Lecture 35. <u>Stratospheric ozone chemistry.</u>

<u>Part 1.</u> **Formation and destruction of stratospheric ozone.**

Objectives:

1. The formation of ozone: Chapman mechanism.

2. Catalytic ozone destruction.

3. Ozone and UV radiation.

Readings: Turco: p. 407-414; Brimblecombe: 190-194.

1. <u>The formation of ozone: Chapman mechanism.</u>

"Bad ozone": in photochemical smog -> health threat

      in the troposphere -> contributes to global warming

"Good ozone": in the stratosphere -> absorbs biologically harmful UV

          radiation emitted by sun.

➢ Most of the Earth's atmosphere ozone (about 90%) is found in the
stratosphere.

<u>Typical ozone concentrations:</u>

in very clean troposphere: 10 – 40 ppb;

in ozone layer at 25-30 km: about 10 ppm;

• The ozone column abundance is typically specified in Dobson units.

One **Dobson unit, DU,** is the thickness that the ozone column would occupy
at standard temperature and pressure (T =273.2 K, P = 1 atm):

$$1 \; DU = 10^{-3} \; atm \; cm = 2.69 \times 10^{16} \; molecules \; cm^{-2}$$

➢ Total column ozone values range from about 290 to 310 DU over the
globe.

In 1930 S.Chapman, a British scientist, proposed a theory of the formation of ozone in the stratosphere (known as **Chapman mechanism**):

Major steps of Chapman mechanism:

1) Above about 30 km altitude, molecular oxygen absorbs solar radiation (wavelength < 242 nm) and photodissociates:

$$O_2 + h\nu \rightarrow O + O$$
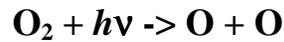
2) The oxygen atom, O, reacts rapidly with O_2 in the presence of a third body, denoted M (M is usually another O_2 or N_2), to form ozone:
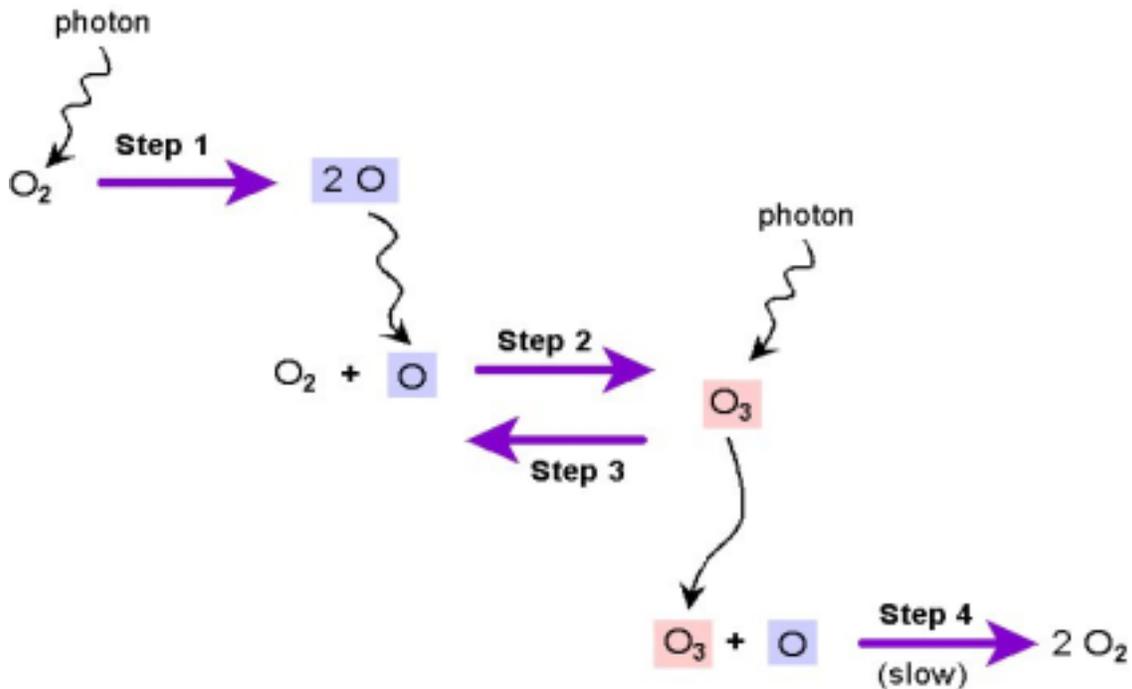
$$O_2 + O + M \rightarrow O_3 + M$$

