

Equation for the buildup of ozone at sunset

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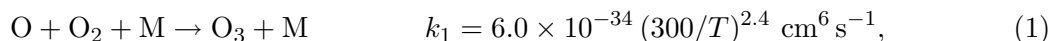
Abstract

The diurnal signature of ozone obtained from MOSAIC units can be used to estimate the rate of net formation of ozone in the mesosphere. The chemical reactions that produce and destroy ozone in the mesosphere predict a characteristic functional form for the concentration of ozone that can be observed in MOSAIC data. In this memo we look at the reactions that produce the increase in mesospheric ozone concentration after sunset, examine theoretical predictions for the nighttime equilibrium ozone concentration, and solve an important differential equation.

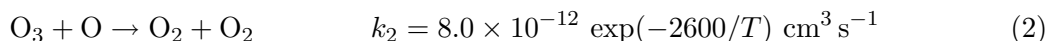
1 Chemical reactions that produce and destroy ozone

The primary processes that produce and destroy mesospheric ozone are covered in Smith & Marsh (2005) and VSRT Memo #040. A brief summary is included below.

Ozone is formed primarily by reaction of atomic and diatomic oxygen in the presence of a third molecule such as nitrogen:



where k_1 indicates the rate constant for the reaction and T is temperature in Kelvin. During the day ozone is destroyed via photodissociation from solar radiation, a process which dominates over formation and other destruction processes. We will not consider daytime ozone concentrations in this memo except to note that the daytime ozone concentration will be much lower than the nighttime value. At night, ozone is destroyed by reactions with atomic oxygen and hydrogen:



where the hydrogen reaction dominates. There is considerable uncertainty in the rate constant k_3 (see VSRT memo #040).

The density of a molecule can be expressed as the density of the atmosphere times the fractional concentration of the molecule. Thus, the formation rate of ozone in the mesosphere is $k_1 O \rho O_2 \rho$, where ρ is the number density in cm^{-3} and O and O_2 refer to the volume mixing ratios (concentrations) of atomic and diatomic oxygen, respectively¹. Putting it all together, we can find an equation for the rate of change of ozone:

$$\frac{d(\text{O}_3 \rho)}{dt} = k_1 O \rho O_2 \rho - k_2 \text{O}_3 \rho O \rho - k_3 \text{O}_3 \rho \text{H} \rho. \quad (4)$$

¹Note the difference between a mass density, which has units of g cm^{-3} , and a number density, which has units of particles per cubic centimeter, or simply cm^{-3} .

By the ideal gas law, $\rho = p/kT$, where p is the pressure and k is Boltzmann's constant (1.38×10^{-16} erg K⁻¹). Typical values for p and T in the mesosphere are 0.001 hPa and 170 K, respectively (see VSRT Memo #040). From Smith & Marsh (2005), typical concentrations of the reactants are $O_2 \approx 0.21$ (as at the surface), $O \approx 0.01$, $H \approx 10^{-6}$, and $O_3 \approx 10^{-5}$. The ozone concentration is much smaller than the concentrations of all the other reactants except for H (the concentration of which is fairly constant throughout the day), so all quantities in equation (4) can be treated as constants except for the ozone concentration that we are solving for. After collecting constants and redefining variables, equation (4) can be reduced to a differential equation of the form

$$\frac{dy}{dx} = a - y. \quad (5)$$

The solution to this equation (see Appendix A) is

$$O_3 = \begin{cases} D & : t < t_0 \\ N + (D - N) \exp(-(t - t_0)/\tau) & : t \geq t_0, \end{cases} \quad (6)$$

where D and N are the day and night equilibrium values of the ozone concentration respectively, τ is a constant indicating how fast the ozone builds up from the daytime to the nighttime value, and t_0 is the time at which the nighttime conditions start to prevail (i.e., when photodissociation turns off because the Sun has set). The solution is shown graphically in Figure 1. The ozone concentration asymptotes to the nighttime equilibrium value N (but can be considered to be effectively equal to N after several times τ).

2 Nighttime equilibrium value of ozone concentration

The nighttime equilibrium ozone concentration N is reached when the rate of ozone formation equals the rate of ozone destruction. In other words, the rate of change of the ozone concentration with time is zero at equilibrium. We can solve for N by setting equation (4) to zero:

$$N = O_{3,\text{equil}} = \frac{k_1 O O_2 \rho}{k_2 O + k_3 H}. \quad (7)$$

From VSRT Memo #040, typical mesospheric numbers for temperature, concentrations of other constituents, etc. can be plugged into equation (7), resulting in a solution of $N \approx 22$ ppm (parts per million). However, this does not appear to be consistent with the ozone concentrations inferred from MOSAIC data. There are several possible explanations for this discrepancy.

