**Solutions to Problem Set #1**

1. Calculate total density in molecules per cm$^3$ from information in table.

The ideal gas law for a unit volume can be expressed as $P = n\,k\,T$ where $P$ is the pressure, $n$ is the total density ([M] in our notation), $k$ is Boltzmann's constant, and $T$ is the absolute temperature. This can be solved for $n = P/kT$. As an example, at P= 100 hPa (first row in table), the pressure in cgs units is $10^5$ g cm$^{-1}$ sec$^{-2}$; Boltzmann's constant is $1.38 \times 10^{-16}$ g cm$^2$ sec$^{-2}$ K$^{-1}$; and T is 194 K.

Thus [M] = $1 \times 10^5/(1.38 \times 10^{-16}\ 194) = 3.74 \times 10^{18}$
units: (g cm$^{-1}$ sec$^{-2}$/(g cm$^2$ sec$^{-2}$ K$^{-1}$ K) = cm$^{-3}$

2. Calculate [$O_2$].

Molecular oxygen is well-mixed at approximately 21% of the total atmosphere. Thus [$O_2$] = 0.21 [M]. At 100 hPa [$O_2$] = 0.21 x 3.74 x $10^{18}$= 7.84 x $10^{17}$ cm$^{-3}$.

3. Calculate [$O$]/[$O_3$].

Ratio of [O] to [$O_3$] is set by fast exchange reactions; photolysis of $O_3$ (hv + $O_3$ → $O_2$ + O) and recombination of O atoms (O + $O_2$ + M → $O_3$ + M). The ratio is given by [O]/[$O_3$] = $J_{O3}/(k_{O,O2,M}$ [$O_2$][M]). At 100 hPa $J_{O3} = J_{O3\rightarrow O1D} + J_{O3\rightarrow O3P} = 4.96 \times 10^{-4}$ sec$^{-1}$ and $k_{O,O2,M} = 6.0 \times 10^{-34}$ (T/300)$^{-2.3} = 1.64 \times 10^{-33}$ cm$^3$ sec$^{-1}$. Multiplying these together with the densities of $O_2$ and M gives a ratio of $1.04 \times 10^{-7}$. About 1 in 10 million of [$O_x$] is in the form of atomic oxygen. The ratio increases as we go upward until it is about 4 in 100 at 0.9 hPa (~50 km altitude).

4. Calculate [$O_3$].

We can solve for the absolute concentration of [$O_3$] in the pure oxygen approximation to the stratospheric ozone system. The result is

[$O_3$] = [$O_2$] ($J_{O2}\ k_{O,O2,M}$ [M]/$k_{O,O3}\ J_{O3}$)$^{1/2}$.

This result can also be written in terms of the ratio R = [O]/[$O_3$] as

[$O_3$] = {$J_{O2}$ [$O_2$]/($k_{O,O3}$ R)}$^{1/2}$.

At 100 hPa, the result is [$O_3$] = { 1 x $10^{-13}$ x 7.84 x$10^{17}$/(1.96 x $10^{-16}$ x 1.04 x $10^{-7}$)}$^{1/2}$ = {3.84 x $10^{27}$}$^{1/2}$ = 6.22 x $10^{13}$ cm$^{-3}$.

5. Calculate [$O$].

[O] can be calculated from $[O_3]$ and the ratio, R, of [O] to $[O_3]$. The result at 100 hPa is $[O] = R [O_3] = 1.04 \times 10^{-7} \times 6.22 \times 10^{13} = 6.44 \times 10^6$ cm$^{-3}$. The O atom concentration increases with increasing altitude, reaching more than $10^{10}$ cm$^{-3}$ at 0.9 hPa.

