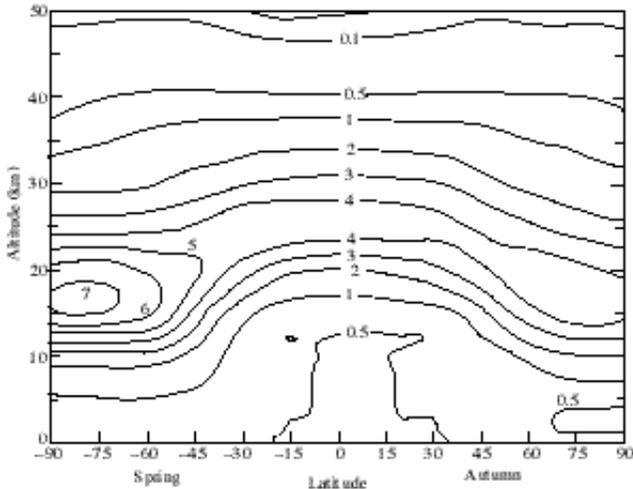


# CHAPTER 10. STRATOSPHERIC OZONE

The stratospheric ozone layer, centered at about 20 km above the surface of the Earth ( [Figure 10-1](#) ), protects life on Earth by absorbing UV radiation from the Sun. In this chapter we examine the mechanisms controlling the abundance of ozone in the stratosphere and the effect of human influence.



**Figure 10-1** The natural ozone layer: vertical and latitudinal distribution of the ozone number density (1012 molecules cm<sup>-3</sup>) at the equinox, based on measurements taken in the 1960s. From Wayne, R.P., *Chemistry of Atmospheres*, Oxford, 1991.

## 10.1 CHAPMAN MECHANISM

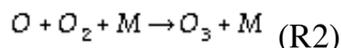
The presence of a high-altitude ozone layer in the atmosphere was first determined in the 1920s from observations of the solar UV spectrum. A theory for the origin of this ozone layer was proposed in 1930 by a British scientist, Sydney Chapman, and is known as the Chapman mechanism. It lays the foundation for current understanding of stratospheric ozone.

### 10.1.1 The mechanism

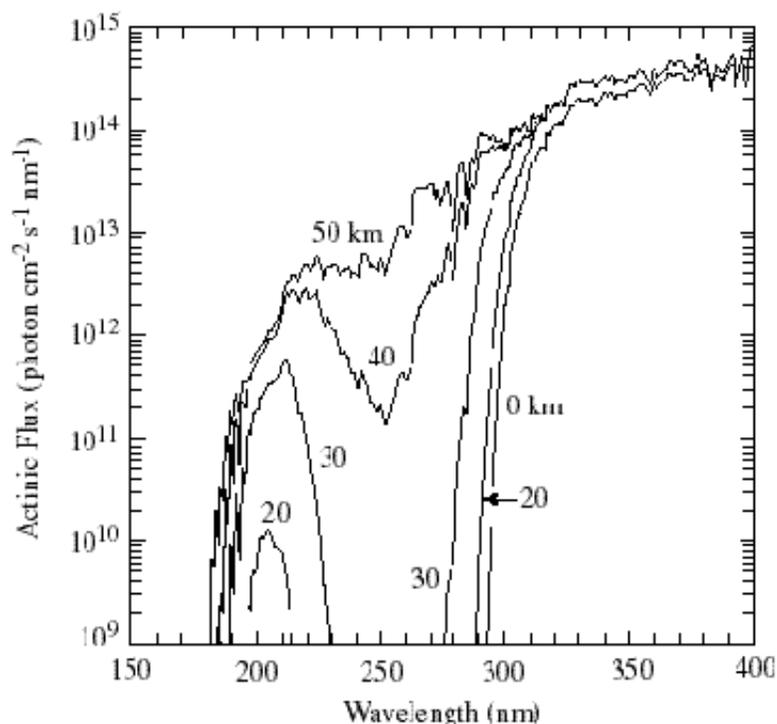
Chapman proposed that the ozone layer originates from the photolysis of atmospheric O<sub>2</sub>. The bond energy of the O<sub>2</sub> molecule (498 kJ mol<sup>-1</sup>) corresponds to the energy of a 240 nm UV photon; only photons of wavelengths less than 240 nm can photolyze the O<sub>2</sub> molecule. Such high-energy photons are present in the solar spectrum at high altitude ( [Figure 10-2](#) ). Photolysis of O<sub>2</sub> yields two O atoms:



where the O atoms are in the ground-level triplet state O(3P) ( [section 9.4](#) ) and are highly reactive due to their two unpaired electrons. They combine rapidly with O<sub>2</sub> to form ozone:

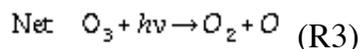
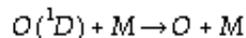
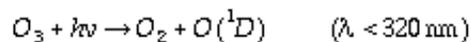


where M is a third body ([section 9.1.2](#)).

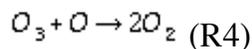


**Figure 10-2 Solar actinic flux at different altitudes, for typical atmospheric conditions and a 30° solar zenith angle. From DeMore, W.B., et al., Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, JPL Publication 97-4, Jet Propulsion Lab, Pasadena, CA, 1997.**

The O<sub>3</sub> molecules produced in reaction (R2) go on to photolyze. Because the bonds in the O<sub>3</sub> molecule are weaker than those in the O<sub>2</sub> molecule, photolysis is achieved with lower-energy photons:



where O(1D) is the O atom in an excited singlet state ([section 9.4](#)) and is rapidly stabilized to O(3P) by collision with N<sub>2</sub> or O<sub>2</sub>. Note that [See](#) is not a terminal sink for O<sub>3</sub> since the O atom product may recombine with O<sub>2</sub> by [See](#) to regenerate O<sub>3</sub>. For O<sub>3</sub> to actually be lost the O atom must undergo another reaction, which in the Chapman mechanism is



## 10.1.2 Steady-state solution

A schematic for the Chapman mechanism is shown in [Figure 10-3](#). Rate constants for reactions (R1) - (R4) have been measured in the laboratory. Reactions (R2) and (R3) are found to be much faster than reactions (R1) and (R4), as might be expected from our discussion above. We thus have a rapid cycle between O and O<sub>3</sub> by reactions (R2) and (R3), and a slower cycle between O<sub>2</sub> and (O+O<sub>3</sub>) by (R1) and (R4). Because of the rapid cycling between O and O<sub>3</sub> it is convenient to refer to the sum of the two as a chemical family, odd oxygen (O<sub>x</sub> = O<sub>3</sub> + O), which is produced by (R1) and consumed by (R4).

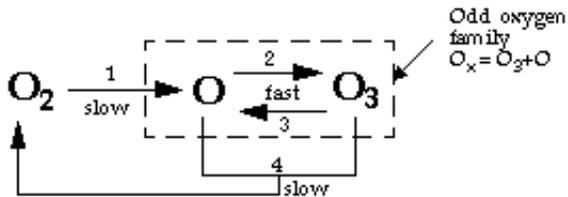


Figure 10-3 The Chapman mechanism

Simple relationships between O<sub>2</sub>, O, and O<sub>3</sub> concentrations can be derived from a chemical steady-state analysis of the Chapman mechanism. As we saw in [section 3.1.2](#), chemical steady state can be assumed for a species if its production and loss rates remain roughly constant over its lifetime. We first examine if chemical steady state is applicable to the shortest-lived species in [Figure 10-3](#), the O atom. The lifetime  $\tau_O$  of the O atom against conversion to O<sub>3</sub> by (R2) is

$$\tau_O = \frac{[O]}{k_2[O][O_2][M]} = \frac{1}{k_2[O_2][M]} \quad (10.1)$$

where we have used the low-pressure limit in the rate expression for (R2), as is appropriate for atmospheric conditions. In equation (10.1), [M] is the air number density  $n_a$ , and [O<sub>2</sub>] = CO<sub>2</sub> $n_a$  where CO<sub>2</sub> = 0.21 mol/mol is the mixing ratio of O<sub>2</sub>. Thus:

$$\tau_O = \frac{1}{k_2 C_{O_2} n_a^2} \quad (10.2)$$

All terms on the right-hand side of (10.2) are known. Substituting numerical values one finds that  $\tau_O$  in the stratosphere is of the order of seconds or less ([See The Chapman mechanism and steady state](#)). Production and loss rates of the O atom depend on the meteorological environment (pressure, temperature, radiation) and on the O<sub>3</sub> abundance, neither of which vary significantly over a time scale of seconds. We can therefore assume chemical steady state for O atoms between production by (R3) and loss by (R2), neglecting reactions (R1) and (R4) which are much slower:

