% agrees with soil data quoted by the Council for Agricultural Science and Technology (1976). Moreover, the long lifetime and low yield would be consistent with the lack of variability for atmospheric N_2O as reported by Weiss, Dowd & Craig (1976) from measurements over the Pacific Ocean, and Goldan *et al.* (1978) from continental measurements. It disagrees however with relatively large variations of the total N_2O column density as measured spectroscopically by Goody (1969). It should be noted that other investigators (Hahn & Junge 1977; Singh, Salas, Shiegeshi & Crawford 1977*b*) using chromatographic techniques find greater variability than that seen by Weiss *et al.* (1976) and Goldan *et al.* (1978). The apparent discrepancies might be attributed to a predominant rôle for continental influences on the budget of atmospheric N_2O. Data from this laboratory (Kaplan *et al.* 1978) indicate that fresh water systems can provide both sources and sinks for N_2O. It would seem possible that aqueous systems could play an important rôle

and that biological uptake might represent a major sink (see, for example, Brice, Eggleton & Penkett 1977), though heterogeneous chemistry could also contribute (Ausloos, Rebbert & Glasgow 1977). The issue is clearly unresolved. The weight of the evidence, in our view, appears to point towards a relatively long lifetime for N_2O, in that it is difficult to account for source strengths or sinks much larger than about 5×10^7 t N per year (McElroy *et al.* 1976).

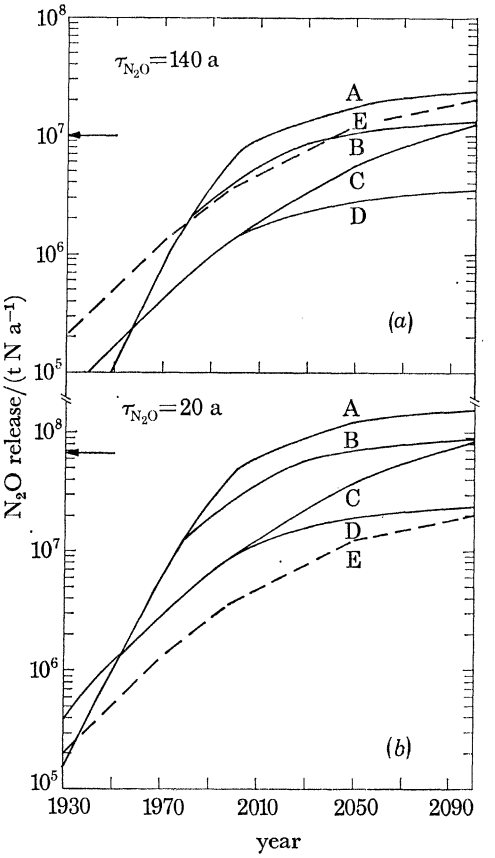

FIGURE 26. Projections for release rates of N_2O, assuming the sources of fixed nitrogen given in figure 23, the delay times for denitrification given in figure 25, a natural fixation rate of 1.6×10^8 t N/a and N_2O lifetimes as shown. The labels are described in figure 23, and the arrows indicate the source of N_2O from natural processes.

Figure 27 shows historical data for industrial sources of several halocarbons which are ultimately released to the atmosphere. We focus here on chlorinated species. The possible impact of brominated compounds is discussed elsewhere (Wofsy *et al.* 1975*b*). The compounds $CFCl_3$ and CF_2Cl_2 are released to the atmosphere on an average of less than a year following manufacture (McCarthy, Bower & Jesson 1977). The data in figure 27 are from McCarthy *et al.* (1977) for $CFCl_3$ and CF_2Cl_2, from Galbali (1976) for CCl_4, and from Neely & Plonka (1978) for CH_3CCl_3. The figure also summarizes models devised to explore possible future release patterns for $CFCl_3$, CF_2Cl_2, CCl_4 and CH_3CCl_3. We consider two models for $CFCl_3$, CF_2Cl_2 and CH_3CCl_3. In model A, release rates are assumed to remain constant at values applicable in 1974. Model B envisages regulation of these compounds and the source is abbreviated accordingly in the period subsequent to 1980 (see figure 27). Trichloroethane is used as an intermediate in the manufacture of vinylidine chloride and as a cleaning solvent, with the latter

accounting for most of the release to the atmosphere. Release rates have grown rapidly in recent years as this compound is used to replace the chloroethylenes C_2Cl_4 and C_2HCl_3. The models in figure 27 envisage continued growth in the release of CH_3CCl_3 until 1980, followed by slow growth thereafter.

