

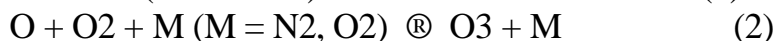
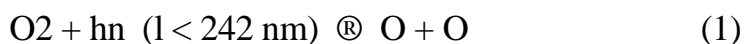
# Dr.Nadia Mohammed

## Stratospheric Chemistry

Stratospheric chemistry became environmental chemistry in the early 1970's when scientists studied the potential stratospheric effects of supersonic aircraft.

They realized that human activity could affect the chemistry of this cold, remote region 10 to 40 km above the Earth. Of greatest concern was the destruction of stratospheric ozone, Earth's protective shield against solar ultraviolet light. This concern sparked a flurry of activity that in 1987 led to an international treaty, the Montreal Protocol, for controlling the production and use of man-made chlorofluorocarbons (CFCs) that affect stratospheric ozone.

Studies of stratospheric chemistry began when Hartley (1881) first proposed ozone's presence in the upper atmosphere. A description of ozone chemistry came later when Chapman proposed the reaction sequence, now called the Chapman mechanism.



The results from this simple model were later found to differ from the observed ozone in two ways. First, the calculated average total ozone column is more than twice as large as measured. The total ozone column is the amount of ozone per unit area of the Earth's surface integrated radially from the surface to space. This difference indicates a problem with the chemistry. Second, the model predicts that ozone concentrations should be largest in the tropics, where the ozone production is greatest whereas observations have shown that the ozone amount is greatest at high latitudes.

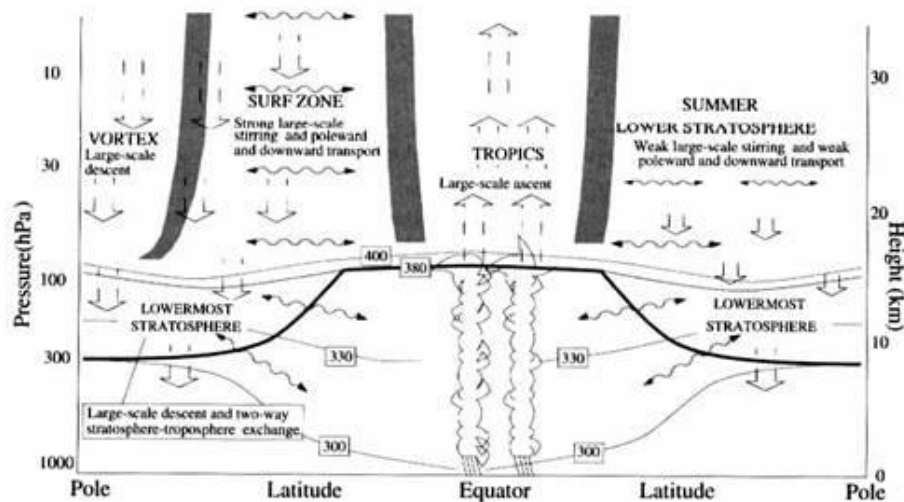
This second difference indicates a problem with ozone transport.

A way to resolve the problem of excess calculated ozone was found in the 1950's, when Hampson (1965) and Bates and Nicolet (1950) proposed that the reactive hydrogen species, hydroxyl (OH) and hydroperoxyl (HO<sub>2</sub>), form a cycle that catalytically destroys ozone. A second cycle involving the reactive nitrogen species, nitrogen dioxide (NO<sub>2</sub>) and nitric oxide (NO), was proposed two decades later.

A few years later, cycles involving reactive chlorine and bromine were proposed. Several other cycles have been found as laboratory studies and atmospheric measurements have uncovered new reactions and chemistry. Adding this chemistry to the Chapman mechanism has greatly improved the agreement between the calculated and observed ozone concentrations.

The differences between the modeled and observed ozone distribution were largely resolved by considering stratospheric transport. Brewer (1949) suggested that the dryness of the stratosphere resulted from air entering the stratosphere in the tropics. Only in the tropics are the temperatures at the tropopause low enough to “freeze-dry” the air to its observed dryness as it enters the stratosphere. Dobson (1956) argued that air entering the stratosphere in the tropics and moving toward high latitudes would create the observed high ozone concentrations there. Once at high latitudes, this air descends back into the troposphere, completing the cycle.

The current view of stratospheric transport is found in the following figure. Note the more rapid descent in the winter hemisphere compared to the summer hemisphere. In fact, mass of air that descends back into the troposphere is almost twice as large in the Northern Hemisphere as it is in the Southern Hemisphere. Note too the weak exchange between the stratosphere and troposphere in the lowermost stratosphere. The gray shaded areas are quasi-barriers to transport between the tropics and the midlatitudes and the winter hemisphere surf zone and the winter vortex.