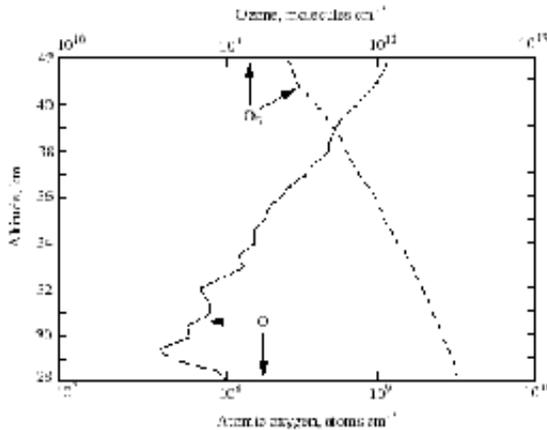
$$k_2[O][O_2][M] = k_3[O_3] \quad (10.3)$$

Rearrangement of (10.3) yields

$$\frac{[O]}{[O_3]} = \frac{k_3}{k_2 C_{O_2} n_a^2} \quad (10.4)$$

Substituting numerical values one finds [O]/[O<sub>3</sub>] << 1 throughout the stratosphere ([See The](#)

[Chapman mechanism and steady state](#) ). Observed concentrations ( [Figure 10-4](#) ) obey closely this steady state.



**Figure 10-4 Simultaneous measurements of O and O<sub>3</sub> concentrations in the stratosphere over Texas in December 1977. Adapted from R.P. Wayne, op. cit.**

An important result of our steady-state analysis for the O atom is that O<sub>3</sub> is the main component of the Ox family:  $[O_x] = [O_3] + [O]^a [O_3]$ . This result has two implications:

- ‡ The concentration of O<sub>3</sub> is controlled by the slow production and loss of Ox from reactions [\(R1\)](#) and [\(R4\)](#) rather than by the fast production and loss of O<sub>3</sub> from reactions [\(R2\)](#) and [\(R3\)](#);
- ‡ The effective lifetime of O<sub>3</sub> against chemical loss is defined by the lifetime of Ox.

The lifetime of Ox is given by:

$$\tau_{Ox} = \frac{[O_x]}{2k_4[O][O_3]} \approx \frac{1}{2k_4[O]} \quad (10.5)$$

where we have included a factor of 2 in the denominator because [\(R4\)](#) consumes two Ox (one O<sub>3</sub> and one O). The factor of 2 can be derived formally from a mass balance equation for Ox as the sum of the mass balance equations for O<sub>3</sub> and O:

$$\begin{aligned} \frac{d}{dt}[O_x] &= \frac{d}{dt}([O_3] + [O]) = \frac{d}{dt}[O_3] + \frac{d}{dt}[O] \\ &= [\text{rate}(2) - \text{rate}(3) - \text{rate}(4)] + [2x \text{rate}(1) + \text{rate}(3) - \text{rate}(2) - \text{rate}(4)] \\ &= 2x \text{rate}(1) - 2x \text{rate}(4) \end{aligned} \quad (10.6)$$

Values of  $t_{Ox}$  computed from [\(10.5\)](#) range from less than a day in the upper stratosphere to several years in the lower stratosphere, reflecting the abundance of O atoms ( [Figure 10-4](#) , [See The Chapman mechanism and steady state](#) ). In the upper stratosphere at least, the lifetime of Ox is sufficiently short that chemical steady state can be assumed to hold. This steady state is defined by

$$2k_1[O_2] = 2k_4[O][O_3] \quad (10.7)$$

Substituting [\(10.4\)](#) into [\(10.7\)](#) yields as solution for [O<sub>3</sub>]:

$$[O_3] = \left( \frac{k_1 k_2}{k_3 k_4} \right)^{\frac{1}{2}} C_{O_2} N_a \quad (10.8)$$

The simplicity of equation (10.8) is deceiving. Calculating [O<sub>3</sub>] from this equation is actually not straightforward because the photolysis rate constants k<sub>1</sub>(z) and k<sub>3</sub>(z) at altitude z depend on the local actinic flux I(z), which is attenuated due to absorption of radiation by the O<sub>2</sub> and O<sub>3</sub> columns overhead. From (9.13), the general expression for a photolysis rate constant is

$$k = \int_{\lambda} q_x(\lambda) \sigma_x(\lambda) I_{\lambda} d\lambda \quad (10.9)$$

The actinic flux I(z) at altitude z is attenuated relative to its value I<sub>0</sub> at the top of the atmosphere by

$$I_{\lambda}(z) = I_{\lambda,0} e^{-\frac{\delta}{\cos \theta}} \quad (10.10)$$

where q is the solar zenith angle, that is the angle between the Sun and the vertical (section 7.6), and d is the optical depth of the atmosphere above z computed from (7.30):

$$\delta = \int_z^{\infty} (\sigma_{O_2}[O_2] + \sigma_{O_3}[O_3]) dz' \quad (10.11)$$

Values of I at UV wavelengths decrease rapidly with decreasing altitude in the stratosphere because of efficient absorption by O<sub>2</sub> and O<sub>3</sub> (Figure 10-2), and k<sub>1</sub> and k<sub>3</sub> decrease correspondingly (Figure 10-5).

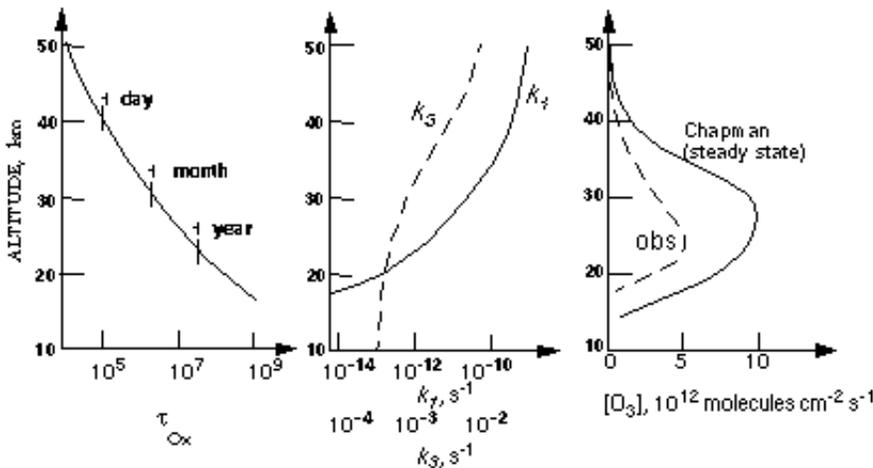


Figure 10-5 Chapman mechanism at low latitudes. Left panel: Lifetime of O<sub>x</sub>. Center panel: O<sub>2</sub> and O<sub>3</sub> photolysis rate constants. Right panel: calculated and observed vertical profiles of O<sub>3</sub> concentrations.

Since k<sub>1</sub>(z) and k<sub>3</sub>(z) depend on the O<sub>3</sub> column overhead through (10.9) - (10.11), equation (10.8) is not explicit for [O<sub>3</sub>] (the right-hand-side depends on [O<sub>3</sub>]). Solution to (10.8) must be obtained numerically by starting from the top of the atmosphere with I = I<sub>0</sub> and [O<sub>3</sub>] = 0, and progressing downward by small increments in the atmosphere, calculating I(z) and the resulting values of k<sub>1</sub>(z), k<sub>3</sub>(z), and [O<sub>3</sub>](z) as one penetrates in the atmosphere.

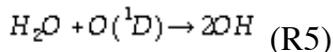
The resulting solution (Figure 10-5, right panel) is able to explain at least qualitatively the observed maximum of O<sub>3</sub> concentrations at 20-30 km altitude. The maximum reflects largely the vertical dependence of O<sub>x</sub> production by (R1), 2k<sub>1</sub>[O<sub>2</sub>], which we have seen is the effective source for O<sub>3</sub>. The O<sub>2</sub> number density decreases exponentially with altitude following the barometric law, while k<sub>1</sub> decreases sharply with decreasing altitude due to absorption of UV radiation by O<sub>3</sub> and O<sub>2</sub>. The product k<sub>1</sub>[O<sub>2</sub>] thus has a maximum value at 20-30 km altitude. See [problem 10.1](#) for an analytical derivation of this maximum.