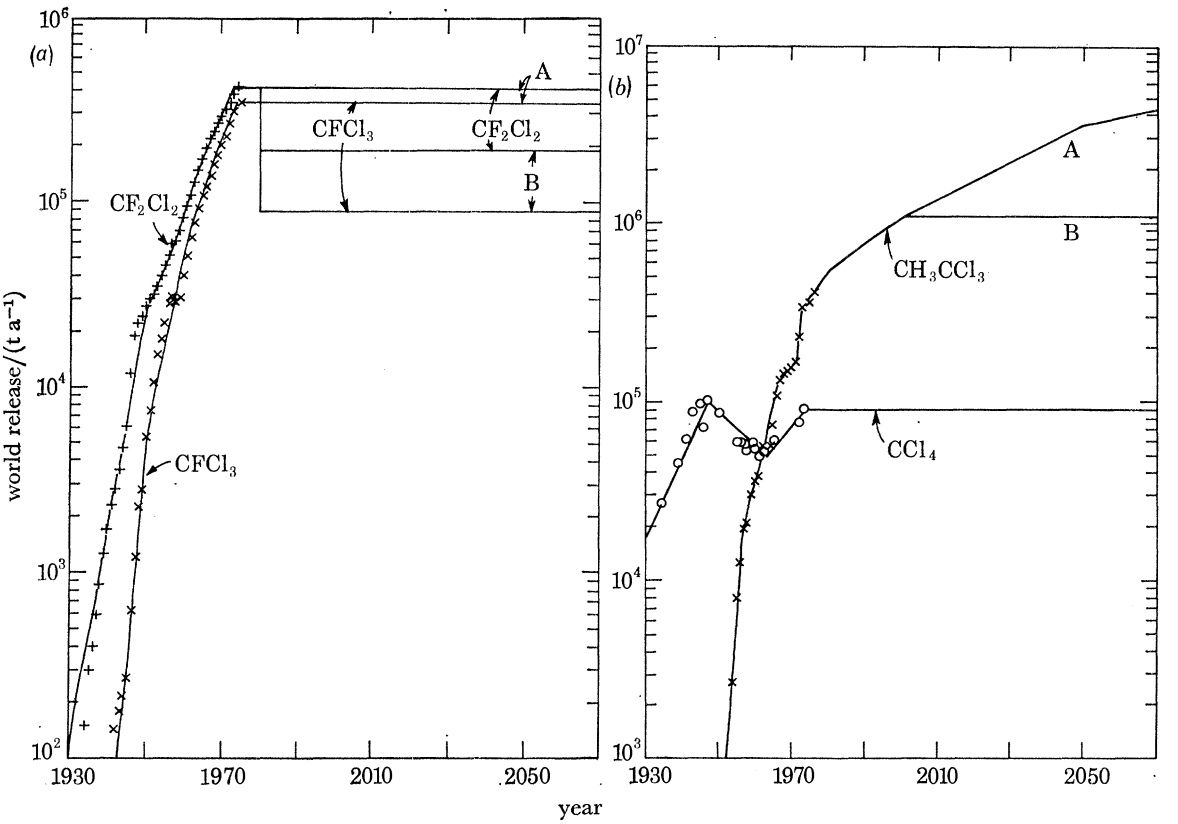

FIGURE 27. (*a*) Historical data and projections for release of $CFCl_3$ (×) and CF_2Cl_2 (+). The data are from McCarthy *et al.* (1977). Model A assumes continued release at 1974 rates, while model B assumes that the use of these compounds as aerosol propellants is discontinued in 1980. (*b*) Historical data and projections for release of CH_3CCl_3 (×) and CCl_4 (○). The data are from Neely & Plonka (1978) and Galbali (1975) respectively. For CH_3CCl_3, the growth patterns given for fossil fuel emissions in figure 24 are adopted; a constant release rate after 1974 is assumed for CCl_4.

5. RESULTS

We shall describe results from a number of models exploring consequences of combustion, anthropogenic changes to the nitrogen cycle and the chlorocarbon release patterns described above. The anthropogenic perturbations will be treated by using the standard chemical model summarized in table 1, with diurnal variations incorporated as described in § 3. We begin with a brief discussion of results obtained for steady state conditions, assuming a range of values for tropospheric N_2O and stratospheric Cl_x.

Figure 28 presents global average column densities of O_3 as functions of the N_2O mixing ratio, for several concentrations of stratospheric Cl_x, calculated by using the one-dimensional diffusion model. It shows the dependence of results on procedures used to treat insolation. The mixing ratios for N_2O and Cl_x in the present atmosphere are taken as 3×10^{-7} and 2.3×10^{-9},

respectively. The value for N_2O reflects the mean surface concentration of the gas. The value for Cl_x reflects conditions at an altitude of 40 km.

The model with diurnally averaged insolation (figure 28*b*) has somewhat less O_3 than the more complete model (figure 28*a*). Differences arise largely at altitudes below 30 km. They may be attributed in part to the larger source of odd oxygen in the standard model due to (20), in part to a reduction in the removal rates for odd oxygen due to

$$OH + O_3 \rightarrow HO_2 + O_2, \tag{41}$$

and

$$O + NO_2 \rightarrow NO + O_2. \tag{42}$$

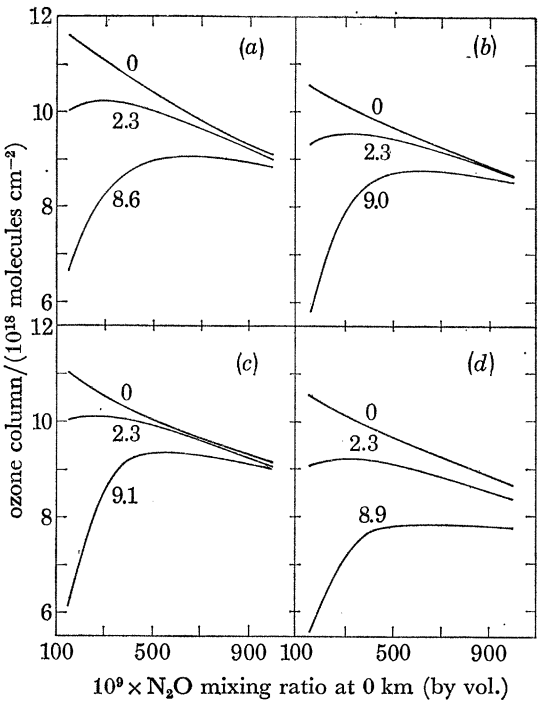

FIGURE 28. Global average column densities of ozone as a function of the tropospheric N_2O mixing ratio. The labels on the curves indicate the Cl_x mixing ratios (unit: parts/10^9 by vol.) at 40 km. The steady state calculations with a Cl_x mixing ratio of *ca.* 8.6/10^9 at 40 km result from $CFCl_3$ and CF_2Cl_2 fluxes of 341 000 t/a and 410 000 t/a respectively, with the boundary conditions for other constituents taken from table 2. A Cl_x mixing ratio of *ca.* 2.3/10^9 corresponds to $CFCl_3$ and CF_2Cl_2 fluxes which are smaller by a factor of 10, and approximate present-day conditions. The results shown in (*a*) are obtained with the full diurnal model described in the text, which includes backscatter of solar radiation from the lower atmosphere. The results in (*b*), (*c*) and (*d*) are calculated with diurnally averaged insolation. (*a*), (*b*) and (*d*) allow for Rayleigh scattering and planetary albedo, while (*c*) does not. (*a*), (*b*) and (*c*) use the standard chemical model given in table 1, while (*d*) assumes that photolysis of $ClNO_3$ follows reaction 10 rather than 9 (see text).

