**PROBLEMS**

11.1 Sources of CO

The two principal sources of CO to the atmosphere are oxidation of CH₄ and combustion. Mean rate constants for oxidation of CH₄ and CO by OH in the troposphere are \( k_1 = 2.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) and \( k_2 = 1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), respectively. Observations indicate mean CO concentrations of 80 ppbv in the northern hemisphere and 50 ppbv in the southern hemisphere, and a globally uniform CH₄ concentration of 1700 ppbv. Calculate the fraction of the CO source in each hemisphere contributed by oxidation of CH₄. Comment on the interhemispheric difference.

11.2 Sources of tropospheric ozone

1. Ozone is supplied to the troposphere by transport from the stratosphere. We estimate here the magnitude of this source by using the two-box model for stratosphere-troposphere exchange introduced in problem 3.3, where \( k_{ST} = 0.7 \text{ yr}^{-1} \) is the transfer rate constant of air from the stratosphere to the troposphere and \( k_{TS} = 0.14 \text{ yr}^{-1} \) is the reverse transfer rate constant from the troposphere to the stratosphere. Observations indicate that the atmosphere contains \( 5 \times 10^{13} \) moles of O₃ and that 90% of that total is in the stratosphere (the remaining 10% is in the troposphere). Calculate the net source of tropospheric O₃ contributed by transport from the stratosphere.

2. Ozone is also produced within the troposphere by oxidation of CO and hydrocarbons (principally CH₄) in the presence of NOₓ. One of the earliest estimates of the global source of ozone in the troposphere was done by scaling the emission inventories of CH₄ and CO. We repeat this calculation here. Consider the following mechanism for oxidation of CH₄ and CO to CO₂ under high-NOₓ conditions:

\[
\begin{align*}
O_2 & \\
CH_4 + OH & \rightarrow CH_3O_2 + H_2O \\
CH_3O_2 + NO & \rightarrow CH_3O + NO_2 \\
CH_3O + O_2 & \rightarrow CH_2O + HO_2 \\
O_2 & \\
NO_2 + h\nu & \rightarrow NO + O_3 \\
HO_2 + NO & \rightarrow OH + NO_2 \\
CH_2O + OH & \rightarrow CHO + H_2O
\end{align*}
\]
2.1 Write a net reaction for the oxidation of CO to CO_2 by the above mechanism. Do the same for the oxidation of CH_4 to CO_2 (some of the reactions may proceed more than once). How many O_3 molecules are produced per molecule of CO oxidized? per molecule of CH_4 oxidized?

2.2 Present-day global emission estimates are 3\times10^{13} moles yr^{-1} for CH_4 and 4\times10^{13} moles yr^{-1} for CO. Using your results from question 2.1, estimate the global production rate of ozone in the troposphere.

2.3 The range of estimates for the global chemical production rate of ozone in the troposphere, as derived from 3-dimensional models of tropospheric chemistry, is 6-10\times10^{13} moles yr^{-1}. Explain how the approach you used in question 2.2 might be expected to overestimate the production rate of ozone.

2.4 Conclude as to the relative importance of transport from the stratosphere and production within the troposphere as sources of tropospheric ozone.

11.3 Oxidizing power of the atmosphere

1. Consider the mechanism for oxidation of CH_4 to CO_2:

\[ \text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2 \]

\[ \text{O}_2 \]

\[ \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{HO}_2 \]

2. Write a net reaction for the oxidation of CO to CO_2 by the above mechanism. Do the same for the oxidation of CH_4 to CO_2 (some of the reactions may proceed more than once). How many O_3 molecules are produced per molecule of CO oxidized? per molecule of CH_4 oxidized?

3. Present-day global emission estimates are 3\times10^{13} moles yr^{-1} for CH_4 and 4\times10^{13} moles yr^{-1} for CO. Using your results from question 2.1, estimate the global production rate of ozone in the troposphere.

4. The range of estimates for the global chemical production rate of ozone in the troposphere, as derived from 3-dimensional models of tropospheric chemistry, is 6-10\times10^{13} moles yr^{-1}. Explain how the approach you used in question 2.2 might be expected to overestimate the production rate of ozone.

5. Conclude as to the relative importance of transport from the stratosphere and production within the troposphere as sources of tropospheric ozone.