Although the Chapman mechanism is successful in reproducing the general shape of the O<sub>3</sub> layer, it overestimates the observed O<sub>3</sub> concentrations by a factor of 2 or more ([Figure 10-5](#)). In the lower stratosphere, a steady state solution to the mechanism would not necessarily be expected because of the long lifetime of O<sub>x</sub>; there, transport may play a dominant role in shaping the O<sub>3</sub> distribution. In the upper stratosphere, however, where the lifetime of O<sub>x</sub> is short, the discrepancy between theory and observations points to a flaw in the theory. Either the source of O<sub>x</sub> in the Chapman mechanism is too large, or the sink is too small. Considering that the source from (R1) is well constrained by spectroscopic data, the logical conclusion is that there must be additional sinks for O<sub>3</sub> not accounted for by the Chapman mechanism. This flaw was not evident until the 1950s, because the relatively poor quality of the stratospheric ozone observations and the uncertainties on the rate constants of reactions (R1) - [See](#) could accommodate the discrepancies between theory and observations. As the experimental data base improved, however, the discrepancy became clear.

## 10.2 CATALYTIC LOSS CYCLES

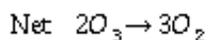
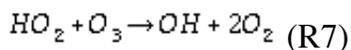
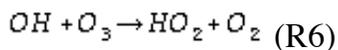
### 10.2.1 Hydrogen oxide radicals (HO<sub>x</sub>)

In the late 1950s it was discovered that catalytic cycles initiated by oxidation of water vapor could represent a significant sink for O<sub>3</sub> in the stratosphere. Water vapor is supplied to the stratosphere by transport from the troposphere, and is also produced within the stratosphere by oxidation of CH<sub>4</sub>. Water vapor mixing ratios in the stratosphere are relatively uniform, in the range 3-5 ppmv. In the stratosphere, water vapor is oxidized by O(1D) produced from (R3):



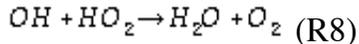
The high-energy O(1D) atoms are necessary to overcome the stability of the H<sub>2</sub>O molecule.

The hydroxyl radical OH produced by [See](#) can react with O<sub>3</sub>, producing the hydroperoxy radical HO<sub>2</sub> which in turn reacts with O<sub>3</sub>:



We refer to the ensemble of OH and HO<sub>2</sub> as the HO<sub>x</sub> chemical family. The sequence of

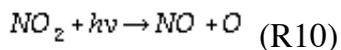
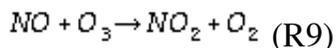
reactions (R6) and (R7) consumes O<sub>3</sub> while conserving HOx. Therefore HOx acts as a catalyst for O<sub>3</sub> loss; production of one HOx molecule by (R5) can result in the loss of a large number of O<sub>3</sub> molecules by cycling of HOx through (R6) and (R7). Termination of the catalytic cycle requires loss of HOx by a reaction such as



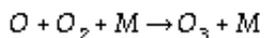
The sequence (R5) - (R8) is a chain reaction for O<sub>3</sub> loss in which (R5) is the initiation step, (R6) - (R7) are the propagation steps, and (R8) is the termination step. There are several variants to the HOx-catalyzed mechanism, involving reactions other than [See - See](#); see [problem 10.4](#). From knowledge of stratospheric water vapor concentrations and rate constants for (R5) - (R8), and assuming chemical steady state for the HOx radicals (a safe assumption in view of their short lifetimes), one can calculate the O<sub>3</sub> loss rate. Such calculations conducted in the 1950s and 1960s found that HOx catalysis was a significant O<sub>3</sub> sink but not sufficient to reconcile the chemical budget of O<sub>3</sub>. Nevertheless, the discovery of HOx catalysis introduced the important new idea that species present at trace levels in the stratosphere could trigger chain reactions destroying O<sub>3</sub>. This concept was to find its crowning application in subsequent work, as described below. Another key advance was the identification of (R5) as a source for the OH radical, a strong oxidant. As we will see in chapter 11, oxidation by OH provides the principal sink for a large number of species emitted in the atmosphere. Finally, recent work has shown that the HOx-catalyzed mechanism represents in fact the dominant sink of O<sub>3</sub> in the lowest part of the stratosphere ([section 10.4](#)).

### 10.2.2 Nitrogen oxide radicals (NOx)

The next breakthrough in our understanding of stratospheric O<sub>3</sub> came about in the late 1960s when the United States and other countries considered the launch of a supersonic aircraft fleet flying in the stratosphere. Atmospheric chemists were called upon to assess the effects of such a fleet on the O<sub>3</sub> layer. An important component of aircraft exhaust is nitric oxide (NO) formed by oxidation of atmospheric N<sub>2</sub> at the high temperatures of the aircraft engine. In the stratosphere NO reacts rapidly with O<sub>3</sub> to produce NO<sub>2</sub>, which then photolyzes:



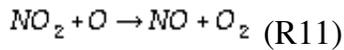
1.



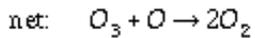
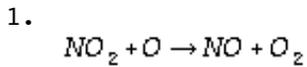
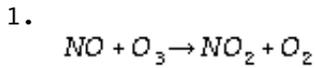
This cycling between NO and NO<sub>2</sub> takes place on a time scale of about one minute during daytime. It has no net effect on O<sub>3</sub> and is called a null cycle. It causes, however, rapid exchange between NO and NO<sub>2</sub>. We refer to the ensemble of NO and NO<sub>2</sub> as a new chemical family, NOx.

Further investigation of NOx chemistry in the stratosphere showed that a fraction of the

NO<sub>2</sub> molecules produced by [\(R9\)](#) reacts with oxygen atoms produced by [\(R3\)](#):



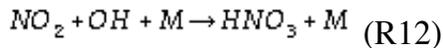
The sequence of reactions [\(R9\)](#) and [\(R11\)](#) represents a catalytic cycle for O<sub>3</sub> loss with a net effect identical to [\(R4\)](#):



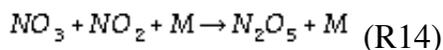
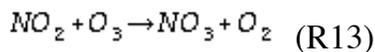
Each cycle consumes two O<sub>x</sub> molecules, which is equivalent to two O<sub>3</sub> molecules (see [section 10.1.2](#)). The rate-limiting step in the cycle is [\(R11\)](#) because NO<sub>2</sub> has the option of either photolyzing (null cycle) or reacting with O (O<sub>3</sub> loss cycle). The O<sub>3</sub> loss rate is therefore given by

$$-\frac{d}{dt}[\text{O}_3] \approx -\frac{d}{dt}[\text{O}_x] = 2k_{11}[\text{NO}_2][\text{O}] \quad (10.12)$$

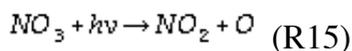
Termination of the catalytic cycle involves loss of NO<sub>x</sub> radicals. In the daytime, NO<sub>x</sub> is oxidized to HNO<sub>3</sub> by the strong radical oxidant OH ([section 10.2.1](#)):



At night OH is absent, because there is no O(1D) to oxidize H<sub>2</sub>O by [\(R5\)](#). Loss of NO<sub>x</sub> at night takes place through the oxidation of NO<sub>2</sub> by O<sub>3</sub> and subsequent conversion of the NO<sub>3</sub> radical to N<sub>2</sub>O<sub>5</sub>:

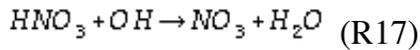
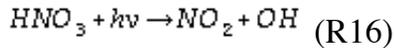


This formation of N<sub>2</sub>O<sub>5</sub> can take place only at night, because during daytime NO<sub>3</sub> is photolyzed back to NO<sub>2</sub> on a time scale of a few seconds:

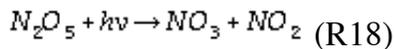
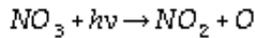


The products of NO<sub>x</sub> oxidation, HNO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, are non-radical species and have

therefore relatively long lifetimes against chemical loss (weeks for HNO<sub>3</sub>, hours to days for N<sub>2</sub>O<sub>5</sub>). They are eventually converted back to NO<sub>x</sub>:

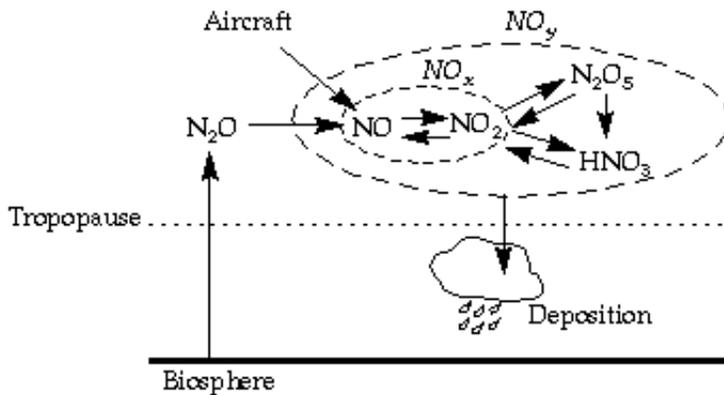


1.