Concentrations of OH, HO_2, O and NO all tend to peak near noon, whereas the concentration of NO_2 attains its highest value soon after sunset. The diurnally averaged model underestimates therefore the sink for odd hydrogen, reaction (3), resulting in a small excess in the average concentrations computed for OH and HO_2. In a similar fashion the diurnally averaged model overestimates the product of O and NO_2 concentrations and underestimates the product of [NO] and [HO_2].

The differences in the variation of O_3 column densities with N_2O exhibited in figure 28*a–c*

reflect the manner in which the computational schemes treat $ClNO_3$, in addition to the reactions noted above. Reaction (42) plays a dominant rôle at high concentrations of N_2O, where chlorine chemistry is effectively suppressed owing to formation of $ClNO_3$. At lower concentrations of N_2O, errors in the treatment of $ClNO_3$ and (42) by the average model are compensatory.

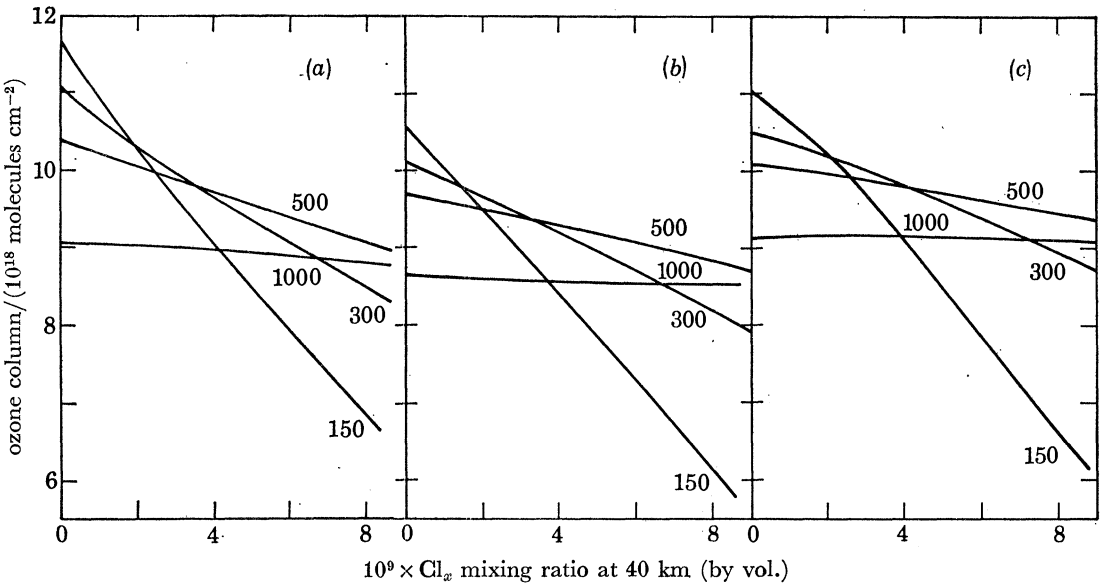

FIGURE 29. Global average column densities of ozone as a function of the Cl_x mixing ratio at 40 km. The labels on the curves refer to the N_2O mixing ratios (unit: parts/10^9 by vol.) at 0 km. The panels (*a*), (*b*), and (*c*) are described in figure 28.

Figure 29 shows calculated values for the integrated column density of O_3, with the standard chemical model, as a function of chlorine concentration at 40 km, for several values of the N_2O mixing ratio in the troposphere. As before, these results were obtained by using the one-dimensional diffusion model. The average insolation model tends to underestimate O_3 depletion for any given perturbation. The incremental effect of chlorine is small in both models for high concentrations of N_2O. This behaviour reflects the importance of $ClNO_3$ and the rôle of the reaction

$$ClO + NO \rightarrow Cl + NO_2, \qquad (43)$$

both of which serve to suppress the concentration of ClO. Differences between the average and diurnal models may be attributed largely to an overestimate of $ClNO_3$ by the average model, as discussed above.

Figures 30–32 show the changes in the concentration of O_3 as a function of altitude which result from perturbations of Cl_x and N_2O. Addition of NO_x leads to a larger decrease in O_3 below 24 km in the standard model as compared with the average insolation model (see figure 31). This difference may be attributed to overestimation of $ClNO_3$ by the average-insolation model.

Figure 32 shows the influence of enhanced concentrations of tropospheric CO and CH_4. Tropospheric ozone increases significantly in response to large enhancements of CO, as a

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consequence of process (35). Increases in ozone also occur in the stratosphere, owing to more efficient termination of the Cl catalytic cycle by the reaction

$$Cl + CH_4 \rightarrow HCl + CH_3. \quad (44)$$

This effect is more marked for large chlorine abundances.

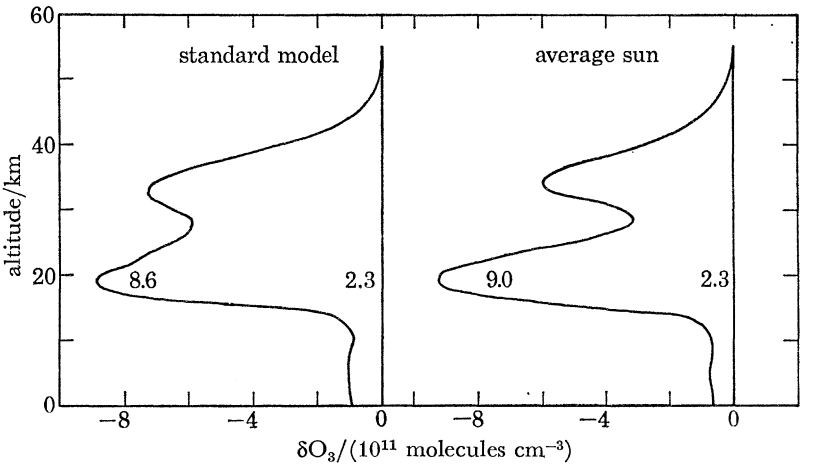

FIGURE 30. Change in the concentration of ozone as a function of altitude for added Cl_x at a fixed NO_x mixing ratio (N_2O at 0 km = $300/10^9$). The labels on the curves indicate the value of Cl_x at 40 km. The left hand panel was calculated with the full diurnal model and the right hand panel with diurnally averaged insolation. The reference profile ($\delta O_3 = 0$) is the calculated ozone for present-day conditions.