**Figure 7-6.** Schematic of the principal regions of the lower stratosphere with distinct transport characteristics. Broad arrows denote the diabatic circulation, wavy arrows denote stirring along isentropic surfaces. The thick solid line starting at about 7 km at the pole and ending at about 15 km at the equator is the tropopause, i.e., the notional boundary between troposphere below and stratosphere above. Isentropic surfaces (300K, 330K, 380K, and 400K) are drawn as thin solid lines in the troposphere and lower stratosphere. Isentropic surfaces in the remainder of the stratosphere may be assumed to be roughly horizontal. See text for further discussion. (from WMO 1998)

This general picture of meridional transport from tropics to high latitudes does not describe the actual paths taken by molecules entering the stratosphere. These paths involve rapid circulation around the globe (weeks), rising in the tropics (months), and transport downward toward the poles (months - years). Parcels of air do not stay intact long, but rather, are mixed with other air parcels by eddies, and lose their identity in a week or so. This mixing occurs on quasi-horizontal surfaces that slope toward the poles. The mixing is quasi-horizontal because horizontal transport is much faster than vertical transport. The surfaces slope toward the poles because forces caused by atmospheric waves act as a suction pump that pulls air upward and poleward from the tropics and pushes air downward at middle-to-high latitudes. This quasi-horizontal mixing is rapid in the middle latitudes, but mixing with the tropics and the wintertime polar region is impeded. The transport of air into, through, and out of the stratosphere has a profound influence on the chemistry.

Depending on the exact path taken by a molecule, it can stay in the stratosphere from a few years (taking a path just above the tropopause) or as many as 6-7 years (taking a path through the mesosphere). A typical value is closer to 3 to 4 years. We can see rate of transport up into the tropical stratosphere by looking at the vertical variation of seasonally varying gases, such as CO<sub>2</sub> and H<sub>2</sub>O. For the rest of the stratosphere, we can find the average lifetime

A whole new dimension was added to studies of stratospheric chemistry in 1985, when observations of rapid springtime ozone loss over Antarctica were first reported by members of the British Antarctic Survey. Quick analyses showed that the known chemical cycles could not be responsible. New chemical mechanisms were proposed that involved chlorine chemistry. Most surprising was the discovery that stratospheric particles composed of water vapor and nitric acid, called polar stratospheric clouds (PSCs), act as sites to produce this halogen-dominated chemistry. The reactions of gases on particles, called heterogeneous chemistry, are now known to be important not just for the polar regions but also for the entire lower stratosphere.

The focus of much of the research in stratospheric chemistry over the last fifty years has been on ozone and the possibility of human influences on it. In this chapter, we give a primer to stratospheric ozone chemistry. First is a description of stratospheric structure and ozone climatology. Second is a brief tutorial on chemical concepts used frequently in atmospheric chemistry. Third is a description of stratospheric ozone chemistry in both the tropics and middle latitudes and in the wintertime polar regions.

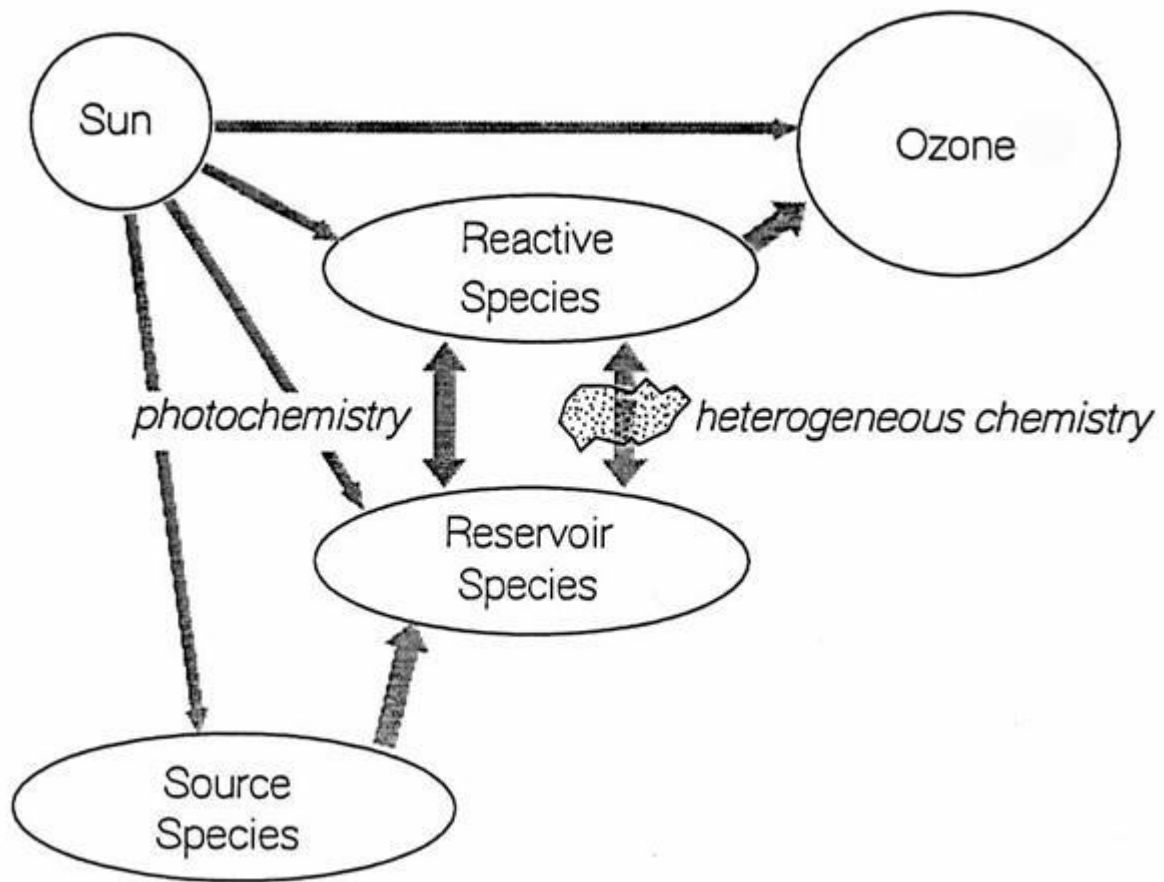
## **The Structure of the Stratosphere**