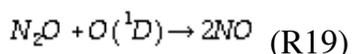
and serve therefore as reservoirs for NO<sub>x</sub>. We refer to the ensemble of NO<sub>x</sub> and its reservoirs as yet another chemical family, NO<sub>y</sub>. Ultimate removal of NO<sub>y</sub> is by transport to the troposphere where HNO<sub>3</sub> is rapidly removed by deposition.

A diagram of the ensemble of processes is shown in [Figure 10-6](#). The loss rate of O<sub>3</sub> can be calculated from knowledge of the aircraft emission rate of NO, the chemical cycling within the NO<sub>y</sub> family, and the residence time of air (and therefore NO<sub>y</sub>) in the stratosphere. Model calculations conducted in the 1970s found that an aircraft fleet in the stratosphere would represent a serious threat to the O<sub>3</sub> layer. This environmental concern, combined with economic considerations, led to scrapping of the supersonic aircraft plan in the United States (the Europeans still built the Concorde).



**Figure 10-6 Sources and sinks of stratospheric NO<sub>x</sub> and NO<sub>y</sub>. The direct conversion of N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub> takes place in aerosols and will be discussed in [section 10.4](#).**

The identification of a NO<sub>x</sub>-catalyzed mechanism for O<sub>3</sub> loss turned out to be a critical lead towards identifying the missing O<sub>3</sub> sink in the Chapman mechanism. Beyond the source from supersonic aircraft, could there be a natural source of NO<sub>x</sub> to the stratosphere? Further work in the early 1970s showed that N<sub>2</sub>O, a low-yield product of nitrification and denitrification processes in the biosphere ([section 6.3](#)), provides such a source. N<sub>2</sub>O is a very stable molecule which has no significant sinks in the troposphere. It is therefore transported to the stratosphere where it encounters high concentrations of O(1D), allowing oxidation to NO by

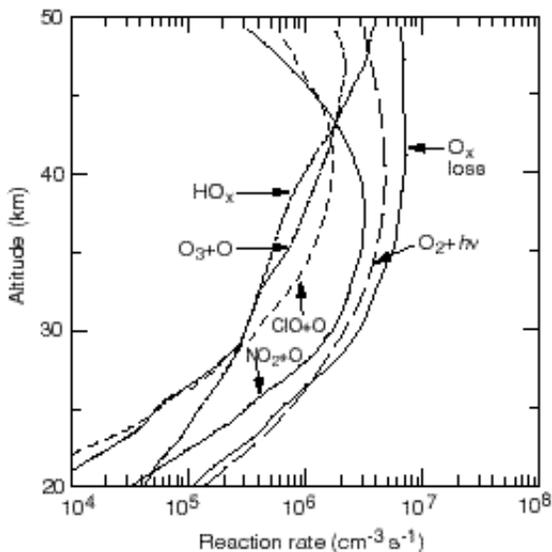


Reaction (R19) actually accounts for only about 5% of loss of N<sub>2</sub>O in the stratosphere; the remaining 95% are converted to N<sub>2</sub> by photolysis and oxidation by O(1D) via an alternate branch. The conversion to N<sub>2</sub> is however of no interest for driving stratospheric chemistry.

On the basis of [Figure 10-6](#), we see that the loss rate of O<sub>3</sub> by the NO<sub>x</sub>-catalyzed mechanism can be calculated from knowledge of the production and loss rates of NO<sub>y</sub>, and of the chemical cycling within the NO<sub>y</sub> family. We examine now our ability to quantify each of these terms:

- **Production rate of NO<sub>y</sub>.** In the natural stratosphere, NO<sub>y</sub> is produced as NO from oxidation of N<sub>2</sub>O by O(1D). The concentration of N<sub>2</sub>O in the stratosphere is readily measurable by spectroscopic methods, and the concentration of O(1D) can be calculated from chemical steady state by reaction (R3), so that the source of NO<sub>y</sub> is well constrained.
- **Loss rate of NO<sub>y</sub>.** The dominant sink for NO<sub>y</sub> in the stratosphere is transport to the troposphere followed by deposition. We saw in chapter 4 that the residence time of air (and hence of NO<sub>y</sub>) in the stratosphere is 1-2 years. Thus the loss rate of NO<sub>y</sub> is relatively well constrained, to within a factor of two.
- **Chemical cycling within the NO<sub>y</sub> family.** The rate of O<sub>3</sub> loss depends on the fraction of NO<sub>y</sub> present as NO<sub>x</sub>, that is, the NO<sub>x</sub>/NO<sub>y</sub> ratio. This ratio can be calculated from the rate equations for the different components of the NO<sub>y</sub> family. Under most conditions, chemical steady state between the different NO<sub>y</sub> components is a good approximation.

We therefore have all the elements needed to calculate the O<sub>3</sub> loss rate from the NO<sub>x</sub>-catalyzed mechanism. When atmospheric chemists did these calculations in the 1970s they found that they could fully account for the missing sink of O<sub>3</sub> in the Chapman mechanism! [Figure 10-7](#) shows results from such a calculation constrained with simultaneous observations of NO<sub>y</sub>, O<sub>3</sub>, H<sub>2</sub>O, and CH<sub>4</sub> through the depth of the stratosphere. The Ox loss rates in this calculation are computed on the basis of the gas-phase mechanisms described above, and the resulting total Ox loss (solid line) is compared to the source of Ox from photolysis of O<sub>2</sub> (long dashes). Results show a close balance between Ox production and loss, with NO<sub>x</sub> catalysis providing the dominant sink in most of the stratosphere. The budget of stratospheric O<sub>3</sub> finally appeared to be closed. Paul Crutzen received the 1995 Nobel Prize in Chemistry for this work.



**Figure 10-7** 24-hour average rates of Ox production and loss computed with a gas-phase chemistry model constrained with simultaneous observations of O<sub>3</sub>, H<sub>2</sub>O, CH<sub>4</sub>, NO<sub>y</sub>, and Cl<sub>y</sub> from the space shuttle. We will see in [section 10.4](#) that consideration of aerosol chemistry modifies greatly the model results in the lower stratosphere. From McElroy, M.B., and R.J. Salawitch, *Science* 243, 763-770, 1989.

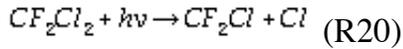
Ice core data show that atmospheric concentrations of N<sub>2</sub>O have risen from 285 ppbv in the 18th century to 310 ppbv today, and present-day atmospheric observations indicate a growth rate of 0.3 % yr<sup>-1</sup> ([Figure 7-1](#)). There is much interest in understanding this rise because of the importance of N<sub>2</sub>O not only as a sink for stratospheric O<sub>3</sub> but also as a greenhouse gas (chapter 7). Table 10.1 gives current estimates of the sources and sinks of atmospheric N<sub>2</sub>O. Although the estimates can provide a balanced budget within their ranges of uncertainty (atmospheric increase <sup>a</sup> sources - sinks), the uncertainties are in fact large. Biogenic sources in the tropical continents, cultivated areas, and the oceans provide the dominant sources of N<sub>2</sub>O. The increase of N<sub>2</sub>O over the past century is thought to be due principally to increasing use of fertilizer for agriculture.