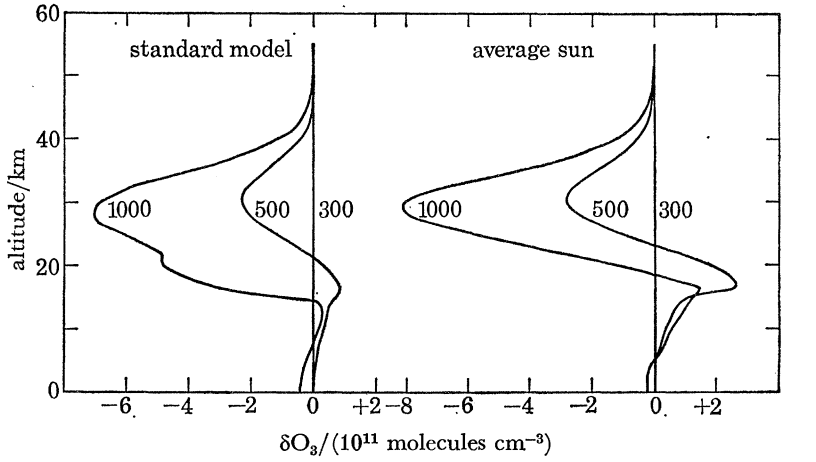

FIGURE 31. Change in the concentration of ozone as a function of altitude for added NO_x at a fixed Cl_x mixing ratio (Cl_x at 40 km = $2.3/10^9$). The labels on the curves show the mixing ratio of N_2O at 0 km. The left hand panel was calculated with the full diurnal model and the right hand panel with diurnally averaged insolation.

We should caution that the computed magnitude of the perturbation to O_3 may be quite sensitive to uncertainties which currently exist in the chemical model. The point is illustrated in figure 33, which may be compared with figures 28*b* and 29*b*. The models are identical in all respects except that: (i) The rate constant for (3) was set equal to 2×10^{-11} cm^3 s^{-1}; (ii) The rate constant for (21) was increased by a factor of 3; and (iii) The rate constant for reaction (41) was increased slightly, with the new rate expression taken as $7.5 \times 10^{-11} \exp(-737/T)$.

Both models provide satisfactory descriptions of the natural atmosphere. The rate adjustments are consistent with experimental uncertainty, yet the character of the response to the perturbations is quite different. We may note for example that results in figure 33 would suggest that the column density of O_3 might increase with increasing N_2O, at current levels of stratospheric Cl_x.

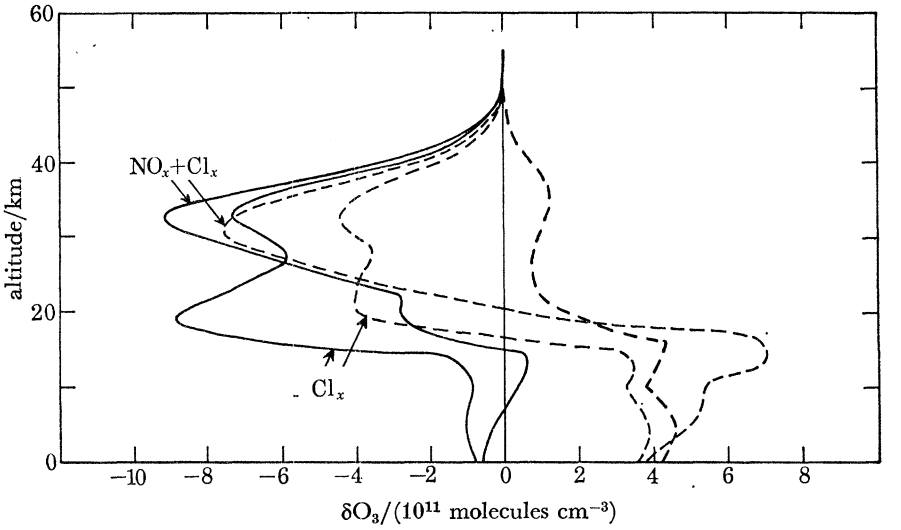

FIGURE 32. Change in ozone number density as a function of altitude for added NO_x, Cl_x, CO and CH_4. The solid curves represent calculations with present-day values for CH_4 and CO, whereas the dashed curves show the influence of increased tropospheric CO and CH_4, by factors of 7 and 2.5 respectively. The curves labelled Cl_x show the ozone changes which result from increasing Cl_x to $8.6/10^9$ at 40 km. The curves labelled NO_x and Cl_x show the additional effect of increasing tropospheric N_2O to $1000/10^9$. The reference profile assumes N_2O at 0 km = $300/10^9$, Cl_x at 40 km = $2.3/10^9$, approximating present-day conditions.

