Homework No. 2 due Monday April 14, 2014 (at beginning of class).
Write out answers in complete sentences. No computation is necessary.

1. What is odd oxygen? How does it relate to ozone?

Odd oxygen is defined to be the combination of atomic oxygen and ozone. Its concentration is defined as $[O_x] = [O] + [O_3]$. *In the troposphere and most of the stratosphere* $[O] << [O_3]$ *so that* $[O_3] \cong [O_x]$. *In the mesosphere atomic oxygen becomes a significant portion of odd oxygen so that its concentration must be considered in deriving ozone from odd oxygen.*

2. What is the primary source for odd oxygen?

The primary source of odd oxygen is the photolysis of O_2 *to produce atomic oxygen atoms that can combine with* O_2 *to form* O_3 *via a 3-body reaction.*

3. What is a typical mixing ratio (mole fraction) of ozone in the stratospheric ozone layer?

In general the mixing ratio of ozone in the stratosphere is in the parts per million range with a peak value of approximately 10 parts per million by volume (ppmv).

4. Temperature increases with increasing altitude in the stratosphere. What is the reason for this behavior?

Ozone in the stratosphere absorbs ultraviolet radiation at wavelengths less than 300 nm. This absorption leads to heating that has a peak value at about 50 km altitude (1 hPa).

5. What is the significance of increasing temperature with altitude in the stratosphere for the transport of chemicals?

Because of heating due to ozone absorption that peaks at the stratopause, the stratosphere is a region that is heated from above making it a permanent inversion layer. This leads to very slow overturning and long lifetimes for chemicals that are injected into the stratosphere. It is a stably-stratified region; hence the name "stratosphere".

6. What are typical mixing ratios for the oxides of nitrogen and chlorine in the stratosphere? Contrast these with the typical mixing ratio of ozone.

Typical mixing ratios for oxides of nitrogen and chlorine are parts per billion (ppbv). These are about a factor of 1000 less than the typical mixing ratio for ozone.

7. Why are the oxides of nitrogen, chlorine, hydrogen and bromine important in the stratosphere?

The oxides of nitrogen, chlorine, hydrogen and bromine are important because they can participate in catalytic cycles that lead to the destruction of ozone. These reactions mimic the natural ozone-loss reaction, $O + O_3 \rightarrow 2O_2$ *(or* $2O_3 \rightarrow 3O_2$*) without themselves being removed from the atmosphere. This allows the parts per billion of oxides to substantially affect the concentration of parts per million of ozone.*

8. What is the role of reactions that form acid anhydrides such as HCl, HNO_3, HBr and HF?

The acid anhydrides serve as temporary reservoirs for the oxides of chlorine, nitrogen, bromine and fluorine. They are formed by reactions such as $Cl + CH_4$ *,* $OH + NO_2 + M$*,* $Br + CH_4$ *, and* $F + CH_4$ *.*

9. What are CFCs? Give a couple of examples.

CFCs are chlorofluorocarbons, carbon-hydrogen compounds in which all of the hydrogen atoms have been replaced by chlorine and fluorine atoms. Examples include CFC-11 ($CFCl_3$*), CFC-12 (*CF_2Cl_2*) and CFC-113 (*CF_3Cl_3*).*

10. Why is the F atom from CFCs not important for ozone depletion?

The reservoir HF is formed by reaction of F atoms with CH_4 *. The HF bond is sufficiently strong that the reaction with OH to release the F atom is endothermic. Thus, once formed, the HF molecule is more like a permanent reservoir than a temporary reservoir. Fluorine is removed from the stratosphere by transport processes before the HF can be returned to a catalytically-active form (F, FO).*

11. What are the important conditions that lead to the formation of the Antarctic ozone hole?

The Antarctic polar night leads to cooling by radiation to space. The region become isolated by circumpolar winds (the polar vortex) that inhibit transport between midlatitudes and the polar region. The vortex becomes both cold and isolated forming a sort of reaction vessel. Cold temperatures lead to the formation of polar stratospheric clouds. These clouds provide surfaces on which heterogeneous reactions can take place, specifically those that return reservoir forms of chlorine (HCl and $ClONO_2$*) back to active forms (Cl and ClO). The actual compound formed in the polar night is* Cl_2*.*

12. What happens to nitrogen oxides in the Antarctic winter?

Nitrogen oxides will form nitric acid during the Antarctic winter. The nitric acid will be taken up as nitric acid tri-hydrate (HNO_3•$3H_2O$) in polar stratospheric clouds. When temperatures get cold enough these particles become incorporated into ice cloud particles that grow to a size that is significant enough to cause them to fall out of the stratosphere removing nitrogen oxides such that it becomes impossible to reform the chlorine nitrate reservoir.

13. What happens to chlorine oxides in the Antarctic winter and spring?

The chlorine oxides are strongly enhanced by the by the reaction of the reservoirs HCl and $ClONO_2$ to form Cl_2. The Cl_2 is photolyzed rapidly when the sun comes up in the Antarctic spring to form Cl atoms. The concentration of chlorine monoxide builds up to around a part per billion allowing the self-reaction of ClO to form the chlorine monoxide dimer Cl_2O_2. The dimer can photolyzed in visible light to form Cl atoms. The chlorine catalytic cycle can then occur without the need for atomic oxygen, which is in very short supply in the lower stratosphere.

14. Why is the Arctic different from the Antarctic with respect to ozone in the "normal" stratosphere? In the "chlorine-perturbed" stratosphere?

The southern hemisphere has a pole-centered land mass (Antarctica) with a circumpolar ocean. The polar vortex that forms during the polar night is relatively undisturbed, leading to strong winds and isolation such that excursions of the polar air into sunlight are rare. By contrast, the northern hemisphere has land masses and mountains that disturb the circumpolar flow. The waves formed propagate upward to disturb the flow of air around the polar vortex, leading to warming that prevents temperatures from getting as cold in the Arctic as they do in the Antarctic. A second impact is that the vortex is stretched and distorted exposing the air to sunlight in the middle of the winter. Finally, temperatures seldom get cold enough to form water-ice that can fall out of the stratosphere and remove the nitrate that is trapped in the particles.

15. What does the Montreal Protocol do to attempt to return stratospheric ozone to "normal"?

The Montreal protocol regulates the production of CFCs to remove the source of chlorine oxides. The CFCs that are the source of chlorine oxides have very long lifetimes in the atmosphere (50 to 100 years). The CFCs that have been released to the atmosphere will slowly decay and the chlorine oxides will decrease with them. As the excess loss of ozone is removed, the amount of ozone in the stratosphere will slowly increase.