### 1. Present-day global budget of N<sub>2</sub>O

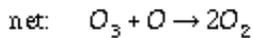
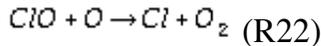
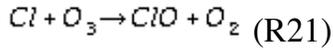
	Rate, Tg N yr <sup>-1</sup> best estimate and range of uncertainty
<b>SOURCES, natural</b>	9 (6-12)
Oceans	3 (1-5)
Tropical soils	4 (3-6)
Temperate soils	2 (0.6-4)
<b>SOURCES, anthropogenic</b>	6 (4-8)
Cultivated soils	4 (2-5)
Biomass burning	0.5 (0.2-1.0)
Chemical industry	1.3 (0.7-1.8)
Livestock	0.4 (0.2-0.5)
<b>SINK Stratosphere</b>	12 (9-16)
<b>ATMOSPHERIC INCREASE</b>	4

### 10.2.3 Chlorine radicals (ClOx)

In 1974, Mario Molina and Sherwood Rowland pointed out the potential for O<sub>3</sub> loss associated with rising atmospheric concentrations of chlorofluorocarbons (CFCs). CFCs are not found in nature; they were first manufactured for industrial purposes in the 1930s and their use increased rapidly in the following decades. During the 1970s and 1980s, atmospheric concentrations of CFCs rose by 2-4% yr<sup>-1</sup> ([Figure 7-1](#)). CFC molecules are inert in the troposphere; they are therefore transported to the stratosphere, where they photolyze to release Cl atoms. For example, in the case of CF<sub>2</sub>Cl<sub>2</sub> (known by the trade name CFC-12):



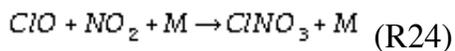
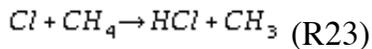
The Cl atoms then trigger a catalytic loss mechanism for O<sub>3</sub> involving cycling between Cl and ClO (the ClO<sub>x</sub> family). The sequence is similar to that of the NO<sub>x</sub>-catalyzed mechanism:



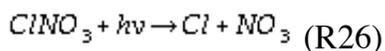
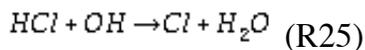
The rate-limiting step for O<sub>3</sub> loss in this cycle is (R22) (see [problem 10.5](#)), so that the O<sub>3</sub> loss rate is

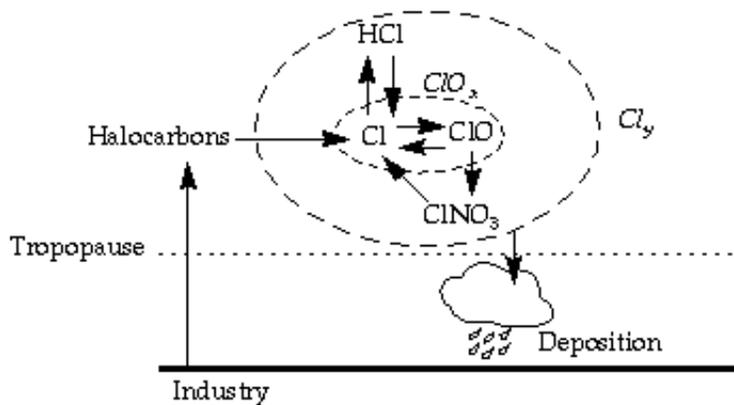
$$-\frac{d}{dt}[O_3] = -\frac{d}{dt}[O_x] = 2k_{22}[ClO][O] \quad (10.13)$$

The catalytic cycle is terminated by conversion of ClO<sub>x</sub> to non-radical chlorine reservoirs, HCl and ClNO<sub>3</sub>:



The lifetime of HCl is typically a few weeks and the lifetime of ClNO<sub>3</sub> is of the order of a day. Eventually these reservoirs return ClO<sub>x</sub>:

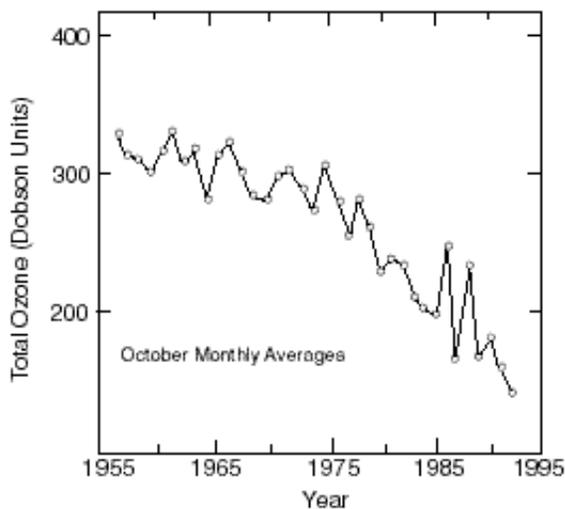




**Figure 10-8 Sources and sinks of stratospheric ClOx and Cly**

We thus define a chemical family Cly as the sum of ClOx and its reservoirs. A diagram of the ensemble of processes is shown in [Figure 10-8](#). Note the similarity to [Figure 10-6](#).

Similarly to the NO<sub>x</sub>-catalyzed mechanism, the rate of O<sub>3</sub> loss by the ClO<sub>x</sub>-catalyzed mechanism can be calculated from knowledge of the concentrations of CFCs and other halocarbons in the stratosphere, the residence time of air in the stratosphere, and the ClO<sub>x</sub>/Cly chemical partitioning. Molina and Rowland warned that ClO<sub>x</sub>-catalyzed O<sub>3</sub> loss would become a significant threat to the O<sub>3</sub> layer as CFC concentrations continued to increase. Their warning, backed up over the next two decades by increasing experimental evidence and compounded by the discovery of the antarctic ozone hole, led to a series of international agreements (beginning with the Montreal protocol in 1987) which eventually resulted in a total ban on CFC production as of 1996. For this work they shared the 1995 Nobel Prize in Chemistry with Paul Crutzen.

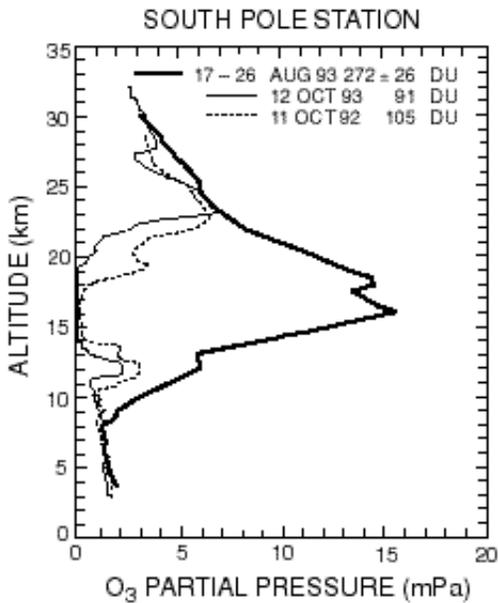


**Figure 10-9 Historical trend in the total ozone column measured spectroscopically over Halley Bay, Antarctica in October, 1957-1992. One Dobson unit (DU) represents a 0.01 mm thick layer of ozone under standard conditions of temperature and pressure; 1 DU = 2.69x10<sup>16</sup> molecules cm<sup>-2</sup>s<sup>-1</sup>. From: Scientific Assessment of Ozone Depletion: 1994, World Meteorological Organization (WMO), Geneva, 1995.**

### 10.3 POLAR OZONE LOSS

In 1985, a team of scientists from the British Antarctic Survey reported that springtime stratospheric O<sub>3</sub> columns over their station at Halley Bay had decreased precipitously since the 1970s ([Figure 10-9](#)). The depletion was confined to the spring months (September-November); no depletion was observed in other seasons. Global satellite data soon confirmed the Halley Bay observations and showed that the depletion of stratospheric O<sub>3</sub>

extended over the totality of the antarctic vortex, a large circumpolar region including most of the southern polar latitudes. The depletion of O<sub>3</sub> has worsened since 1985, and springtime O<sub>3</sub> columns over Antarctica today are less than half of what they were in the 1960s ([Figure 10-9](#)). Measured vertical profiles show that the depletion of O<sub>3</sub> is essentially total in the lowest region of the stratosphere between 10 and 20 km ([Figure 10-10](#)), which normally would contain most of the total O<sub>3</sub> column in polar spring ([Figure 10-1](#)).

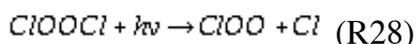
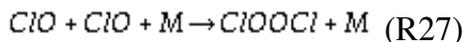


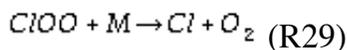
**Figure 10-10** Vertical profiles of ozone over Antarctica measured by chemical sondes. In August the ozone hole has not developed yet, while in October it is fully developed. From Harris, N.R.P., et al., *Ozone measurements*, in WMO, op. cit..

Discovery of this "antarctic ozone hole" (as it was named in the popular press) was a shock to atmospheric chemists, who thought by then that the factors controlling stratospheric O<sub>3</sub> were relatively well understood. The established mechanisms presented in sections [See CHAPMAN MECHANISM](#) and [See CATALYTIC LOSS CYCLES](#) could not explain the O<sub>3</sub> depletion observed over Antarctica. Under the low light conditions in that region, concentrations of O atoms are very low, so that reactions ([R11](#)) and ([R22](#)) cannot operate at a significant rate. This severe failure of theory sent atmospheric chemists scrambling to understand what processes were missing from their understanding of stratospheric chemistry, and whether the appearance of the antarctic O<sub>3</sub> hole could be a bellwether of future catastrophic changes in stratospheric O<sub>3</sub> levels over other regions of the world.