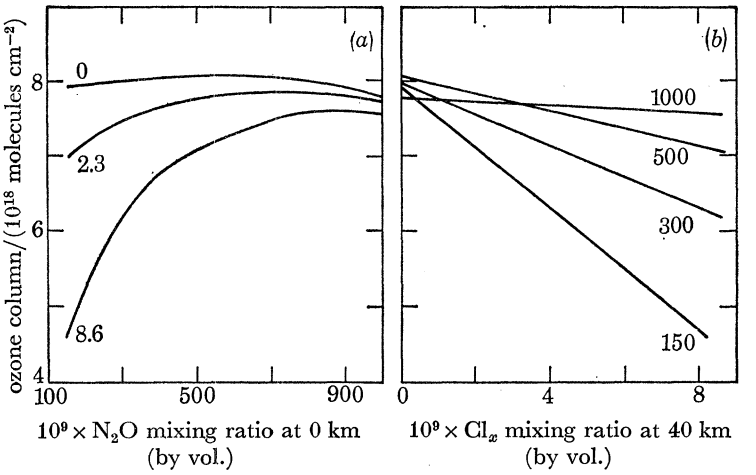

FIGURE 33. Global average ozone column densities as a function of N_2O and Cl_x. The curves are labelled as in figures 28 and 29. These results were calculated with diurnally averaged insolation as in figure 28*b*. The modified rates for reactions 3, 21 and 41 described in the text were used.

Inherent limitations of the one-dimensional diffusion model were discussed earlier. The model should provide a satisfactory description of O_3 above about 28 km, but cannot account for the distribution of O_3 at lower levels, where dynamical effects are predominant and inadequately described by one dimensional diffusion. One-dimensional diffusion models have

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been applied to the assessment of O_3 perturbations, despite these limitations, with the hope that the models should satisfactorily simulate fractional changes to total O_3. As an alternate approach one might assume that the transition from chemical to dynamical control of O_3 should occur over a narrow altitude range. Models might be used therefore to estimate the fractional change in the concentration of O_3 at the transition boundary and observed concentrations of O_3 at lower levels might be scaled appropriately to reflect the influence of perturbations. This procedure is useful to the extent that O_3 may be regarded as a passive tracer in the dynamical region, and to the extent that we can identify a well defined boundary separating zones of chemistry and dynamics (see McElroy *et al.* 1974).

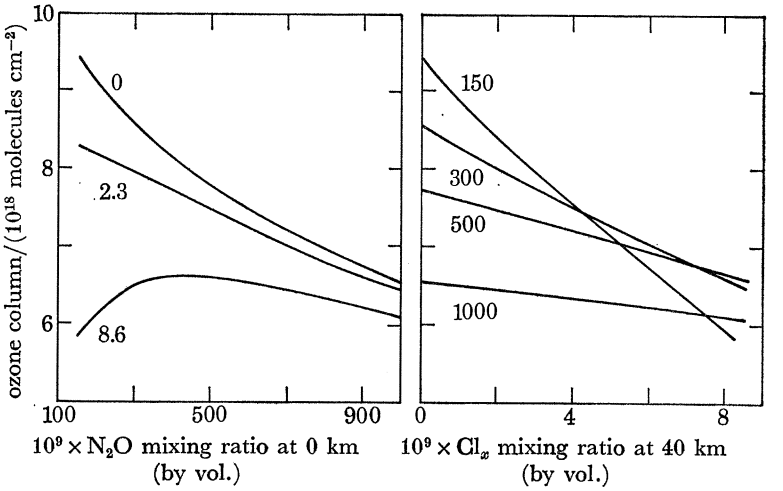

FIGURE 34. Global average ozone column densities as a function of N_2O and Cl_x. The curves are labelled as in figures 28 and 29. The full diurnal model was employed above 28 km, and the scaling procedure applied below that level (see text).

The relative influences of chemistry and dynamics may be evaluated by comparison of relevant time constants. The chemical time constant may be defined as the time required for photolytic production of a given concentration of O_3,

$$\tau = [O_3]/2J_{O_2}[O_2], \tag{45}$$

where J_{O_2} is the rate (unit: s^{-1}) for photodissociation of O_2. Chemical time constants for the unperturbed system are shown for several latitudes in figure 35. Consideration of the observational data for O_3 indicates that dynamical time constants cannot exceed about 3 months, and are most probably smaller than this by at least a factor of 3 (Oort & Rasmussen 1971). Implications for O_3 perturbations are summarized in figure 34.

A comparison of figure 34 with figures 28 and 29 suggests that differences between models are most pronounced in their response to low concentrations of NO_x. The variance between results obtained with the diffusion and scaling approaches provide some subjective estimate of the inherent uncertainty. The diffusion model allows for enhancement of the source for perturbed O_3 at low altitudes, a contribution omitted in the scaling model. On the other hand, the scaling model should account to some extent for the complex influence of global dynamics, and has the additional benefit that results should be reliable in the limit of small perturbations.

We turn our attention now to specific human influences on the atmosphere, emphasizing

possible effects on O_3. We shall make use of the one-dimensional diffusion model, while presenting sufficient information to allow the reader to gauge modifications which would arise with a scaling approach. We consider a variety of models as summarized in table 3. Models describing perturbations associated with combustion are labelled A. Models incorporating effects of chlorocarbons and N_2O from recombination of fixed N are designated by symbols B and C, respectively. Numerals are used to distinguish specific models employed to describe possible human influences in each of these broad categories.

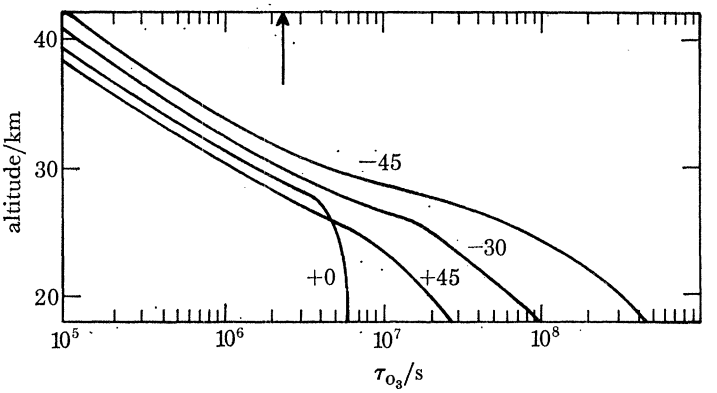

FIGURE 35. The chemical lifetime of ozone (equation (45)) is shown as a function of altitude, for 20° solar declination, and the latitudes marked on the curves. The arrow indicates a lifetime of one month.