NOTE: above reaction is the only reaction that produces ozone in the atmosphere!!!

3) Ozone absorbs solar radiation (in the wavelength range of 240 to 320 nm) and decomposes back to O_2 and O:

$$O_3 + h\nu \rightarrow O_2 + O$$
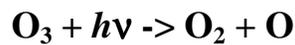
4) Additionally, ozone can react with atomic oxygen to regenerate two molecules of O_2:

$$O_3 + O \rightarrow O_2 + O_2$$

Let's consider the dynamic behavior of reactions (1) –(4).

Rate of reaction (1) = $Rate_1 = J_{O2}\,[O_2]$, where J_{O2} is the photolysis rate constant of the reaction (1).

NOTE: photochemistry, photolysis rate constant, actinic flux, spectral absorption cross section of O_3 and O_2 were introduced in Lecture 7.

Rate of reaction (2) = $Rate_2 = k_2\,[O]\,[O_2]\,[M]$

Rate of reaction (3) = $Rate_3 = J_{O3}\,[O_3]$

Rate of reaction (4) = $Rate_4 = k_4\,[O]\,[O_3]$

Thus, the rate of formation of ozone is

$$d[O_3]/dt = k_2\,[O]\,[O_2]\,[M] - J_{O3}\,[O_3] - k_4\,[O]\,[O_3]$$

and the balance of oxygen atom is

$$d[O]/dt = 2J_{O2}\,[O_2] - k_2\,[O]\,[O_2]\,[M] + J_{O3}\,[O_3] - k_4\,[O]\,[O_3]$$

Comparing the rates of the reactions (1)-(4) for typical stratospheric conditions, we find that $Rate_2$ and $Rate_3$ are greatly exceed $Rate_1$ and $Rate_4$.

- Because the reactions (2)-(3) are very rapid, these reactions rapidly interconvert O and O_3. Thus, O and O_3 can be considered as a single species O_x, called **odd oxygen**:
  $O_x = O + O_3$

Under steady-state conditions, it can be shown that $Rate_1 = Rate_4$ or

$$J_{O2}\,[O_2] = k_4\,[O]\,[O_3] \text{ or } J_{O2}\,[O_2] = k_4\,[O_x]^2 ,$$

Thus, the steady-state concentration of odd oxygen is given

$$[O_x] = (J_{O2}\,[O_2] / k_4)^{1/2}$$

- Since over 99% of the odd oxygen is in the form of O_3, the Chapman mechanism predicts that local stratospheric ozone concentrations are proportional to the square root of O_2 photolysis rate.

