Ozone Depletion

In the late 1970s, it was noticed that there were dramatic drops in atmospheric ozone (O_3) in the stratosphere. Ozone is toxic, but at higher elevations it can absorb UV radiation from space. It was realized that the reason for this enormous drop was the presence of halogen (fluorine, bromine, etc...) radicals in the stratosphere due to chemicals such as CFCs (refrigerants). The goal of this problem is to show you how a simple model can predict how a very small concentration of these radicals can have a catastrophic effect.

To begin, let us consider the natural "ozone cycle". An ozone molecule begins its life when a high energy photon interacts with an oxygen molecule and splits it into two oxygen radicals:

$$\mathrm{O_2} \xrightarrow{\mu} \mathrm{O} + \mathrm{O}$$

Then this oxygen radical can create ozone by colliding with an oxygen molecule:

$$\mathrm{O_2} + \mathrm{O} \underset{\alpha}{\overset{\beta}{\rightleftharpoons}} \mathrm{O_3}$$

The ozone and oxygen radicals can also combine:

$$\mathrm{O_3} + \mathrm{O} \xrightarrow{\lambda} \mathrm{O_2} + \mathrm{O_2}$$

Let's focus at first at what happens at ground level. Here, we can neglect μ, and we expect ozone at any substantial concentration to decay. Denote $[\mathrm{O_3}] = x$, $[\mathrm{O_2}] = y$, $[\mathrm{O}] = z$ for simplicity.

(a) Show that with the assumption that z is in steady state, the dynamics reduce to a first order system. What does the steady-state assumption imply about time scales?

(b) Show that the decay rate of ozone depends on the concentration of oxygen (you do not need to find $y(x)$, however).[1] What is the fixed point, and is it stable?

Next, let us see what happens in the upper atmosphere, where μ is actually fairly large. For simplicity, you may set $\alpha = 0$ for the remainder of this problem, as it will not provide a fundamental role in the reactions. Maintain the approximation that $\dot{z} = 0$.

(c) Show that x and y are linearly related in steady-state, and coefficient of proportionality.

(d) Empirically, it is known that $x \approx 10^{-6} y$ in the natural ozone cycle. What does this imply about the rates β and/or λ? Comment on what this means physically.

Now, why are the halogen radicals so dangerous. Let's consider an example with chlorine. A chlorine radical is formed when a molecule such as $\mathrm{CFCl_3}$ is hit by a high energy photon, and a Cl radical gets

[1] This is unusual – most "easy" reactions do not have product-dependent rates!

knocked off. This radical may then undergo the following pair of reactions (for simplicity, assume they have the same rate):

$$O_3 + Cl \xrightarrow{\sigma} ClO + O_2$$

$$O_3 + ClO \xrightarrow{\sigma} Cl + O_2 + O_2$$

Denote c the total concentration of chlorine radicals, either in Cl or ClO, and assume these catalysts are in steady-state.

(e) Show that, including the chlorine reactions, again x and y are linearly proportional, but with a new coefficient of proportionality. Find the new coefficient.

(f) It is known that $\sigma \sim 10^7\ s^{-1} \cdot M^{-1}$, $c \approx 10^{-9}$ M, and $\mu \approx 10^{-10}\ s^{-1}$. By how many orders of magnitude does the ozone concentration in steady-state drop under the presence of the chlorine radicals? Comment on your result.