11.3 Oxidizing power of the atmosphere

1. Consider the mechanism for oxidation of CH_4 to CO_2:

\[ \text{CH}_4 + \text{OH} \xrightarrow[O_2]{2} \text{CH}_3\text{O}_2 + \text{H}_2\text{O} \] (1)

\[ \text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2 \] (2a)

\[ \text{CH}_3\text{O}_2 + \text{NO} \xrightarrow[O_2]{2} \text{CH}_2\text{O} + \text{NO}_2 \] (2b)

\[ \text{CH}_3\text{OOH} + \text{hv} \rightarrow \text{CH}_2\text{O} + \text{HO}_2 + \text{OH} \] (3a)

\[ \text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{CH}_2\text{O} + \text{OH} + \text{H}_2\text{O} \] (3b)

\[ \text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O} \] (3c)

\[ \text{CH}_2\text{O} + \text{hv} \rightarrow \text{CO} + 2\text{HO}_2 \] (4a)

\[ \text{CH}_2\text{O} + \text{hv} \rightarrow \text{CO} + \text{H}_2 \] (4b)
Assume the following branching ratios: (2:1) for loss of CH$_3$O$_2$ by (2a:2b), (1:1:1) for loss of CH$_3$OOH by (3a:3b:3c), (2:1:1) for loss of CH$_2$O by (4a:4b:4c). These ratios are typical of lower tropospheric air in the tropics.

1.1 Show that $9/7 = 1.29$ molecules of CH$_3$O$_2$ are produced in the oxidation of one molecule of methane to CO$_2$. (1st hint: Reaction (3c) recycles CH$_3$O$_2$. 2nd hint: $1/(1-x) = 1 + x + x^2 + ...$).

1.2. Which reactions in the mechanism consume OH? Which reactions produce OH? What is the net number of OH molecules consumed in the oxidation of one molecule of methane to CO$_2$?

1.3. What is the net number of HO$_2$ molecules produced in the oxidation of one molecule of methane to CO$_2$?

1.4. What is the net number of HO$_x$ molecules consumed in the oxidation of one molecule of methane to CO$_2$? Could modifications in the branching ratios of (2), (3), (4) turn the oxidation of methane into a net source of HO$_x$? How so? How would it be possible to modify the branching ratios?

2. We go on to examine the efficiency with which the HO$_2$ produced from methane oxidation is recycled back to OH. The following reactions are important:

\[
HO_2 + NO \rightarrow OH + NO_2 \quad (6a)
\]
\[
HO_2 + O_3 \rightarrow OH + 2O_2 \quad (6b)
\]
\[
HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (6c)
\]
\[
H_2O_2 + h\nu \rightarrow 2OH \quad (7a)
\]
\[
H_2O_2 + OH \rightarrow HO_2 + H_2O \quad (7b)
\]

Assume branching ratios (1:1:2) for loss of HO$_2$ by (6a:6b:6c) and (1:1) for loss of H$_2$O$_2$ by (7a:7b).

2.1. What net fraction of HO$_2$ molecules is recycled to OH?
2.2. Taking into account this recycling, how many OH molecules are actually lost in the oxidation of one molecule of methane to CO₂? How many OH molecules are actually lost in the oxidation of one molecule of CO to CO₂?

2.3. The global average CH₄ and CO emission fluxes are estimated to be 1.2 and 1.9x10¹¹ molecules cm⁻² s⁻¹, respectively. Assume a fixed global average OH source from O₃ photolysis of 2.9x10¹¹ molecules cm⁻² s⁻¹ in the troposphere, and fixed branching ratios taken from above for all reactions in the mechanism. Based on the mechanism, would OH be titrated if CH₄ emissions doubled? If CO emissions doubled?

2.4. In fact the branching ratios would change if OH concentrations changed. How could these changes help in providing stability to OH? Which branching ratio is most critical for ensuring OH stability?

11.4 OH concentrations in the past

There has been interest in using Greenland ice core measurements of methane (CH₄) and formaldehyde (CH₂O) to derive OH concentrations in the past.

1. The main sink for CH₂O in the Arctic is photolysis, with a mean rate constant \( k = 1 \times 10^{-5} \text{ s}^{-1} \). Oxidation of CH₄ is the only significant source of CH₂O. Show that the steady-state concentration of CH₂O is given by

\[
[\text{CH}_2\text{O}] = \frac{k'}{k}[\text{CH}_4][OH]
\]

where \( k' = 2.0 \times 10^{-12} \exp(-1700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) is the rate constant for oxidation of methane by OH.