Figure 35.1 Zonally averaged rate of ozone formation (molecule cm^{-3} s^{-1}) from the photolysis of O_2 (Johnson, 1975).
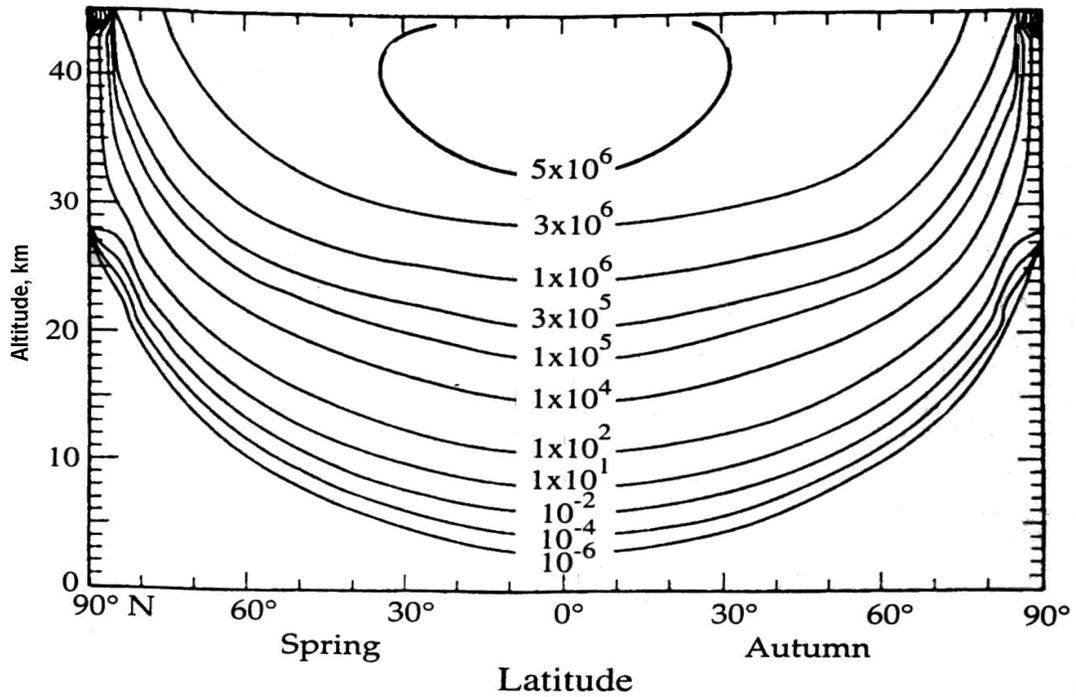

Figure 35.2 Actual zonally averaged ozone concentrations (in units of 10^{12} molecule cm^{-3}) for March 22, (Johnson, 1975).
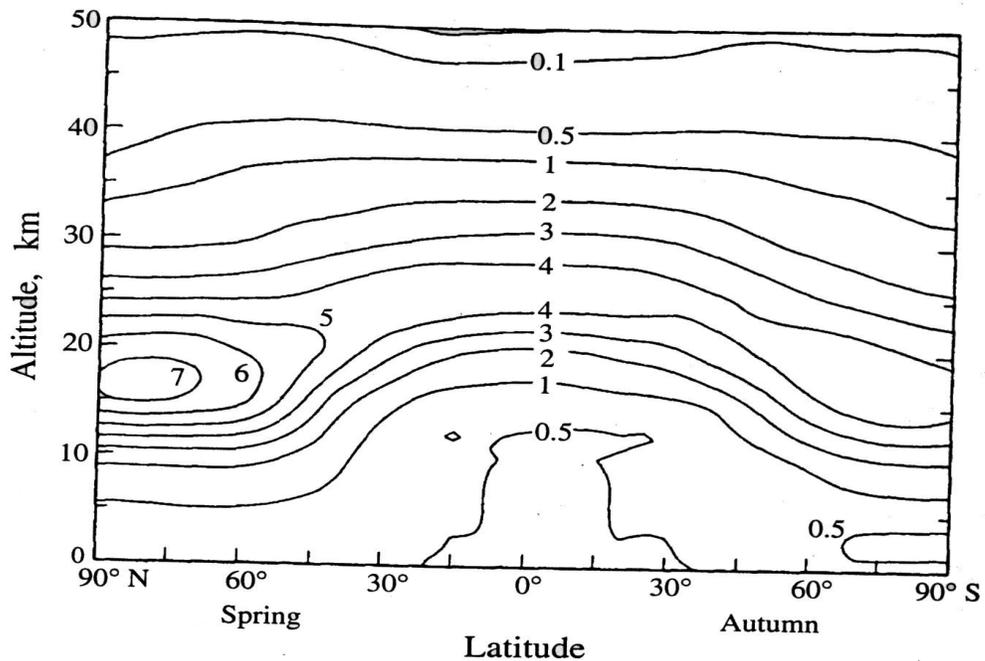
Figure 35.1 shows that ozone production is highest near the equator and increases with increasing altitude, reflecting the dependence on latitudinal variation of solar intensity and zenith angle.