TABLE 3. DESCRIPTION OF MODELS

	combustion
A1	CO, H_2 from curves A, figure 24
A2	CO, H_2 from curves A, figure 24, N_2O from curve E, figure 26*a*
A3	CO, H_2 from curves B, figure 24
A4	CO, H_2 from curves B, figure 24, N_2O from curve E, figure 26*a*
	halocarbons
B1	$CFCl_3$, CF_2Cl_2 from curves A, figure 27
B2	$CFCl_3$, CF_2Cl_2, CCl_4, CH_3CCl_3 from curves A, figure 27
B3	$CFCl_3$, CF_2Cl_2 from curves B, figure 27
B4	$CFCl_3$, CF_2Cl_2, CCl_4, CH_3CCl_3 from curves B, figure 27
	nitrogen
C1	N_2O from curves A, C, E, figure 26*a*
C2	N_2O from curves A, C, E, figure 26*b*
C3	N_2O from curves B, D, E, figure 26*a*

Possible effects of combustion are summarized in figure 36. Models A1 and A2 indicate the influence of direct releases of CO and H_2. Models A3 and A4 show incremental effects associated with combustion-related releases of N_2O. The increase of total ozone arises principally from enhanced concentrations of the gas in the troposphere, as shown in figures 32 and 37. In the stratosphere, the mixing ratio of Cl_x increases in response to reduced concentrations of tropospheric OH. This process compensates for the reduced efficiency of the Cl_x catalytic cycle, due to enhanced levels of CH_4 as discussed above. Anticipated changes in atmospheric N_2O, CH_4, CO, CH_3Cl and stratospheric Cl_x are given in figure 36*b*.

Figure 38 summarizes possible effects of chlorocarbons, for both high (upper panel) and low (lower panel) emission rates. Release of $CFCl_3$ and CF_2Cl_2 at constant rates of 341 000 t a^{-1}

and 410000 t a^{-1} might be expected to lead to reductions in column O_3 by as much as 5% by the year 2000, growing to 15% by 2100. The results shown here were obtained with a model which assumed that stratospheric photolysis was the only removal process for $CFCl_3$ and CF_2Cl_2. The perturbation to ozone would be smaller if there were additional important sinks (cf. Ausloos *et al.* 1977). Inclusion of CO and H_2 emissions diminishes the perturbations to total

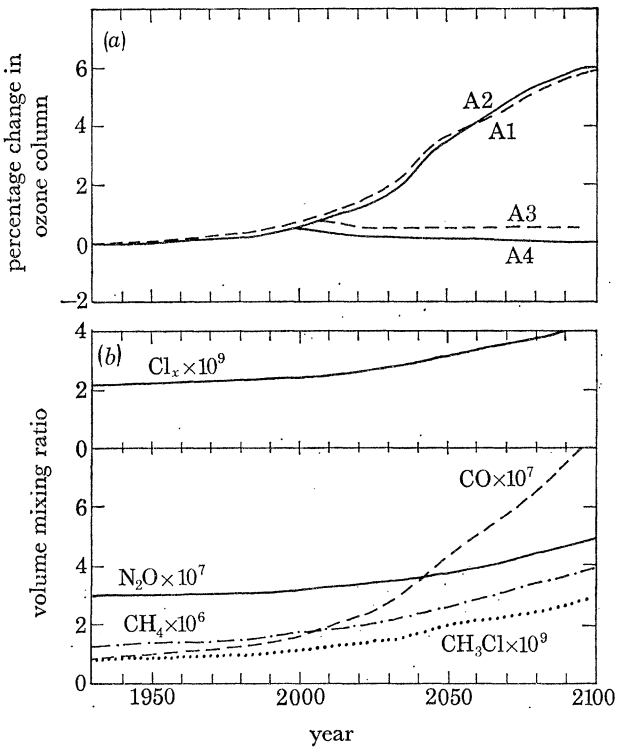

FIGURE 36.

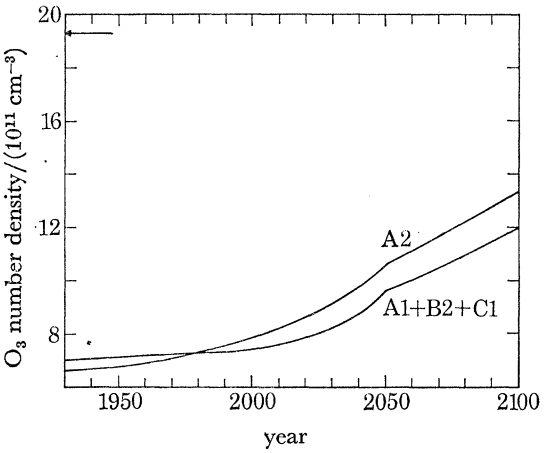

FIGURE 37.

FIGURE 36. (*a*) Changes in the global average ozone column associated with combustion. A1–A4 include emissions of CO and H_2, while A2 and A4 include also the combustion relates source of N_2O. The labels on the curves are described in detail in table 3. (*b*) Time history for the mixing ratios of N_2O, CO, CH_4 and CH_3Cl at 0 km and Cl_x at 40 km for model A2.

FIGURE 37. Changes in the ozone number density at 0 km, arising from combustion related emissions (A2) and multiple perturbations (A1 + B2 + Cl). The labels on the curves are described in table 3. The arrow indicates the present E.P.A. National Ambient Air Quality Standard for ground level ozone of 80 parts/10^9 (by vol.)

ozone, as discussed above. The validity of these models is particularly suspect for large perturbations, in that we do not allow for feedback on atmospheric structure and dynamics due to large changes in O_3. Mixing ratios for CH_4, $CFCl_3$, CF_2Cl_2, CH_3CCl_3 and Cl_x are given in figure 39 for models B2 and B4.