The stratosphere extends from the tropopause, a temperature minimum near 15 km in the tropics and 10 km at high latitudes, to the stratopause, a temperature maximum, at about 50 km. Temperatures at the tropopause are generally 190-215 K, while temperatures at the stratopause are 240-250 K. Although stratospheric temperatures increase everywhere with height, the temperature values depend upon the location and the season, particularly in the lower stratosphere and upper stratosphere.

Stratospheric temperatures increase with height because stratospheric ozone and, to a lesser extent, molecular oxygen absorb ultraviolet sunlight and convert some of the energy into molecular kinetic energy, or heat. The stratospheric temperature structure gives the stratosphere its stability.

## **Stratospheric Chemical Species**

Chemical species for each chemical family have different functions in stratospheric chemistry, as in the following figure. The source species are generally those chemicals that live long enough in the troposphere to survive transport to the stratosphere. Once they reach the stratosphere, source species are destroyed, either directly by absorption of solar ultraviolet light, or by chemical reactions that are initiated by solar UV. Some products of the photochemical destruction of the source species are either reactive or reservoir species. In this chapter, “reactive” indicates free radicals and other chemical species that are photolyzed into free radicals within minutes. “Reservoir” indicates species such as acids and nitrates that are exchanged with free radicals by reactions or photolysis, but generally over a period of hours to months. All reactive and reservoir species are “trace” species, and have volume mixing ratios of less than 20 parts per billion by volume (ppbv =  $10^{-9}$ ) in air.



## Chemistry of the Tropics and Middle Latitudes

### Source Gases

The source gases for all of the chemical families originate at Earth's surface, even molecular oxygen.

**Oxygen Species.** Photolysis of  $O_2$  is the only source of  $O_3$  and  $O$ ,  $O_x$ , in the stratosphere. Local sources of  $NO_x$  in the lower stratosphere can act as  $O_x$  sources by the photochemical smog reactions, but these are a smaller source than the photolysis of  $O_2$ .

**Hydrogen Species.** Hydrogen has two main sources: H<sub>2</sub>O and CH<sub>4</sub>. The O(<sup>1</sup>D) produced by O<sub>3</sub> photolysis reacts with H<sub>2</sub>O to produce 2 OH molecules. Methane is oxidized by OH and undergoes an oxidation sequence that leads to CO<sub>2</sub> and H<sub>2</sub>O. This sequence creates about two water molecules from each fully oxidized CH<sub>4</sub> molecule. The result is that the sum of mixing ratios of 2 x CH<sub>4</sub> + H<sub>2</sub>O is approximately constant at 6 -7 ppmv throughout the stratosphere.

**Nitrogen Species.** Reactive and reservoir nitrogen, called NO<sub>y</sub>, has three sources in the stratosphere.....

**Chlorine Species.** The main source gases of stratospheric chlorine are the long-lived chlorofluorocarbons (CFCs), the anthropogenic methyl chloroform (CH<sub>3</sub>CCl<sub>3</sub>)..... **Bromine Species**

**Other Halogen Species.** The major source of stratospheric fluorine is the CFCs. The fluorine atoms, once released from the CFCs by photochemistry, rapidly is incorporated into HF, which does not participate in stratospheric chemistry. Source molecules such as SF<sub>6</sub>, C<sub>2</sub>F<sub>6</sub>, and CF<sub>4</sub>, which are being used more widely, are very stable and have lifetimes of thousands of years. Fluorine plays essentially no known role in stratospheric chemistry.