Figure 35.2 shows that actual ozone concentrations are highest at northern latitudes, there is a north-south asymmetry.

- Thus measurements show that the regions of highest ozone concentrations do not coincide with the location of the highest rate of formation of O_3. It is because the horizontal and vertical transport redistributes stratospheric air masses causing redistribution of ozone concentrations.

➢ Measurements indicated that the actual amount of ozone in the stratosphere is about a factor of 2 less that what is predicted by the Chapman mechanism. Thus, it must be concluded that significant additional ozone destruction pathways are present beyond the reaction (4).

2. Catalytic ozone destruction.

1950: Bates and Nicolet proposed the idea of a catalytic loss process involving hydrogen radicals, HO_x ($HO_x = H + OH + HO_2$)

NOTE: The formation of OH in the stratosphere was discussed in Lecture 8.

1970-1971: Crutsen and Johnson revealed the role of nitrogen oxides in the stratospheric catalytic chemistry ($NO_x = NO + NO_2$);

1974-1975: Stolarski, Ciceroni, Molina and Rowland elucidated the effect of chlorine-containing compounds in the stratospheric catalytic chemistry (discussed in Lecture 36).
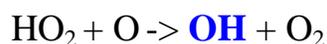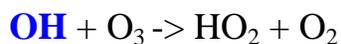
In general form, the ozone destruction in a catalytic cycle is

$$\mathbf{X} + O_3 \rightarrow XO + O_2$$

$$XO + O \rightarrow \mathbf{X} + O_2$$

$$\textbf{Net: } O_3 + O \rightarrow O_2 + O_2$$
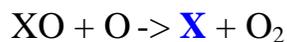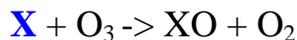
where X is the free radical catalyst.

$\mathbf{X}$ can be H, OH, NO, Cl and Br.

Example, if X = OH we have OH catalytic ozone destruction cycle

$$\mathbf{OH} + O_3 \rightarrow HO_2 + O_2$$

$$HO_2 + O \rightarrow \mathbf{OH} + O_2$$

$$\textbf{Net: } O_3 + O \rightarrow O_2 + O_2$$

where HO_2 is the hydroperoxy radical.

Let's consider NO catalytic ozone destruction cycle

$$\mathbf{NO} + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow \mathbf{NO} + O_2$$

$$\textbf{Net: } O_3 + O \rightarrow O_2 + O_2$$
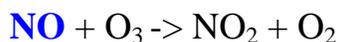
- The principal source of NO_x in the stratosphere is N_2O.

How it works:

About 90% of $\mathbf{N_2O}$ in the stratosphere is destroyed by photolysis

$$\mathbf{N_2O} + h\nu \rightarrow N_2 + O(^1D)$$
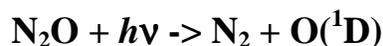
The remainder reacts with the singlet-D oxygen atom, $\mathbf{O(^1D)}$:

$$\mathbf{N_2O} + \mathbf{O(^1D)} \rightarrow 2\ \mathbf{NO}$$

- N_2O has both natural and anthropogenic sources.

NOTE: $\mathbf{N_2O}$ is an important greenhouse gas (discussed in Lectures 33-34).

Thus, if N_2O emission from anthropogenic sources increases => more NO in the stratosphere => ozone depletion (because of NO catalytic ozone destruction cycle)
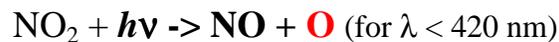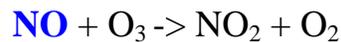

- Another potential sources of NO in the stratosphere: supersonic transport (SST).