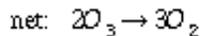
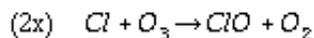
### 10.3.1 Mechanism for ozone loss

Several aircraft missions were conducted in the late 1980s to understand the causes of the antarctic ozone depletion. These studies found the depletion of O<sub>3</sub> to be associated with exceptionally high ClO, a result confirmed by satellite data. Parallel laboratory experiments showed that at such high ClO concentrations, a new catalytic cycle involving self-reaction of ClO could account for most of the observed O<sub>3</sub> depletion:





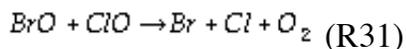
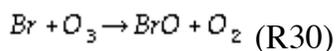
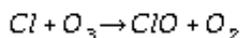
1.



The key behind discovery of this catalytic cycle was the laboratory observation that photolysis of the ClO dimer (ClOCl) takes place at the O-Cl bond rather than at the weaker O-O bond. It was previously expected that photolysis would take place at the O-O bond, regenerating ClO and leading to a null cycle. The rate of O<sub>3</sub> loss in the catalytic cycle is found to be limited by [\(R27\)](#) and is therefore quadratic in [ClO]; it does not depend on the abundance of O atoms, in contrast to the ClO<sub>x</sub>-catalyzed mechanism described in the previous section.

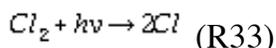
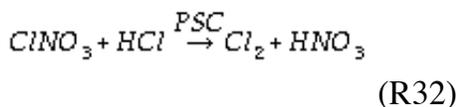
Another catalytic cycle found to be important in the depletion of O<sub>3</sub> during antarctic spring involves Br radicals produced in the stratosphere by photolysis and oxidation of anthropogenic Br-containing gases such as CH<sub>3</sub>Br (see [problem 6.4](#)):

1.



Again, this catalytic cycle is made significant by the high concentrations of ClO over Antarctica. According to current models, the ClO+ClO mechanism accounts for about 70% of total O<sub>3</sub> loss in the antarctic ozone hole; the remaining 30% is accounted for by the BrO+ClO mechanism.

Why are ClO concentrations over Antarctica so high? Further research in the 1990s demonstrated the critical role of reactions taking place in stratospheric aerosols at low temperature. Temperatures in the wintertime antarctic stratosphere are sufficiently cold to cause formation of persistent ice-like clouds called polar stratospheric clouds (PSCs) in the lower part of the stratosphere. The PSC particles provide surfaces for conversion of the ClO<sub>x</sub> reservoirs HCl and ClNO<sub>3</sub> to Cl<sub>2</sub>, which then rapidly photolyzes to produce ClO<sub>x</sub>:

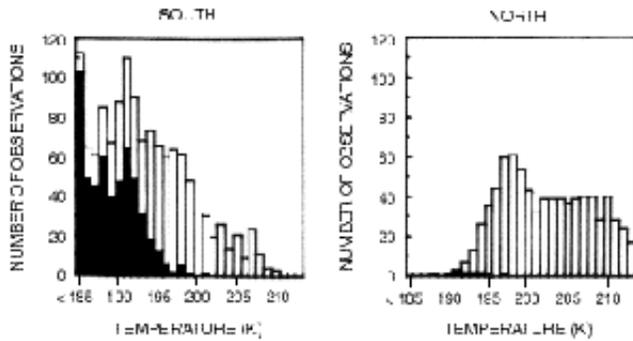


Reaction [\(R32\)](#) is so fast that it can be regarded as quantitative; either ClNO<sub>3</sub> or HCl is completely titrated. Whereas in most of the stratosphere the ClO<sub>x</sub>/Cl<sub>y</sub> molar ratio is less than 0.1, in the antarctic vortex it exceeds 0.5 and can approach unity. Recent research

indicates that (R32) proceeds rapidly not only on PSC surfaces but also in the aqueous H<sub>2</sub>SO<sub>4</sub> aerosols present ubiquitously in the stratosphere ( [section 8.1](#) ) when the temperatures fall to the values observed in antarctic winter (below 200 K). Low temperature rather than the presence of PSCs appears to be the critical factor for (R32) to take place. Nevertheless, as we will see below, PSCs play a critical role in the development of the O<sub>3</sub> hole by providing a mechanism for removal of HNO<sub>3</sub> from the stratosphere.

### 10.3.2 PSC formation

Because the stratosphere is extremely dry, condensation of water vapor to form ice clouds requires extremely low temperatures. The stratospheric mixing ratio of water vapor is relatively uniform at 3-5 ppmv. In the lower stratosphere at 100 hPa (16 km altitude), this mixing ratio corresponds to a water vapor pressure of 3-5x10<sup>-4</sup> hPa. The frost point at that vapor pressure is 185-190 K; such low temperatures are almost never reached except in antarctic winter. When temperatures do fall below 190 K, PSCs are systematically observed. Observations show however that PSCs start to form at a higher temperature, about 197 K ( [Figure 10-11](#) ), and this higher temperature threshold for PSC formation is responsible for the large extent of the O<sub>3</sub> hole.



**Figure 10-11** Frequency distributions of temperature (total bars) and PSC occurrence (shaded bars) in the winter lower stratosphere of each hemisphere at 65o-80o latitude. Adapted from McCormick, M.P., et al., *J. Atmos. Sci.*, **39**, 1387, 1982.

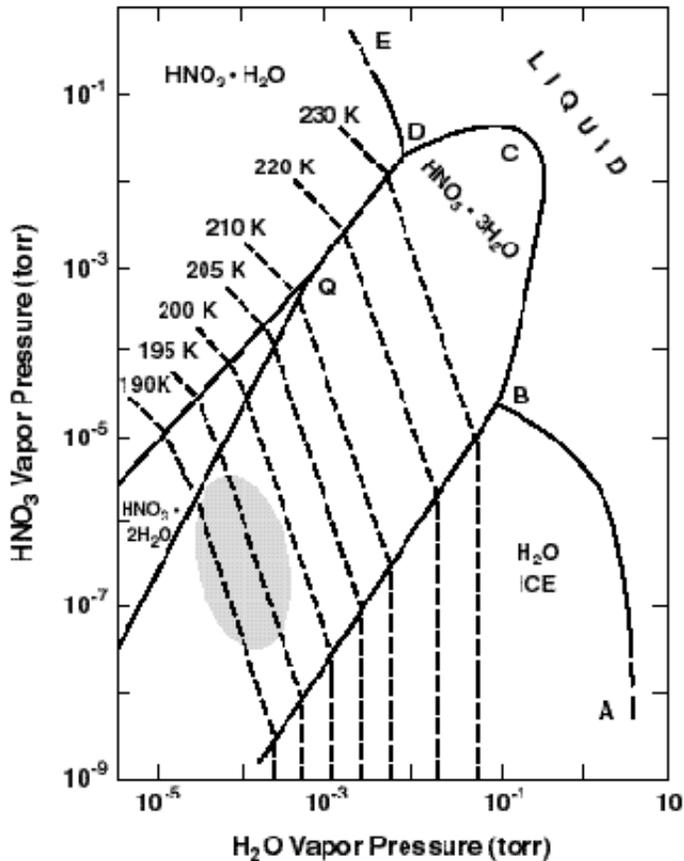
Discovery of the antarctic ozone hole spurred intense research into the thermodynamics of PSC formation. It was soon established that the stratosphere contains sufficiently high concentrations of HNO<sub>3</sub> that solid HNO<sub>3</sub>-H<sub>2</sub>O phases may form at temperatures higher than the frost point of water. These solid phases are:

- HNO<sub>3</sub>·3H<sub>2</sub>O - Nitric acid trihydrate (NAT)
- HNO<sub>3</sub>·2H<sub>2</sub>O - Nitric acid dihydrate (NAD)
- HNO<sub>3</sub>·H<sub>2</sub>O - Nitric acid monohydrate (NAM)