6. Calculate the mixing ratio (mole fraction) of $O_3$ in parts per million.

The mixing ratio is just the ratio of the concentration $[O_3]$ to the total concentration of molecules [M]. The result at 100 hPa is $6.22 \times 10^{13}/3.74 \times 10^{18} = 1.67 \times 10^{-5}$. Converted to parts per million this is 16.7 ppmv (parts per million by volume).

| Press (hPa) | Temp (K) | $J_{O2}$ (sec-1) | $J_{O3\rightarrow O1D}$ (sec-1) | $J_{O3\rightarrow O3P}$ (sec-1) | [M] (cm-3) | $[O_2]$ (cm-3) | $[O_3]$ (cm-3) | [O] (cm-3) | $[O]/[O_3]$ | $f_{O3}$ (ppmv) |
|---|---|---|---|---|---|---|---|---|---|---|
| 100 | 194 | 1.00E-13 | 3.60E-05 | 4.60E-04 | 3.74E+18 | 7.84E+17 | 6.22E+13 | 6.44E+06 | 1.04E-07 | 16.7 |
| 52 | 212 | 8.70E-13 | 3.50E-05 | 4.60E-04 | 1.78E+18 | 3.73E+17 | 3.47E+13 | 1.94E+07 | 5.60E-07 | 19.5 |
| 31 | 218 | 3.70E-12 | 4.50E-05 | 4.60E-04 | 1.03E+18 | 2.16E+17 | 2.65E+13 | 4.80E+07 | 1.81E-06 | 25.7 |
| 18 | 223 | 1.90E-11 | 7.50E-05 | 4.70E-04 | 5.85E+17 | 1.23E+17 | 2.17E+13 | 1.38E+08 | 6.39E-06 | 37.0 |
| 10 | 227 | 6.80E-11 | 1.50E-04 | 4.90E-04 | 3.19E+17 | 6.70E+16 | 1.38E+13 | 3.61E+08 | 2.62E-05 | 43.1 |
| 5.6 | 232 | 2.30E-10 | 3.40E-04 | 5.20E-04 | 1.75E+17 | 3.67E+16 | 7.84E+12 | 9.68E+08 | 1.24E-04 | 44.8 |
| 2.4 | 251 | 7.10E-10 | 1.40E-03 | 6.60E-04 | 6.93E+16 | 1.46E+16 | 1.45E+12 | 3.27E+09 | 2.26E-03 | 20.9 |
| 0.9 | 255 | 1.50E-09 | 4.00E-03 | 9.60E-04 | 2.56E+16 | 5.37E+15 | 2.80E+11 | 1.16E+10 | 4.14E-02 | 10.9 |

| Press (hPa) | Temp (K) | $J_{NO2}$ (sec-1) | $[NO]/[NO2]$ | Frac Cat | TauNO | TauNO2 | NO2 | NOx |
|---|---|---|---|---|---|---|---|---|
| 100 | 194 | 1.00E-02 | 1.10E-01 | 7.71E-03 | 1.09E+01 | 9.92E+01 | 1.01E+09 | 1.12E+09 |
| 52 | 212 | 1.00E-02 | 1.09E-01 | 2.17E-02 | 1.06E+01 | 9.78E+01 | 1.46E+09 | 1.62E+09 |
| 31 | 218 | 1.00E-02 | 1.22E-01 | 5.13E-02 | 1.16E+01 | 9.49E+01 | 1.48E+09 | 1.66E+09 |
| 18 | 223 | 1.00E-02 | 1.42E-01 | 1.34E-01 | 1.23E+01 | 8.66E+01 | 1.51E+09 | 1.73E+09 |
| 10 | 227 | 1.00E-02 | 2.42E-01 | 2.85E-01 | 1.73E+01 | 7.15E+01 | 1.14E+09 | 1.42E+09 |
| 5.6 | 232 | 1.00E-02 | 5.48E-01 | 5.13E-01 | 2.66E+01 | 4.87E+01 | 8.01E+08 | 1.24E+09 |
| 2.4 | 251 | 1.00E-02 | 4.05E+00 | 7.74E-01 | 9.13E+01 | 2.26E+01 | 3.01E+08 | 1.52E+09 |
| 0.9 | 255 | 1.00E-02 | 5.65E+01 | 9.23E-01 | 4.33E+02 | 7.65E+00 | 6.68E+07 | 3.84E+09 |

7. What is the time constant for conversion of NO to $NO_2$?

The rate of change of NO due to its reaction with $O_3$ is $d[NO]/dt = - k_{O3,NO} [O_3][NO]$. Rearranging gives $d[NO]/[NO] = - k_{O3,NO} [O_3]dt$. Integrating both sides leads to an exponential solution $[NO]=[NO]_0 \exp(-k_{O3,NO} [O_3]t)$. Defining $\tau = 1/(k_{O3,NO}[O_3])$ this can be rewritten as $[NO]=[NO]_0 \exp(-t/\tau)$. We thus recognize $\tau$ as the characteristic decay time of [NO] due to its reaction with $O_3$. When $\tau =1$ the NO density is reduced to $1/e$ of its original density $[NO]_0$ by reaction with $O_3$.