1. The flux scale calibration may be incorrect. From VSRT Memo #040, the conversion factor between antenna temperature of the MOSAIC unit at Chelmsford High School and ozone concentration is assumed to be 2.88 mK/ppm.
2. As noted in VSRT Memo #040, there is considerable uncertainty in k_3 , the rate constant for the destruction of ozone with atomic hydrogen. Since reaction (3) dominates over reaction (2) (i.e., $k_3 H \gg k_2 O$), the error in N may be dominated by the error in k_3 .
3. We have assumed that the signal in the peak of the MOSAIC spectrum comes from a single thin layer of the mesosphere near a pressure of 0.001 hPa. However, the mesosphere is not infinitely thin, and contributions from layers of different pressure and temperature may be important.

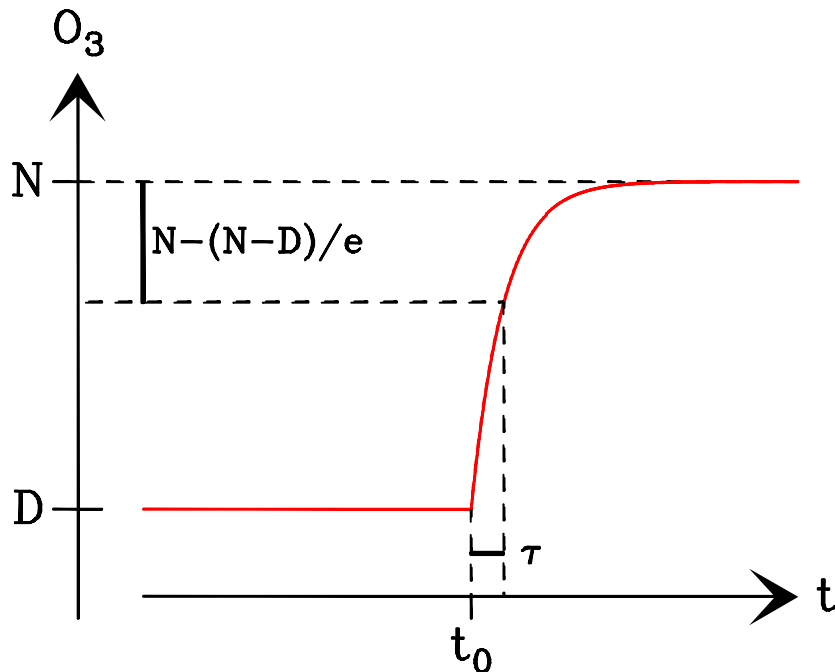


Figure 1: Solution to equation (6). The time constant τ indicates the e -folding time (i.e., the time for the function to go all but $1/e$ of the way from its initial to its final value).

Given these uncertainties (and because we want to study the behavior of mesospheric ozone), the theoretical nighttime equilibrium value of the ozone concentration should be treated as a quantity to be determined rather than as a quantity to calibrate the flux scale of MOSAIC systems.

Appendix A: Solution to the differential equation

To solve equation (5), we multiply both sides of the equation by e^x and collect terms containing a y on the left-hand side.

$$\frac{dy}{dx}e^x + ye^x = ae^x. \quad (8)$$

We can now define a new variable $Y = ye^x$. By the chain rule

$$\frac{dY}{dx} = \frac{dy}{dx}e^x + ye^x, \quad (9)$$

so

$$\frac{dY}{dx} = ae^x. \quad (10)$$

If a is a constant, then

$$ye^x = y(0) + a \int_0^x e^z dz \quad (11)$$

(where z is a dummy variable for integration), and

$$\begin{aligned} y &= y(0)e^{-x} + a(1 - e^{-x}) \\ &= a + (y(0) - a)e^{-x}. \end{aligned} \tag{12}$$

Equation 6 uses this last form.

A brief aside: Equation (5) is a scientifically important equation. It is sometimes called the radiative transfer equation because, with a change of variables, it represents the behavior of a ray of light as it passes through a medium (such as a cloud) with absorption and emission:

$$\frac{dI}{d\tau} = -I + S, \tag{13}$$

where I is the intensity of light passing through a medium, τ is the optical depth of the medium (effectively a length multiplied by an absorption coefficient)², and S is the source function of radiation produced by the medium. From the first form of equation 12, it can be seen that if the optical depth is low, background radiation is slightly attenuated. As the optical depth increases, the background radiation is quickly absorbed, and only the cloud's own emission is seen. For further details, see *Radiative Processes in Astrophysics* by Rybicki & Lightman.

Reference

Smith, A. K., & Marsh, D. R. (2005), *Processes that account for the ozone maximum at the mesopause*, J. Geophys. Res., 110, D23305, doi:10.1029/2005JD006298

²This is not the same τ as in Section 1.