The possible impact of agricultural and combustion related sources of N_2O is summarized in figure 40. We may note that results for model C1 are similar to those for C2. The O_3 perturbation is relatively insensitive to the choice of lifetime for atmospheric N_2O, owing to time delays built into our model of the nitrogen cycle. We have assumed that recombination of fixed N is the major natural source of atmospheric N_2O and that the yield for production of anthropogenic N_2O is similar to that for the natural system. On the other hand, waters polluted by human nitrogen are often biologically active and have been observed to provide significant prompt sources of atmospheric N_2O (Kaplan *et al.* 1978). Assessment of human influence on

N_2O is difficult given the gaps in our understanding of processes which affect the cycle of this gas. The impact on O_3 could be larger, or smaller, than suggested in figure 40. An upper limit to the effect might be estimated if we assume a small natural source for N_2O, with immediate conversion of anthropogenic nitrogen to this gas. A limit based on this consideration is included in figure 40. This model would imply an increase of N_2O from 160 parts in 10^9 in 1940 to $300/10^9$ today.

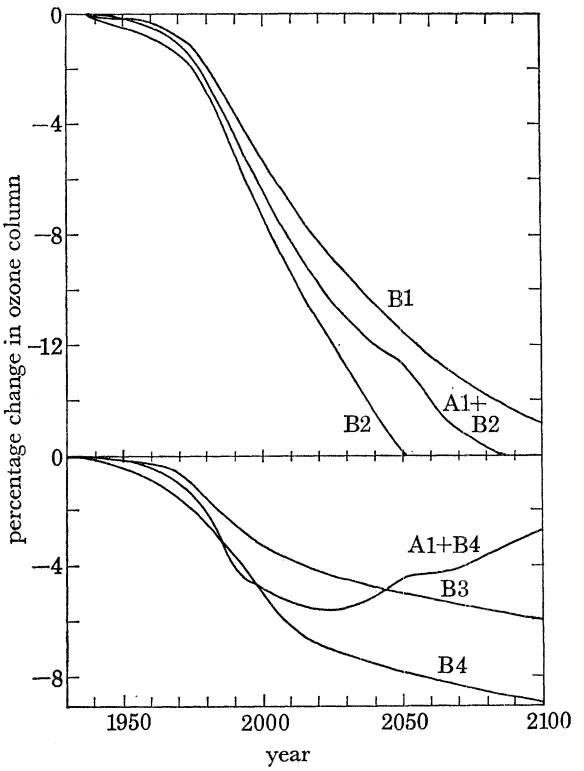

FIGURE 38.

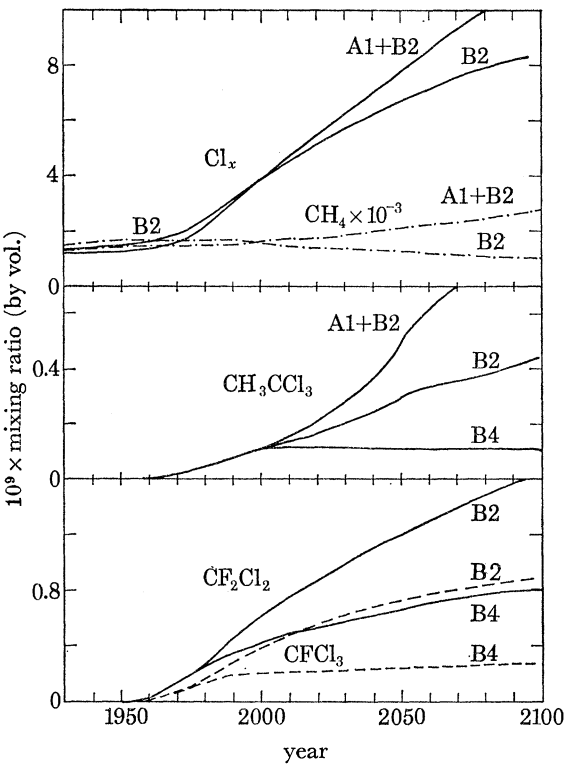

FIGURE 39.

FIGURE 38. Changes in the global average ozone column associated with chlorocarbon use (B1–B4) and combustion (A1). The upper panel employs the high emission rates for chlorocarbons given in figure 27 while the lower panel assumes some regulation of chlorocarbon emissions. The labels on the curves are described in table 3.

FIGURE 39. Mixing ratios for Cl_x (at 40 km) and CH_4, CH_3CCl_3, CF_2Cl_2 and $CFCl_3$ (at 0 km) for the models in figure 38. The upper panel illustrates the consequences of adding combustion emissions (A1) to the chlorocarbon emissions (B2); the lower panel compares the results of the high and low emission rates in figure 27 (B2 and B4) on the abundances of $CFCl_3$ and CF_2Cl_2, while the middle panel shows both effects for CH_3CCl_3.

The behaviour of O_3 in response to multiple coupled perturbations is illustrated in figure 41. We adopt, as a baseline, an atmosphere subject to what may be regarded as the least discretionary of human influences, combustion and agriculture (curve A1 + C1). The figure summarizes then the additional effects which might arise due to various chlorocarbon release patterns. It is clear that the influence of a combination of human practices is intrinsically non-linear as regards the effect on O_3. As seen earlier, a constant release of $CFCl_3$ and CF_2Cl_2 at rates prevalent in 1974 might be expected to cause a reduction of column O_3 by about 15% in the year 2100. Indeed the net perturbation in the fully coupled system is less than that which we derive for the chlorine perturbation alone, 8% as compared to 15%. The 'baseline'

calculation shows the ozone column abundance increasing with time. The additional ozone is present in the troposphere, rather than the stratosphere (see figures 32 and 37). The impact of such a perturbation to tropospheric ozone clearly requires careful study.

