Week 4 Questions, summarized!

1. Homework Problem 7 asked us to determine the energy released from a composite reaction to form formaldehyde from hydroxide and methane. Why was it necessary to include the fifth reaction in the string of composite reactions? Producing OH and NO2 from HO2 and NO is not an intermediate step in the reaction and does not involve the overall reactants or products, so this extra reaction seems irrelevant.

   The main point of the problem was just to give examples of heats of formation, and how those might be related to the rate of a reaction (as a lead-in to calculations of rate constants using Arrhenius expressions). So it was, in a sense, somewhat arbitrary where I cut off the reaction sequence (or extended it).

2. How does assuming a steady-state of an intermediate product (AB*) relate to AB* having a short lifetime and reacting as soon as it is produced, as described in page 156 of the text?

   I tend to think of this in the opposite sense, that species with short lifetimes are typically in steady state (as long as there is both a source and a sink, of course). The steady state assumption, then, is just a way to simplifying calculations of complex reaction schemes.

3. Sunlight must drive a lot of reactions in the atmosphere, how many, are there specific molecules that are of interest?

   The answer depends on what you are trying to do. If you want rough estimates of things, like ozone loss, acid rain, etc. you can use subsets of the full set of important molecules. Sometimes, dozens of species are enough to get the rough answer. But if you are trying to deduce subtle changes in the atmosphere, or you want highly accurate results, you might need 100s to 1000s of molecules to do the job.

4. How quickly does O2 become O3 in the atmosphere?

   This depends on altitude. Above 50 km, the O_2 photolysis rate coefficient is about 10^{-9} s^{-1}. So this would mean that a typical O_2 molecule is photolyzed every 31 years. In the troposphere, the photolysis rate coefficient is smaller than 10^{-14} s^{-1}, so an O_2 molecule can survive 3 million years without being photolyzed (so, clearly something else much be making ozone in the troposphere).

5. What ion-ion or ion-molecule reactions are important and where in the atmosphere do they occur?

   This is a good question! In the upper atmosphere, say, above 80 km, pretty much all the important reactions are ion-molecule (ion-ion are somewhat rare, mainly because ions are so reactive that their concentrations are small, so the product of two small numbers is very small). Examples of important reactions are:

$$N_2^+ + O_2 \rightarrow N_2 + O_2^+$$

$$H^+ + O \rightarrow O^+ + H$$

$$N_2^+ + O \rightarrow N + NO^+$$

$$O_2^+ + N_2 \rightarrow NO + NO^+$$

And there are also a lot of interesting reactions with electrons.

6. Do termolecular reactions in the troposphere usually follow the low-pressure or high-pressure limit? Or is it completely reaction-dependent?

Most reactions are closer to their high-pressure limits than low-pressure, but it really depends on complexity of the molecules that are reacting. Simpler molecules are far from their high-pressure limits, whereas complex molecules with a larger number of degrees of freedom can be at their high-pressure limits. In a sense, it doesn't really matter, insofar as a termolecular reaction is just one with a more complicated formula for a reaction rate coefficient. In the end, we just worry about the two reactants, A and B, and less about the M that is quenching the intermediate.

7. Will we have to derive reaction rate equations for homework or the exam?

Yes!

8. What is polychromatic radiation, or rather what is it in regards to our atmosphere?

This really is referring to the solar spectrum, which spans the ultraviolet to the infrared. It's really just visible and shorter wavelengths that result in interesting chemistry, though.

9. Would you be able to spend a little more time on the important things?

Sorry! I hope I'm doing a bit more of that now. Let me know if you feel otherwise!

10. With regard to pollutants, how does the lifetime affect the impact of the pollutant? For example there are pollutants that are bad and have a long lifetime, but are there a lot of pollutants with short lifetimes that could be worse?

It isn't strictly a "if short lived, more important or less important" relationship. Some short-lived compounds are not important, some are very important, and the same is true for long-lived. So it really depends on the question.

11. I am very confused with units in R for problem #11. I guess I am missing something in H=RT/g, but I kept getting [km kg] or other units...