2. The Table below shows the concentrations (ppbv) of CH₂O and CH₄ in Greenland for three historical periods: present, pre-industrial (1600 A.D.), and last glaciation (18,000 B.C.).

<table>
<thead>
<tr>
<th></th>
<th>[CH₄]</th>
<th>[CH₂O]</th>
<th>T, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present</td>
<td>1700</td>
<td>0.10</td>
<td>260</td>
</tr>
<tr>
<td>Preindustrial</td>
<td>740</td>
<td>0.050</td>
<td>260</td>
</tr>
<tr>
<td>Glacial</td>
<td>410</td>
<td>0.010</td>
<td>250</td>
</tr>
</tbody>
</table>

2.1. Compute the OH concentration (molecules cm⁻³) over Greenland for each period.

2.2. How do you interpret the difference in OH concentrations between pre-industrial times and today?
2.3. One possible explanation for the difference in OH concentrations between glacial and pre-industrial times is that stratospheric ozone concentrations were higher in glacial times. Why would that be? How would that affect OH concentrations?


11. 5 Acetone in the upper troposphere

Recent measurements have revealed the ubiquitous presence of high concentrations of acetone in the upper troposphere, raising interest in the possible implications for tropospheric O₃. Acetone is emitted to the atmosphere by both biogenic and anthropogenic sources, and is removed from the atmosphere mainly by photolysis (λ < 360 nm). Consider the following mechanism for complete oxidation of acetone to CO₂ in the atmosphere:

\[
CH_3C(O)CH_3 + h\nu \rightarrow CH_3C(O)OO + CH_3O_2 \quad (1)
\]

\[
CH_3C(O)OO + NO \rightarrow CH_3O_2 + CO_2 + NO_2 \quad (2)
\]

\[
NO_2 + h\nu \rightarrow NO + O_3 \quad (3)
\]

\[
CH_3O_2 + NO \rightarrow CH_3O + HO_2 + NO_2 \quad (4)
\]

\[
CH_2O + h\nu \rightarrow CO + 2HO_2 \quad (5)
\]

\[
CO + OH \rightarrow CO_2 + HO_2 \quad (6)
\]

\[
HO_2 + NO \rightarrow OH + NO_2 \quad (7)
\]

We assume in this problem a typical lifetime of 1 month for acetone \(k_1 = 3.7 \times 10^{-7} \text{ s}^{-1}\).

1. How many O₃ molecules and how many HOₓ molecules are produced in the complete oxidation of one molecule of acetone to CO₂ by reactions (1)-(7)? (note that some of the reactions may proceed more than once)
2. The source of HO\textsubscript{x} from photolysis of acetone can be compared to the source from photolysis of O\textsubscript{3}:

\begin{equation}
O_3 + h\nu \rightarrow O_2 + O(\overset{1}{D}) \tag{8}
\end{equation}

\begin{equation}
O(\overset{1}{D}) + M \rightarrow O + M \tag{9}
\end{equation}

\begin{equation}
O(\overset{1}{D}) + H_2O \rightarrow 2OH \tag{10}
\end{equation}

with rate constants $k_8 = 1.0 \times 10^{-5}$ s\textsuperscript{-1}, $k_9 = 3.6 \times 10^{-11}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}, $k_{10} = 2.2 \times 10^{-10}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}. For typical conditions at 10 km altitude with 67 ppmv H\textsubscript{2}O, 50 ppbv O\textsubscript{3}, 0.5 ppbv acetone, and an air density $[M] = 8 \times 10^{18}$ molecules cm\textsuperscript{-3}, compare the source of HO\textsubscript{x} from reaction (10) to that from conversion of acetone to CO\textsubscript{2}.

3. You should have found in question 2 that photolysis of acetone is an important source of HO\textsubscript{x} in the upper troposphere. One finds by contrast that it is a negligible source of HO\textsubscript{x} in the lower troposphere or in the stratosphere. Why?

4. The upper troposphere also contains 100 ppbv CO. The lifetime of CO against oxidation by OH is estimated to be 3 months.

4.1. How many molecules of O\textsubscript{3} and of HO\textsubscript{x} are produced in the oxidation of one molecule of CO to CO\textsubscript{2}?

4.2. Compare the O\textsubscript{3} production rates resulting from the oxidation of CO and from the photolysis of acetone. Do you conclude that O\textsubscript{3} production in the upper troposphere is insensitive to changes in the concentration of acetone? Briefly explain.


