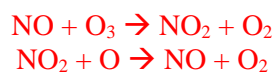


Week 8 Questions, summarized!

1. Do large solar flares ever affect ozone levels in the stratosphere (with any significance)?
2. Has this ever been measured / would it even be possible?

Yes! As far as I understand the basic impacts, additional high energy radiation impinging on the upper part of the stratosphere can produce some ozone, but perhaps more importantly, production of nitric oxide (NO) by the deposition of high energy radiation (I believe by dissociating nitrogen, or N₂) can destroy ozone through catalytic reactions:



Here is a useful resource on the impacts of solar flares on the upper atmosphere.

<https://www.sciencedaily.com/releases/2001/08/010802080620.htm>

3. I don't understand the significance of some symbols that follow certain elements or compounds. For example O₂(1Δ) or O(1D) in hw 12. I think I've seen some sigmas too, and it appeared on the exam. I know that for this class I can just match the symbols and copy the value from the table, but can you explain what these mean?

Ah, well. This is a great question, and one that I've tried to gloss over, so my apologies! Basically, there are a few very important aspects of atomic and molecular orbitals that govern their properties – things like electronic energy, angular momentum, and electron spin. We talk about “electron configurations” and “molecular energy states”, and it is a bit of a complicated process by which spectroscopists know what orbital a particular electron is in (and even saying that an electron is in an “orbital” is construct of quantum mechanics that helps to explain some features of molecular spectroscopy).

There are also some issues related to coupling of orbitals (even more complicated) that feed into these labels called “term symbols.” There is no easy way to give a crash course on these symbols. But here is a link to a video that might help to illustrate how these symbols are determined (don't expect to understand much. This stuff is difficult!):

<https://www.youtube.com/watch?v=D4QxlGAPIWs>

For this class, what matters most is that you recognize that molecules have lots of electrons and those electrons can occupy various orbitals in the molecule. In addition, the electrons have spin, and there are various ways to configure those spins. Some orbital and spin configurations have lower energies than others (meaning that when you put those electrons into the molecule, more energy is released). To reach higher energy levels, the molecule requires the absorption of energy. This can come from collisions, but more likely it will come from absorption of a photon. When a photon is absorbed, only certain transitions are allowed – these are called “allowed” transitions. Other transitions (called “forbidden”) are not allowed because of some property of the molecule that can't be conserved in the process of absorbing the photon.

So because photolysis involves the absorption of a photon, we have to take note of the various states of a molecule, the energies of those states (which determines the frequency of light that can be absorbed), and the “quantum rules” for absorbing photons. It is often those quantum rules that determine whether or not a molecule will absorb light of a particular frequency. Then, we need to follow the evolution of the energy in the molecule. Sometimes, the energy isn’t partitioned into a single bond, and the molecule will vibrate and rotate many times before falling apart, or it might even reradiate a photon and return to the ground state. When this occurs, we tend to see strong “bands” in the absorption spectrum. And if the molecule doesn’t fall apart, it will not “photodissociate” at that frequency. For such a process, we have a quantum “yield” of zero. That is, no fragments are produced by the absorption of the light.

4. I was wondering if you could explain the evolution and current view points on the peak oil theory.

Hmm. This is a good one! I think I’ll have to spend some time to review, but my understanding at this stage is that the easy oil has been discovered, and this is what people were thinking back in the 1960s and 1970s – that as this oil was extracted, it would be more difficult to find new oil deposits, and that eventually oil production would decrease. As we know, technology has allowed for extraction of oil from places where it was impossible to extract oil before. These ‘finds’ have been very productive – a good example is the oil shale of Canada and off-shore deposits. But it’s also been the case that new large deposits are discovered that upend the view that conventional oil will soon peak. Here’s a list of the world’s largest oil fields. My own view is that the ‘age of oil’ will end before we run out of oil because we will start producing cheaper energy (e.g., from renewables), and “peak oil” won’t really mean anything.

https://en.wikipedia.org/wiki/List_of_oil_fields

5. Can you run down the "pieces come together slide again?" Presentation ATOC 3500-Week 8/9. Catalytic Cycles and Stratospheric Ozone Part 3.

The main point of the figure was to show you how to put together the “pieces” that explain how a molecule released at the surface gets to the stratosphere and ultimately destroys ozone. Each step, taken by itself, represents a lot of physics and chemistry. It’s the sum total of all these steps that is needed to make the case for the “human-caused” depletion of ozone.