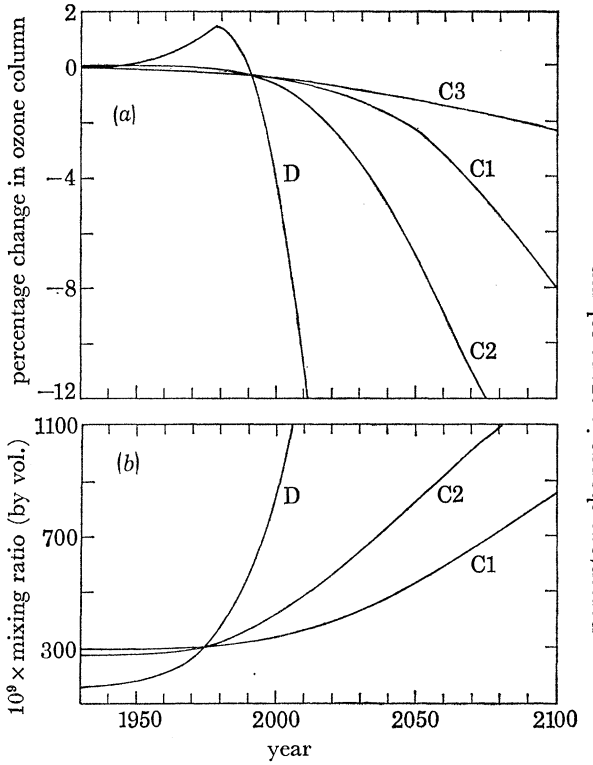

FIGURE 40.

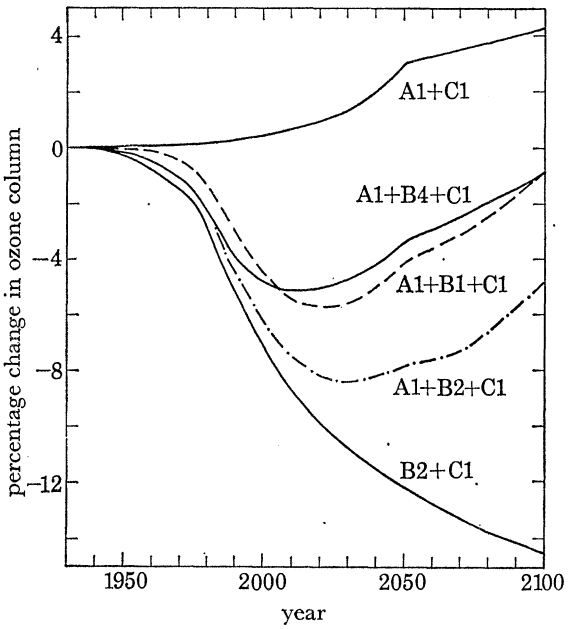

FIGURE 41.

FIGURE 40. (*a*) Changes in the global average ozone column associated with agricultural and combustion related sources of N_2O. The labels are described in table 3. Cl, C3 and D employ a 140 a lifetime for N_2O, and curve C2 a 20 a lifetime. Curve D is the result of an upper limit calculation which allows for immediate conversion of anthropogenically fixed nitrogen to N_2O in 100% yield. (*b*) Associated changes in N_2O at 0 km for selected models in (*a*).

FIGURE 41. Changes in the global average ozone column associated with multiple perturbations (due to combustion (A), chlorocarbon use (B) and fertilizer use (C)). The labels are described in table 3.

6. CONCLUDING REMARKS

Human activities associated with combustion, food production, and chlorocarbon industries may be expected to significantly perturb the chemistry of the atmosphere on a global scale. Increases in the mean concentrations of CO, CO_2, $CFCl_3$, CF_2Cl_2 and CH_3CCl_3 are already apparent, and detectable changes should be evident for N_2O, CH_4, CH_3Cl and O_3 within the next fifty years. The average column abundance of O_3 could decrease by more than 10% by the year 2100 if present trends should continue, and tropospheric ozone may be significantly enhanced.

Assessment of Man's impact on the atmosphere requires a comprehensive model which must simulate, not only essential aspects of atmospheric chemistry and dynamics, but also the manner in which the atmosphere interacts with land, hydrosphere and biosphere. Our understanding of these systems is fragmentary. Human influences are strongly interactive, with

feedbacks which are both positive and negative. Chlorocarbon emissions will enhance the supply of chlorine to the stratosphere. The associated reduction in O_3 may be offset however to some extent by an increase in the stratospheric burdens of NO_x and CH_4 induced by other anthropogenic activity.

Our treatment of human effects on the atmosphere is necessarily incomplete. We ignore for example direct and indirect consequences associated with human exploitation of land, fresh waters, estuaries and oceans and it is clear that these activities could have a predominant influence on the coupled biosphere–atmosphere system.

Our discussion here has sought to describe the atmosphere as an isolated compartment, investigating the consequence for O_3 of various gas exchanges across the lower boundary. Even this limited problem poses major difficulties.

Our model does not account for the present global distribution of O_3. The deficiencies may be attributed in part to uncertainties in our understanding of atmospheric chemistry, in part to the inadequacy of our model for atmospheric dynamics. Lifetimes for N_2O, O_3 and halocarbons may be affected by heterogeneous processes in the troposphere. The abundance and distribution of tropospheric OH is poorly determined and of central importance, in that reactions with OH regulate the stratospheric concentrations of CH_4, CH_3Cl and CH_3CCl_3. Factors which influence the concentration of stratospheric H_2O are not defined. The observed variability of stratospheric ClO is puzzling, and raises the possibility of a major gap in our description of the chlorine cycle. Our models do not allow for coupling of dynamics and chemistry, which might influence the residence time of gases in the perturbed stratosphere.

Finally we should emphasize that our understanding of N_2O and the global nitrogen cycle is seriously incomplete. This problem merits special attention in that the concentration of N_2O may be affected by non-discretionary human activity and in that N_2O plays a key rôle in many important areas of atmospheric chemistry.

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