[Figure 10-12](#) is a phase diagram for the binary HNO<sub>3</sub>-H<sub>2</sub>O system. The diagram shows the thermodynamically stable phases of the system as a function of PHNO<sub>3</sub> and PH<sub>2</sub>O. There are six different phases in the diagram: NAT, NAD, NAM, H<sub>2</sub>O ice, liquid HNO<sub>3</sub>-H<sub>2</sub>O solution, and gas. The presence of a gas phase is implicit in the choice of PHNO<sub>3</sub> and PH<sub>2</sub>O as coordinates. From the phase rule, the number n of independent variables defining the thermodynamically stable phases(s) of the system is

$$n = c + 2 - p \quad (10.14)$$

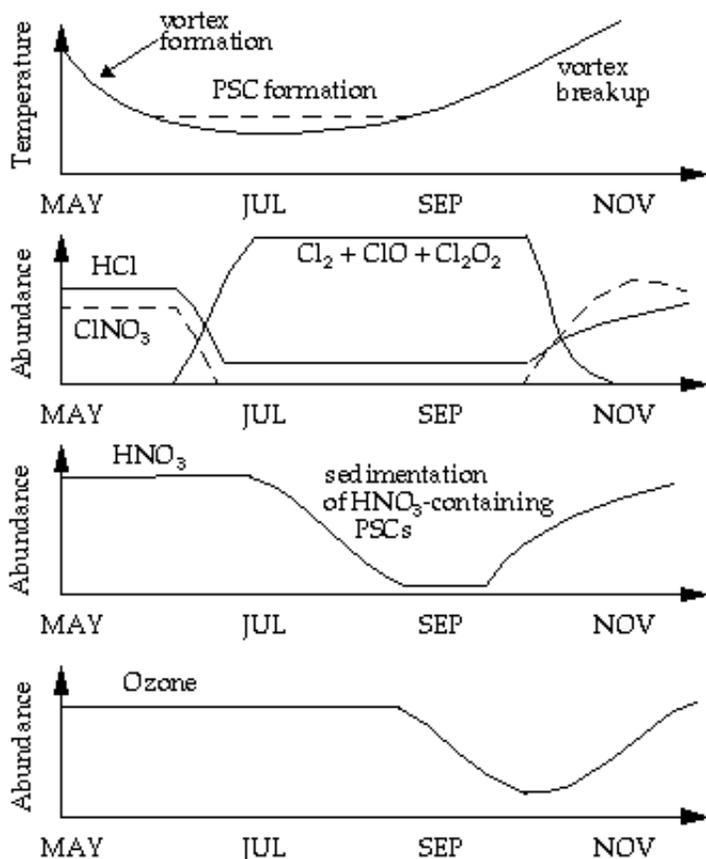
where  $c$  is the number of components of the system (here two:  $\text{HNO}_3$  and  $\text{H}_2\text{O}$ ), and  $p$  is the number of phases present at equilibrium. Equilibrium of a PSC phase with the gas phase ( $p = 2$ ) is defined by two independent variables ( $n = 2$ ). If we are given the  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  vapor pressures (representing two independent variables), then we can define unambiguously the composition of the thermodynamically stable PSC and the temperature at which it forms. That is the information given in [Figure 10-12](#).



**Figure 10-12 Phase diagram for the  $\text{HNO}_3$ - $\text{H}_2\text{O}$  system. The shaded area identifies typical ranges of  $\text{PHNO}_3$  and  $\text{PH}_2\text{O}$  in the lower stratosphere.**

The shaded region in [Figure 10-12](#) indicates the typical ranges of  $\text{PHNO}_3$  and  $\text{PH}_2\text{O}$  in the lower stratosphere. We see that condensation of NAT is possible at temperatures as high as 197 K, consistent with the PSC observations. It appears from [Figure 10-12](#) that NAT represents the principal form of PSCs; pure water ice PSCs can also form under particularly cold conditions ([problem 10.10](#)). Recent investigations show that additional PSC phases form in the ternary  $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  system.

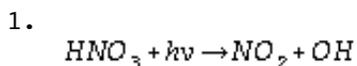
### 10.3.3 Chronology of the ozone hole



**Figure 10-13 Chronology of the antarctic ozone hole**

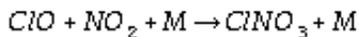
The chronology of the antarctic ozone hole is illustrated in [Figure 10-13](#). It begins with the formation of the antarctic vortex in austral fall (May). As we saw in chapter 4, there is a strong westerly circulation at southern midlatitudes resulting from the contrast in heating between the tropics and polar regions. Because of the lack of topography or land-ocean contrast to disturb the westerly flow at southern midlatitudes, little meridional transport takes place and the antarctic atmosphere is effectively isolated from lower latitudes. This isolation is most pronounced during winter, when the latitudinal heating gradient is strongest. The isolated antarctic air mass in winter is called the antarctic vortex because of the strong circumpolar circulation.

By June, temperatures in the antarctic vortex have dropped to values sufficiently low for PSC formation. Reaction ([R32](#)) then converts HCl and ClNO<sub>3</sub> to Cl<sub>2</sub>, which photolyzes to yield Cl atoms. In the winter, however, loss of O<sub>3</sub> is limited by the lack of solar radiation to photolyze the ClOOC<sub>2</sub> dimer produced in ([R27](#)). Significant depletion of O<sub>3</sub> begins only in September when sufficient light is available for ClOOC<sub>2</sub> photolysis to take place rapidly. By September, however, temperatures have risen sufficiently that all PSCs have evaporated. One would then expect HNO<sub>3</sub> in the vortex to scavenge ClO<sub>x</sub> by



followed by

- 1.

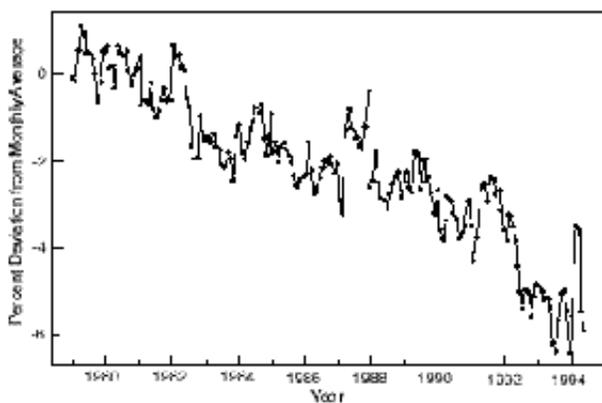


suppressing O<sub>3</sub> loss. This removal of ClO<sub>x</sub> is found to be inefficient, however, because observed HNO<sub>3</sub> concentrations in the springtime antarctic vortex are exceedingly low ( [Figure 10-13](#) ). Depletion of HNO<sub>3</sub> from the antarctic stratosphere is caused by sedimentation of HNO<sub>3</sub>-containing PSC particles over the course of the winter; it is still not understood how the PSC particles grow to sufficiently large sizes to undergo sedimentation. Better understanding of this sedimentation process is critical for assessing the temporal extent of the antarctic ozone hole, and also for predicting the possibility of similar O<sub>3</sub> depletion taking place in the arctic.

There is indeed much concern at present over the possibility of an O<sub>3</sub> hole developing in the arctic. Temperatures in arctic winter occasionally fall to values sufficiently low for PSCs to form and for HCl and ClNO<sub>3</sub> to be converted to ClO<sub>x</sub> ( [Figure 10-11](#) ), but these conditions are generally not persistent enough to allow removal of HNO<sub>3</sub> by PSC sedimentation. As a result, O<sub>3</sub> depletion in arctic spring is suppressed by  $(R16) + (R24)$ . If extensive PSC sedimentation were to take place in arctic winter, one would expect the subsequent development of a springtime arctic O<sub>3</sub> hole. Observations indicate that the arctic stratosphere has cooled in recent years, and a strong correlation is found between this cooling and increased O<sub>3</sub> depletion. One proposed explanation for the cooling is increase in the concentrations of greenhouse gases. Greenhouse gases in the stratosphere have a net cooling effect (in contrast to the troposphere) because they radiate away the heat generated from the absorption of UV by O<sub>3</sub>. Continued cooling of the arctic stratosphere over the next decades could possibly cause the development of an "arctic ozone hole" even as chlorine levels decrease due to the ban on CFCs. This situation is being closely watched by atmospheric chemists.