R is a confusing quantity. It's really just a constant that is used to get the right dimensions in the ideal gas law. So PV = nRT has units of pressure, volume, amount (n) and temperature. So R has to be in the units that are appropriate for the particular problem. I like using Atmospheres for pressure, Kelvin for temperature, Liters for volume, and moles for quantity. In this case, R would be in units of "L Atm mol^{-1} K^{-1}." But if you want to derive a quantity in "molecules per cubic centimeter", you have to find R in different units. Easy enough to do the conversions, but you still have to work through them (or hope someone has done it for you already).

12. I just found in chapter 2 that H= R*T/(M*g), is that why I kept getting kg*km? I am confused...

So if R is written in the right units, you don't need to worry about mass. If R is in units that include mass, you'd need to divide it back out. What do we mean by mass? A mole of N_2 weighs 28 grams. So if you use "moles" in R, you won't have mass. But if you use mass in R, you'd need to divide by the molecular weight of air, which is 29 g mol^{-1}. The key here is just to be careful with the units of R. I wish it were easier!

13. What does the Paris Agreement means for the future of climate policy and the climate itself, and what effects can the recent news you shared in class regarding the US and China signing along have on the future of the agreement?

I think the biggest breakthrough with Paris is that finally something might get done, rather than just constant meetings with no real progress. I.e. "getting things done" is the new mantra. India just signed too, so that puts the wheels into motion.

14. How could this election year and its outcomes and the years to come affect the future of this agreement and similar orders, agreements, and regulations soon to be or already in place?

The Paris agreement seems to fall outside the political sphere this time around. I personally think that not much will change with a new administration. A lot of Paris is about "voluntary" and " "non-binding" measures. Let's hope that this leads to some progress and people see that it is possible to help the environment and still grow the economy.

15. Why is O-singlet-D called that? I don't understand the nomenclature for electronic states (but the px2py2pz0 does make sense)

Well, it's a little tricky. I'm not sure I can explain it easily, except that the "singlet" refers to total electron spin (zero, in this case, is called "singlet'). Triplet refers to two electrons with spins in the same direction (so a total of "one" for spin, since each spin is considered ½). The D refers to total angular momentum of the occupied orbitals, and that is a little more difficult to explain.

16. In your BrO paper, the reaction list looked bimolecular. Where was the termoleculer reaction part of that paper? Also in my Stat Thermo class I am just starting to look at those potential energy figures like your one in the paper and they don't totally make sense there, but I'm hoping they will make sense in a few weeks.

If you mean the BrO + ClO → BrCl + O_2, it's the step that quenches the BrOOCl intermediate that would cause the overall scheme to appear "termolecular." But as I noted in class, one of the things I did in my dissertation was to show that a termolecular reaction is really made up of a series of bimolecular steps, and it's just the complicated reaction scheme that needs a pressure-dependent term to explain how the rate varies with total pressure. Each step can be treated as a bimolecular reaction.

17. How do molecules like HO2 form? You mentioned that molecules like these aren't very stable, which makes sense, since basic chemistry tells me that a single hydrogen atom can't bond with two oxygens. Does it have to do with radicals?

HO_2 is formed a few ways. We'll get to this soon. They aren't very stable, which is why they are so important for keeping chain reactions going. And yes, neutral hydrogen has only one electron, and that, by definition is called a radical. But in the case of HO_2, it's the O that is the reactive end, since H is bonded to one of the Os.

18. Clouds appear to be relatively coherent structures. Do chemicals "pockets" form and move in similar fashions, or is a uniform distribution pretty accurate?

I’m not so sure clouds are as coherent as you think. Clouds are just condensed water…that is, they are portions of the atmosphere where the temperature is below the saturation point. When you are in a cloud, there is a lot of variability in the water, just like outside a cloud. For example, at a given temperature outside a cloud, the water vapor in the air can vary from nearly nothing (i.e., very low relative humidity) to 99% of saturation, and the air looks cloud-free. In a cloud, there can be some parts that have lots of water and some that are very close to saturation…say 101% of saturation. These will all have cloud droplets, so they look “coherent” as you say, but they are still very different air masses, in terms of their composition.