### 11.6 Transport, rainout, and chemistry in the marine upper troposphere

We consider a simple dynamical model for the upper troposphere over the tropical oceans where direct transfer from the lower troposphere to the upper troposphere by deep convective clouds is balanced by large-scale subsidence. Let $k_{ij}$ represent the first-order rate constant for transfer of air from layer $i$ to layer $j$. 

1. We estimate the residence time of air in the upper troposphere in this model by using methyl iodide (CH$_3$I) as a tracer of transport. Methyl iodide is emitted from the oceans and has a lifetime of 4 days against photolysis. Mean CH$_3$I concentrations are 0.36 pptv in the lower troposphere and 0.10 pptv in the upper troposphere. Assuming steady state for CH$_3$I in the upper troposphere, show that the residence time of air in the upper troposphere is 10 days.

2. Deep convection provides a means for rapid transport of gases from the lower to the upper troposphere, but water-soluble gases are scavenged during transport by precipitation in the deep convective cloud. Consider a gas X with Henry's law constant $K_X$ (M atm$^{-1}$) in a cloud of liquid water content $L$ (volume of liquid water per volume of air). Show that the dimensionless fractionation $f$ of X between the cloudwater (aq) and the gas phase (g) is given by

$$f = \frac{[X]_{aq}}{[X]_g} = K_X L R T$$

where the concentrations [ ] are moles per unit volume of air, $R$ is the gas constant, and $T$ is temperature.

3. Calculate $f$ for the peroxides H$_2$O$_2$ ($K_{H2O2} = 2 \times 10^5$ M atm$^{-1}$) and CH$_3$OOH ($K_{CH3OOH} = 3 \times 10^3$ M atm$^{-1}$) for a typical cloud liquid water content $L = 1 \times 10^{-6}$ m$^3$ water/m$^3$ air and temperature $T = 250$ K (be careful with units!). Your results should show that H$_2$O$_2$ but not CH$_3$OOH is efficiently scavenged in deep convection.

4. Observed mean concentrations of CH$_3$OOH are 1100 pptv in the lower...
troposphere and 80 pptv in the upper troposphere. Calculate the net source of CH$_3$OOH (molecules cm$^{-3}$ s$^{-1}$) to the upper troposphere associated with deep convection. Use an air density $n_a = 4 \times 10^{18}$ molecules cm$^{-3}$ for the upper troposphere.

5. In the upper troposphere, CH$_3$OOH photolyzes or reacts with OH, and the resulting CH$_2$O also photolyzes or reacts with OH:

\[
O_2 + CH_3OOH + h\nu \rightarrow CH_2O + HO_2 + OH \quad (1a)
\]
\[
CH_3OOH + OH \rightarrow CH_2O + OH + H_2O \quad (1b)
\]
\[
CH_2O + h\nu \rightarrow CO + H_2 \quad (2a)
\]
\[
2O_2 + CH_2O + h\nu \rightarrow CO + 2HO_2 \quad (2b)
\]
\[
CH_2O + OH \rightarrow CO + HO_2 + H_2O \quad (2c)
\]

Branching ratios are (1:1) for (1a:1b) and (1:1:1) for (2a:2b:2c). Calculate the yield of HO$_x$ per molecule of CH$_3$OOH injected to the upper troposphere, and from there the total HO$_x$ source in the upper troposphere resulting from deep convective injection of CH$_3$OOH. Compare to a typical HO$_x$ source of $1 \times 10^4$ molecules cm$^{-3}$ s$^{-1}$ in the upper troposphere from the O($^1$D)+H$_2$O reaction. Is convective injection of CH$_3$OOH an important source of HO$_x$ in the upper troposphere?

[To know more: Prather, M.J., and D.J. Jacob, A persistent imbalance in HO$_x$ and NO$_x$ photochemistry of the upper troposphere driven by deep tropical convection, Geophys. Res. Lett., 24, 3189-3192, 1997.]

