

Atmospheric Chemistry: Quiz #2. 16 April 2014

1. Stratospheric ozone absorbs ultraviolet radiation. This absorption leads to heating of the stratosphere, creating a permanent inversion layer in which temperature increases with altitude. The peak mixing ratio of ozone occurs at approximately 35 km altitude. The peak temperature occurs at the higher altitude of 50 km. Why is the temperature maximum at this higher altitude?

***Atmospheric density falls off exponentially with altitude with a 7-8 km scale height. Thus the density at 50 km is about  $1/e^2$  smaller than the density at 35 km ( $1/e^2 \approx 0.13$ ). The same amount of heating at 50 km would have an 8 times larger effect on temperature (the heat capacity of a less dense atmosphere is smaller). This is partially counteracted by the falloff of the density of ozone between 35 and 50 km. Another effect that contributes to the difference is that ozone between 50 and 35 km absorbs some of the radiation that can contribute to heating at the lower altitude.***

2. Describe the sequence of events that occur to cause the Antarctic ozone depletion (ozone hole) in the spring of each year. What are the key meteorological conditions? What happens to nitric acid and the nitrogen oxides? What happens to chlorine and the chlorine oxides? What triggers the timing for the rapid ozone depletion? What causes the depletion to end?

***Southern polar vortex is isolated and dark. Radiation to space cools the stratosphere to the point where polar stratospheric clouds can form. The first clouds to form consist of nitric acid trihydrate ( $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ ) that condenses at temperatures near 195K. In the dark,  $\text{NO}_x$  is mostly in the form of  $\text{HNO}_3$  and  $\text{ClONO}_2$ . The  $\text{HNO}_3$  is incorporated into the clouds and not available for reaction. When the temperatures go below 188K, water-ice clouds can form much larger particles that fall out and take the  $\text{HNO}_3$  with them both dehydrating and denitrifying the polar stratosphere. The surfaces of these clouds lead to heterogeneous reactions of chlorine reservoirs,  $\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 (\text{gas}) + \text{HNO}_3 (\text{solid})$ . The  $\text{Cl}_2$  accumulates in the polar night and the  $\text{HNO}_3$  is stuck on the particle. When the sun comes up in the spring,  $\text{Cl}_2$  is rapidly photolyzed to  $\text{Cl}$  atoms, triggering the beginning of polar ozone depletion. The draining of the chlorine reservoirs to active chlorine can increase active chlorine by as much as a factor of 100 leading to sufficient chlorine for the self-reaction  $\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2\text{O}_2$ , which is followed by  $\text{Cl}_2\text{O}_2 + h\nu \rightarrow \text{Cl} + \text{ClOO}$ .  $\text{ClOO}$  falls apart to  $\text{Cl} + \text{O}_2$ . Thus chlorine goes through a catalytic cycle that doesn't require atomic oxygen, which is in short supply in the lower stratosphere. The depletion ends when there is no more ozone or when the vortex breaks up mixing in air from midlatitudes with  $\text{NO}_x$ ,  $\text{O}_3$  and other molecules.***

3. How can volcanoes affect stratospheric ozone? What is the key chemical? How does it reach the stratosphere? What happens to form small particles? Why are “small” particles important? What is the sequence of reactions that occur because of the presence of volcanic particles in the stratosphere?

***Volcanoes affect ozone by injecting gases directly into the stratosphere. The key chemical is sulfur dioxide, SO<sub>2</sub>. SO<sub>2</sub> is converted to sulfuric acid, H<sub>2</sub>SO<sub>4</sub> by a series of reactions. H<sub>2</sub>SO<sub>4</sub> coagulates to form small particles. “Small” particles are important because they act like gases in the stratosphere and are not removed by gravitational settling. Small particles also have more surface area per unit volume for heterogeneous reactions. The key heterogeneous reaction is N<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O → 2 HNO<sub>3</sub>. This reduces NO<sub>x</sub> thus reducing the catalysis of ozone depletion by NO<sub>x</sub> reactions (leading to a potential increase in ozone). The NO<sub>x</sub> reduction also leads to a decrease in the interference of NO<sub>x</sub> in both the ClO<sub>x</sub> and HO<sub>x</sub> catalytic ozone-destruction cycles. Thus volcanic eruptions have competing effects; at low chlorine amounts ozone destruction is more favored. At high chlorine amounts, volcanoes may cause a net increase in ozone.***

4. Reaction with hydroxyl radicals is the main removal process in the troposphere for most hydrocarbons released at the surface. What is the expression for the lifetime of a hydrocarbon due to reaction with hydroxyl?

$$\tau_{OH,HC} = 1/(k_{OH,HC} [OH])$$

5. a) What is the lifetime of CH<sub>4</sub> due to reaction with hydroxyl if the rate coefficient is 2 x 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup> and the OH concentration is 2 x 10<sup>6</sup> molecules cm<sup>-3</sup>? Express the answer in years (1 year = 3.15 x 10<sup>7</sup> sec).

$$\tau_{OH,CH_4} = 1/(k_{OH,CH_4} [OH])$$

$$\tau_{OH,CH_4} = 1/(2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \cdot 2 \times 10^6 \text{ molecule cm}^{-3}) = 0.25 \times 10^9 \text{ sec} = 7.9 \text{ years}$$

b) What is the lifetime of ethane due to reaction with hydroxyl?  
(k<sub>OH,C<sub>2</sub>H<sub>6</sub></sub> = 1.3 x 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>)

$$\tau_{OH,C_2H_6} = 1/(k_{OH,C_2H_6} [OH])$$

$$\tau_{OH,C_2H_6} = 1/(1.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \cdot 2 \times 10^6 \text{ molecule cm}^{-3}) = 0.38 \times 10^7 \text{ sec} = 0.12 \text{ years} = 1.5 \text{ months}$$