## 10.4 AEROSOL CHEMISTRY

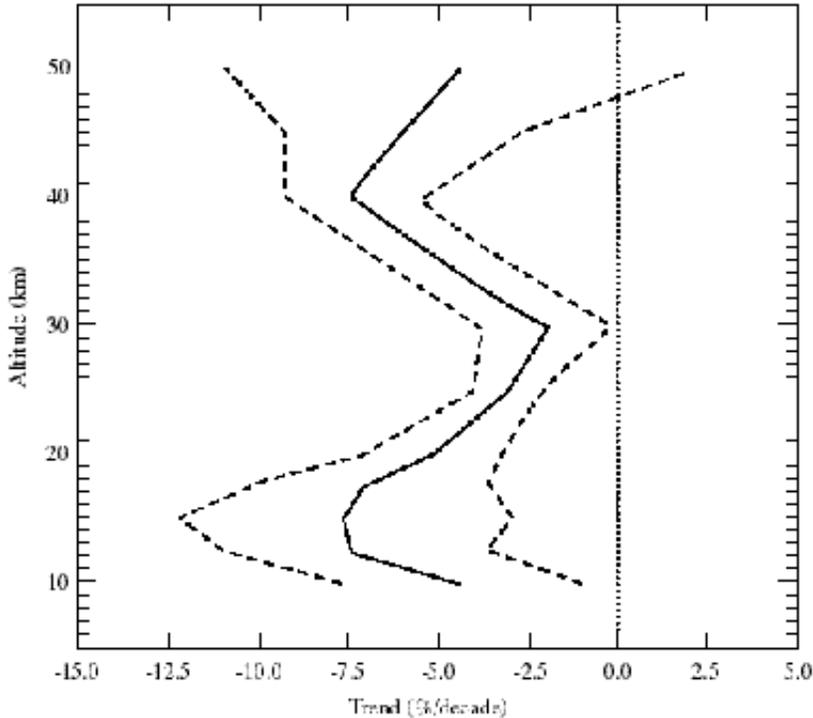
Another major challenge to our understanding of stratospheric chemistry emerged in the early 1990s when long-term observations of O<sub>3</sub> columns from satellites and ground stations revealed large declines in O<sub>3</sub> extending outside the polar regions. The observations ( [Figure 10-14](#) ) indicate a ~6% decrease from 1979 to 1995 in the global mean stratospheric O<sub>3</sub> column at 60oS-60oN, with most of the decrease taking place at midlatitudes.



**Figure 10-14** Trend in the global ozone column at 60oS-60oN for the 1979-1995 period. From WMO, op. cit.

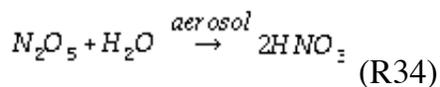
This large decline of O<sub>3</sub> was again a surprise. It was not forecast by the standard gas-phase chemistry models based on the mechanisms in [section 10.2](#) , which predicted only a ~0.1% yr<sup>-1</sup> decrease in the O<sub>3</sub> column for the 1979-1995 period. The models also predicted that

most of the O<sub>3</sub> loss would take place in the upper part of the stratosphere, where CFCs photolyze, but observations show that most of the decrease in the O<sub>3</sub> column actually has taken place in the lowermost stratosphere below 20-km altitude ( [Figure 10-15](#) ). This severe failure of the models cannot be explained by the polar chemistry discussed in [section 10.3](#) because temperatures at midlatitudes are too high. Dilution of the antarctic ozone hole when the polar vortex breaks up in summer is not a viable explanation either because it would induce a seasonality and hemispheric asymmetry in the trend that is not seen in the observations.



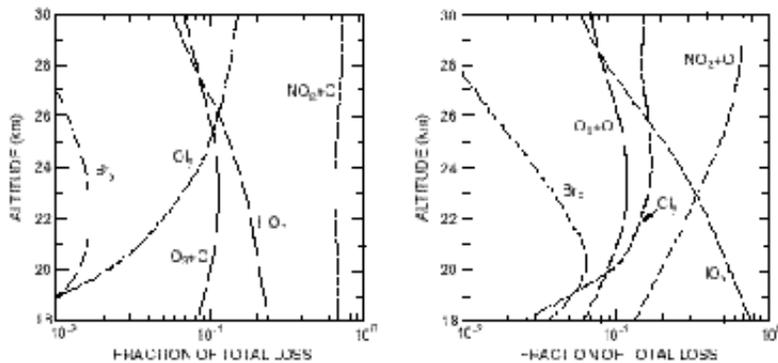
**Figure 10-15 Vertical distribution of the O<sub>3</sub> trend at northern midlatitudes for the period 1980-1996: best estimate (solid line) and uncertainties (dashed lines). Adapted from Scientific Assessment of Ozone Depletion: 1998, WMO. Geneva, 1999.**

Recent research indicates that aerosol chemistry in the lower stratosphere could provide at least a partial explanation for the observed long-term trends of O<sub>3</sub> at midlatitudes. Laboratory experiments have shown that the aqueous H<sub>2</sub>SO<sub>4</sub> aerosol ubiquitously present in the lower stratosphere ( [section 8.1](#) ) provides a medium for the rapid hydrolysis of N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub>:



From the standpoint of the NO<sub>x</sub>-catalyzed O<sub>3</sub> loss mechanism discussed in [section 10.2.2](#) , [\(R34\)](#) simply converts NO<sub>y</sub> from one inactive reservoir form to the other. However, HNO<sub>3</sub> is a longer-lived reservoir than N<sub>2</sub>O<sub>5</sub>, so that conversion of N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub> slows down the regeneration of NO<sub>x</sub> and hence decreases the NO<sub>x</sub>/NO<sub>y</sub> ratio. Although one might expect O<sub>3</sub> loss to be suppressed as a result, the actual picture is more complicated. Lower NO<sub>x</sub> concentrations slow down the deactivation of ClO<sub>x</sub> by conversion to ClONO<sub>2</sub> ([R24](#)), so that ClO<sub>x</sub>-catalyzed O<sub>3</sub> loss increases. Also, a fraction of HNO<sub>3</sub> produced by [\(R34\)](#) eventually photolyzes by [\(R16\)](#), and the sequence [\(R34\)](#) + [\(R16\)](#) provides a source of HO<sub>x</sub> that enhances the HO<sub>x</sub>-catalyzed O<sub>3</sub> loss discussed in [section 10.2.1](#) .

When all these processes are considered, one finds in model calculations that (*R34*) has little net effect on the overall rate of O<sub>3</sub> loss in the lower stratosphere, because the slow-down of the NO<sub>x</sub>-catalyzed loss is balanced by the speed-up of the HO<sub>x</sub>- and ClO<sub>x</sub>-catalyzed losses; in this manner, the gas-phase models of the 1980s were lulled into a false sense of comfort by their ability to balance Ox production and loss ( [Figure 10-7](#) ). The occurrence of (*R34*) implies a much larger sensitivity of O<sub>3</sub> to chlorine levels, which have increased rapidly over the past two decades. [Figure 10-16](#) illustrates this point with model calculations of the relative contributions of different catalytic cycles for O<sub>3</sub> loss, considering gas-phase reactions only (left panel) and including (*R34*) (right panel). Whether or not the enhanced sensitivity to chlorine arising from (*R34*) can explain the observed long-term trends of O<sub>3</sub> ( [Figure 10-14](#) ) is still unclear.



**Figure 10-16** Effect of N<sub>2</sub>O<sub>5</sub> hydrolysis in aerosols on model calculations of ozone loss in the lower stratosphere at midlatitudes. The Figure shows the fractional contributions of individual processes to the total loss of O<sub>3</sub> in model calculations conducted without (left panel) and with (right panel) hydrolysis of N<sub>2</sub>O<sub>5</sub> in aerosols. From McElroy, M.B., et al., *The changing stratosphere*, Planet. Space Sci., 40, 373-401, 1992.

Field observations over the past five years have provided ample evidence that N<sub>2</sub>O<sub>5</sub> hydrolysis in aerosols does indeed take place rapidly in the stratosphere. The observed NO<sub>x</sub>/NO<sub>y</sub> ratio in the lower stratosphere at midlatitudes is lower than expected from purely gas-phase chemistry mechanisms, and more consistent with a mechanism including (*R34*). In addition, the observed ClO/Cl<sub>y</sub> ratio is higher than expected from the gas-phase models, because of the slower ClNO<sub>3</sub> formation resulting from the lower NO<sub>x</sub> levels. Aircraft observations following the Mt. Pinatubo eruption in 1991 indicated large decreases of the NO<sub>x</sub>/NO<sub>y</sub> ratio and increases of the ClO/Cl<sub>y</sub> ratio, as would be expected from (*R34*) taking place on the volcanic aerosols. The resulting enhancement of ClO is thought to be responsible in part for the large decrease in the O<sub>3</sub> column in 1992, the year following the eruption ( [Figure 10-14](#) ).

Further reading:

McElroy, M.B., R.J. Salawitch, and K.R. Minschwaner, *The changing stratosphere*, Planet. Space Sci., 40, 373-401, 1992. Catalytic loss cycles.

Warneck, P., *Chemistry of the Natural Atmosphere*, Academic Press, New York, 1988. Historical survey, photochemistry of O<sub>2</sub> and O<sub>3</sub>.

World Meteorological Organization, *Scientific assessment of ozone depletion: 1998*, WMO, Geneva, 1999. Polar ozone loss, ozone trends.