At 100 hPa, the result is $\tau = 1/(1.47 \times 10^{-15} \times 6.22 \times 10^{13}) =10.9$ sec. By 0.9 hPa, the time constant has slowed to 433 sec. These are very fast compared to the time scales for transport of chemical species as we will see later in the course. Note that the time constants for $NO_2$ to return to NO are in the 20-100 sec range. Thus, the conversion back and forth is rapid compared to transport times and the ratio of concentrations is determined by the steady-state chemical equations.

8. What fraction of the cycles of NO to $NO_2$ and back lead to catalysis?

The key is when the $NO_x$ is in the form of $NO_2$, does the $NO_2$ go back to NO through the null cycle by absorbing a photon, or does it go back by reacting with an O atom to complete a catalytic cycle? This is determined by the rate of the reaction with O atoms compared to the total rate of $NO_2$ conversion to NO by both photolysis and the reactions with O atoms.

Thus, frac(catalysis) = $k_{O,NO2}$ [O]/($k_{O,NO2}$ [O] + $J_{NO2}$), where [$NO_2$] in the numerator and denominator have been cancelled. At 100 hPa, the result is

frac(catalysis) = $1.21 \times 10^{-11} \times 6.44 \times 10^6$/($1 \times 10^{-2} + 1.21 \times 10^{-11} \times 6.44 \times 10^6$) = 7.71 $\times 10^{-3}$ or about 1 in 120 cycles. By 0.9 hPa, the O atoms concentration has increased by more than 3 orders of magnitude and we get the result that 92% of the cycles lead to catalysis.

9. What is the ratio of [NO] to [$NO_2$]?

The ratio is calculated from the assumption that [NO] and [$NO_2$] are in photochemical steady state. The steady state can be derived from the continuity equation of [NO] or that for [$NO_2$] using only the intra-conversion equations for these two molecules. The resulting equation is

$k_{O3,NO}[O_3][NO] = k_{O,NO2}[O][NO_2] + J_{NO2}[NO_2]$

The ratio is then [NO]/[$NO_2$] = ($k_{O,NO2}[O]+J_{NO2}$)/($k_{O,3NO}[O_3]$). This could also be expressed in terms of lifetimes as [NO]/[$NO_2$]=$\tau_{NO}/\tau_{NO2}$. Note that $\tau_{NO2}$ = $1/(k_{O,NO2}[O]+J_{NO2})$ could be expressed in terms of the individual lifetimes for each of these reactions. With a little algebra it is easy to show that $1/\tau_{NO2} = 1/\tau_{NO2,O} + 1/\tau_{NO2,hv}$.

At 100 hPa we get: [NO]/[$NO_2$] = ($1.21 \times 10^{-11} \times 6.44 \times 10^6 + 1 \times 10^{-2}$)/($1.47 \times 10^{-15} \times 6.22 \times 10^{13}$) = 0.11.

10. What $NO_x$ concentration is necessary to make the ozone ($O_x$) loss due to its catalytic cycle equal the pure oxygen loss?

We can calculate the necessary [$NO_2$] by equating the two loss terms giving $k_{O,O3}[O_3]=k_{O,NO2}[NO_2]$. We have cancelled the factor 2 in front of each loss and the [O] in each loss term. We thus need [$NO_2$] = [$O_3$] $k_{O,O3}/k_{O,NO2}$. At 100 hPa we have [$NO_2$] = $6.22 \times 10^{13} \times 1.96 \times 10^{-16}/1.21 \times 10^{-11}$ = $1.01 \times 10^9$ cm$^{-3}$. We can convert to total [$NO_x$] by multiplying by [$NO_x$]/[$NO_2$]=([NO]+[$NO_2$])/[$NO_2$]=1+[NO]/[$NO_2$]. From the previous answer we have, at 100 hPa, 1+[NO]/[$NO_2$]=1.11 so that the necessary [$NO_x$] is $1.12 \times 10^9$ cm$^{-3}$.