6. Will there be extra credit?

I’m not sure anyone will need it – that is, my plan is to be generous in the awarding of points for problems, so that a test by itself won’t make or break a grade.

7. What would be the most plausible way to fix the ozone hole issue (if possible) and how many years would it take to "restore" it?

Well, you know the old adage – that the best fix for a problem is to avoid creating it in the first place. But since the horse is already out of the barn, it’s too late to close the door. Some people have suggested putting NO_x into the ozone hole, to titrate out the chlorine (remember, part of the process that creates the ozone hole is the sedimentation of ice/nitric acid, which removes NO_x, and that leads to enhancements of ozone-destroying chlorine). But NO_x also destroys ozone, so

it's unclear whether adding NO_x might trigger some other process that we haven't considered. So it would be wise to try to understand some of these non-linear feedbacks before trying to solve the problem with more chemicals. Also, if you estimate the mass of material that you need to add to offset the ozone loss, it is a HUGE number. Millions or billions of tons. That might make things unfeasible just from the implementation point of view. Finally, temperatures are important for the ozone hole (they help with the formation of the polar vortex and they cause polar stratospheric clouds to form). And temperatures in the stratosphere are dropping as we add greenhouse gases (a complicated process I will try to mention soon).

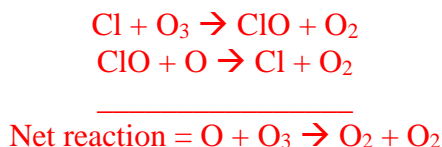
8. I have been reading about the NO_x chemistry in the atmosphere. Are we going to talk about it in class as well? I find it a little bit confusing.

Yes. Let's defer for now. We'll dive into NO_x more when we talk about acid rain and tropospheric smog. Maybe that will be a good time to revisit all the important things NO_x does.

9. I'm still not really sure I understand when you say that one reaction with O destroys two ozone molecules. How does that happen?

So this is really a bit of hand-waving, in that one needs to look at each reaction individually and sum up those that destroy ozone, add back those that produce ozone, and ignore those that do nothing. This is what we mean by "production and loss" (or "P" and "L") when we talk about modeling the concentration of a particular molecule.

But there is one handy (not necessarily 100% accurate) way of explaining that "two ozone molecules are destroyed each time a catalytic cycle occurs." Consider chlorine:



We have defined "odd oxygen" to deal with the fact that any time there is an O atom it will form ozone. So by the converse, removing an O atom by this reaction removes a potential ozone molecule. So this "explains" why this sequence of reactions ends up destroying two ozone molecules. But an easier way to represent this is to consider where the O atom usually comes from:



When we add this third reaction to the chlorine cycle, we get a net reaction that looks like:



You might wonder why I didn't just say this in class. Part of my reluctance to show the catalytic cycle as three steps is that (1) it's easier to just show two, and remember that

whenever you see an oxygen atom, think of it as an ozone that is just missing O₂. But (2), the true result of a catalytic involves a few more considerations that aren't really worth going into, but they have to do with partitioning of the various forms of a radical. When we start digging deeper into this, we really need a model to calculate the exact ozone loss, which could be 1.95 molecules per reaction cycle or even something larger than 2. So it really won't matter if we try to represent it symbolically. We'll need a computer to get it right. (3) Finally, and perhaps most importantly, since there are true catalytic cycles that have a net reaction that is $O_3 + O_3 \rightarrow O_2 + O_2 + O_2$, which doesn't necessarily require sunlight, and because O atoms come from photolysis of ozone, which does require sunlight, I don't like to mix these up. So I prefer to just remember that when I see an O atom, I just consider it a potential ozone molecule, so that if an O atom is destroyed in a reaction, it's pretty much the same as destroying another ozone molecule.

10. What are the sources of other halogens that destroy ozone?

So there are many chlorine containing compounds, the majority of which are man-made. But one, methyl chloride (CHCl₃), comes predominantly from the ocean (it is produced by phytoplankton), and it is responsible for significant ozone loss. We don't consider this a problem, because it was part of the natural balance before humans began increasing the abundances of other, non-naturally occurring forms of chlorine. Bromine, obviously is another halogen to consider. Human sources include halons used in some extinguishers, methyl bromide, a fumigant, and some minor compounds used in industrial processes. There are also some natural emissions of bromine, similar to those of chlorine, including methyl bromide. About half of the atmospheric methyl bromide comes from human practices and half are natural, making it difficult to attribute ozone losses to humans alone.