NOTE: chlorine chemistry will be discussed in Lecture 36.

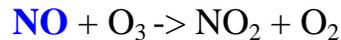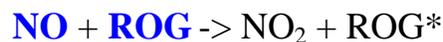Compare ozone formation in the free troposphere, in photochemical smog and in the stratosphere:

Free troposphere:

NO from natural sources

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + h\nu \rightarrow NO + O \text{ (for } \lambda < 420 \text{ nm)}$$

$$O_2 + O + M \rightarrow O_3 + M$$

Photochemical smog:

NO and **ROG** (reactive organic compounds) from car emission

$$NO + ROG \rightarrow NO_2 + ROG*$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + h\nu \rightarrow NO + O \text{ (for } \lambda < 420 \text{ nm)}$$

$$O_2 + O + M \rightarrow O_3 + M$$

Stratosphere:

$$O_2 + h\nu \rightarrow O + O \text{ (for } \lambda < 242 \text{ nm)}$$
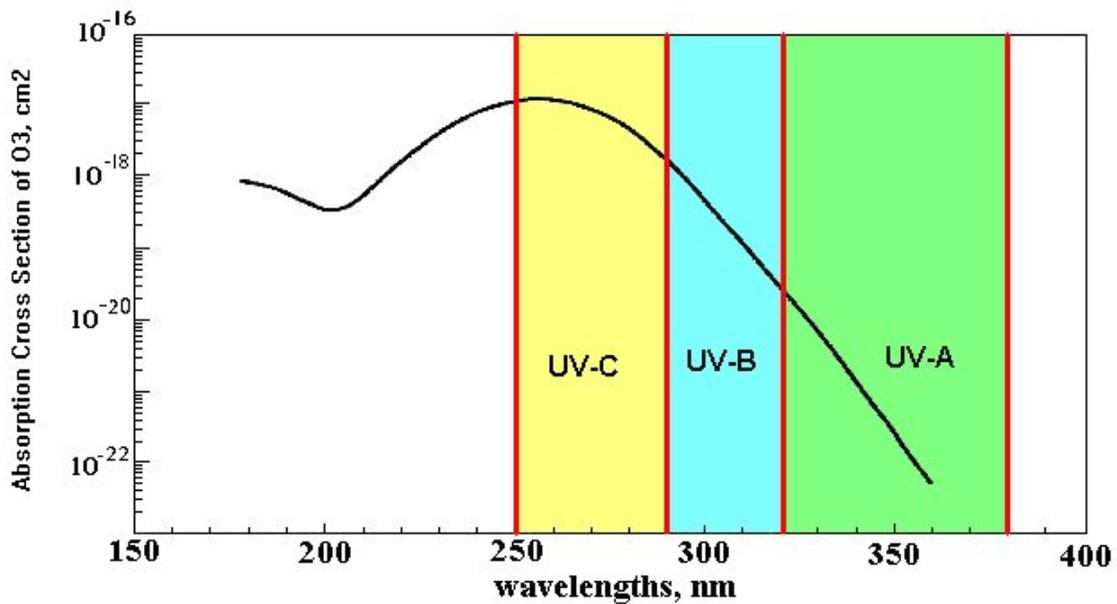
$$O_2 + O + M \rightarrow O_3 + M$$

3. <u>Ozone and UV radiation.</u>

"Good ozone": in the stratosphere -> absorbs biologically harmful UV

radiation emitted by sun.

Figure 35.3 Absorption cross section for ozone at T = 273 K (DeMore et al., 1994) and wavelength regions of near UV radiation.

The health effects depend on UV radiation regions:

UV-A: 320 nm $< \lambda <$ 380 nm

Cause detrimental health consequences

UV-B: 290 nm $< \lambda <$ 320 nm

Biologically hazardous

UV-C: 250 nm $< \lambda <$ 290 nm

Extremely hazardous to people