11. What makes different radicals such as Ox, HOx, ClOx, and NOx contribute to Ozone loss at different altitudes? Does this have anything to do with their lifetimes?

It isn't so much the lifetimes that matter, but rather the rates of the various reactions that lead to ozone destruction. Each radical has an abundance that is determined by a complex series of reactions, and this abundance, along with the relevant rate constants, determine the rate of ozone loss. Some radicals are more abundant higher in altitude, some lower in altitude. So this is what controls the relative rates of ozone destruction by the various radical families.

12. Why is the ozone hole above the Antarctica, not other parts of the earth? The CFCs responsible for Ozone loss shouldn't be everywhere in the atmosphere?

Yes, so the CFCs are pretty uniformly distributed throughout the stratosphere. Once there, they photolyze in sunlight to release chlorine atoms, which then undergo a series of chemical reactions that produce various species. We call the CFCs "organic chlorine" and the breakdown products "inorganic chlorine." When inorganic forms of chlorine react with methane and NO_x in the atmosphere they form HCl (hydrochloric acid) and ClONO₂ (chlorine nitrate). These species

don't normally destroy ozone. But in the winter polar stratosphere, HCl and ClONO₂ react on surfaces of polar stratospheric clouds that form in the cold temperatures to produce Cl₂, a compound that rapidly photolyzes when dim sunlight returns to Antarctica in springtime. The chlorine atoms then destroy ozone via a catalytic cycle involving ClO + ClO → ClOCl, as we worked out in Problem 18, and ozone keeps being destroyed until something stops the ClO from reforming. Normally, NO_x is what reacts with ClO to stop ozone destruction, but over Antarctica NO_x is removed by the polar stratospheric clouds, which fall out just like snow. The only way to stop ozone depletion, then, is for air that has lots of NO_x to mix back in. This takes many months, which leaves plenty of time for chlorine to destroy nearly all of the ozone that is present.

So ozone "holes" only form in air masses that have NO_x removed by some sort of heterogeneous reaction, which also takes chlorine from HCl and ClONO₂ and turns it into ClO. This happens every year over Antarctica and some years over the Arctic. It isn't as frequent over the Arctic because temperatures are warmer, so polar stratospheric clouds aren't as frequent, and less NO_x is removed by sedimentation.

13. In problem 17, we were supposed to compare the rates to JPL values. The JPL tables on pages 14-39 make no mention of J or a photolysis rate constant. How were these determined?

So the place to look in the JPL book is way at the back, where J values (or J coefficients) are plotted, rather than tabulated. Let me know if you still can't find them. These are determined by taking the integral of the product of solar flux, absorption cross section, and quantum yield, just like we did in Problem 17, and doing the integral at high resolution so that the results are accurate.

14. When we calculate the energy required for photolysis by calculating the change of enthalpy for a reaction, we end up with a given wavelength based on the energy of a photon. Will any photon with this wavelength or lower (higher energy) excite this? Or do certain molecules need a specific range. I know you mentioned that O₂ requires UV...

No. Only photons with energies that correspond to "allowed transitions" of the molecule will occur. There are lots of wavelengths of light that aren't absorbed by molecules. This is why most molecules are transparent in the visible, and we can't see them, even though visible light can break the molecular bond. It turns out that the energy of photons in the visible and infrared portion of the spectrum isn't enough to excite the molecule into an upper electronic state, and so the molecule simply ignores those photons. Most molecules, however, absorb in the ultraviolet. So this is why we look carefully at the behavior of the molecule we are examining at the cutoff for solar UV – 300 to 310 nm. If a molecule will absorb wavelengths longer than 310 nm, it will pretty much photolyze everywhere there is sunlight. If not, the molecule might survive long enough to travel to the stratosphere. But once in the stratosphere, it will be rapidly broken down by the UV light that is present there.

15. I would like to learn more about the absorption spectra, where the shape comes from (min values look like a hill).

Ok great! I'd probably have to steer you to some reading material, simply because I probably can't do the problem justice with the time that I can devote to getting things in a proper format. I'll try to look for a good source, and put up a link.

16. I would also be interested in more infos about rotational, vibrational energy storage in molecules. (No math, just simplified models, visualizations to get a better feeling for what is going on)

Ditto – let me look for a good resource.