### 11.7 Bromine chemistry in the troposphere

Events of rapid O$_3$ depletion are observed in arctic surface air in spring, with concentrations dropping from 40 ppbv (normal) to less than 5 ppbv in just a few days. These O$_3$ depletion events are associated with elevated bromine which appears to originate from the volatilization of sea salt bromide deposited on the ice pack. In this problem we examine the mechanism for Br-catalyzed O$_3$ loss thought to operate in arctic surface air. Consider a surface air parcel in the arctic at the onset of an O$_3$ depletion event. The air parcel contains 40 ppbv O$_3$, 50 pptv Br$_y$ (sum of Br, BrO, HOBBr, and HBr), 10 pptv CH$_2$O, $3 \times 10^7$ molecules cm$^{-3}$ HO$_2$, and $1 \times 10^5$ molecules cm$^{-3}$ OH. The air density in the parcel is $3 \times 10^{19}$ molecules
cm$^{-3}$. Bromine chemistry is described by the reactions:

\begin{align}
    Br + O_3 & \rightarrow BrO + O_2 & (1) \\
    BrO + hv & \rightarrow Br + O_3 & (2) \\
    BrO + BrO & \rightarrow 2Br + O_2 & (3) \\
    Br + CH_2O & \rightarrow HBr + CHO & (4) \\
    BrO + HO_2 & \rightarrow HOBr + O_2 & (5) \\
    HBr + OH & \rightarrow Br + H_2O & (6) \\
    HOBr + hv & \rightarrow OH + Br & (7)
\end{align}

with rate constants $k_1 = 6 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $k_2 = 1 \times 10^{-2}$ s$^{-1}$, $k_3 = 3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $k_4 = 6 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $k_5 = 5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $k_6 = 1.1 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, and $k_7 = 1 \times 10^{-4}$ s$^{-1}$.

1. Draw a diagram of the Br$_y$ cycle. Identify a catalytic cycle for O$_3$ loss consisting of only two reactions, and highlight this cycle in your diagram.

2. Show that reaction (2) is the principal sink for BrO. What is the rate-limiting reaction for O$_3$ loss in the catalytic mechanism you described in question 1? Briefly explain.

3. Write an equation for the O$_3$ loss rate ($-d[O_3]/dt$) in the catalytic mechanism as a function of [BrO]. What would the O$_3$ loss rate be if BrO were the main contributor to total bromine (that is, if [BrO] = 50 ppt)? Would you predict near-total ozone depletion in a few days?

4. Ozone loss can in fact be slowed down by formation of HBr or HOBr.

4.1 Explain briefly why.

4.2 Assuming steady-state for all bromine species, calculate the concentrations of HOBr, HBr, BrO, and Br in the air parcel. How does the resulting O$_3$ loss rate compare to the value you computed in question 3? Would you still predict near-total O$_3$ depletion in a few days?

4.3 It has been proposed that O$_3$ depletion could be enhanced by reaction of HOBr with HBr in the Arctic aerosol followed by photolysis of Br$_2$: 

\[ HOBr + HBr \rightarrow BrO + Br + H_2O \]
How would these two reactions help to explain the observed O₃ depletion? Draw a parallel to similar reactions occurring in the stratosphere.


11.8 Nighttime oxidation of NOₓ

Nighttime loss of NOₓ in the lower troposphere proceeds by:

\[
\begin{align*}
NO + O_3 & \rightarrow NO_2 + O_2 \\
NO_2 + O_3 & \rightarrow NO_3 + O_2 \\
NO_2 + NO_3 + M & \rightleftharpoons N_2O_5 + M
\end{align*}
\]

\[
N_2O_5 \rightarrow 2HNO_3
\]

Reaction (3) is viewed as an equilibrium process with constant \( K_3 = [N_2O_5]/([NO_3][NO_2]) = 3.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \). Other reactions have rate constants \( k_1 = 3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), \( k_2 = 2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), and \( k_4 = 3 \times 10^{-4} \text{ s}^{-1} \).

Consider an air parcel with a temperature of 280 K, pressure of 900 hPa, and constant concentrations of 40 ppbv O₃ and 0.1 ppbv NOₓ.

1. The above mechanism for NOₓ loss operates only at night. Explain why.

2. At night, almost all of NOₓ is present as NO₂ (the NO/NOₓ concentration ratio is negligibly small). Explain why.

3. Let NO₃* represent the chemical family composed of NO₃ and N₂O₅, that is, \([NO₃^*] = [NO₃] + [N₂O₅]\). Calculate the lifetime of NO₃* at night.

4. Assuming that NO₃* is in chemical steady state at night (your answer to question 3 should justify this assumption), and that the night lasts 12 hours, calculate the 24-hour average lifetime of NOₓ against oxidation to HNO₃ by the above mechanism. Compare to the typical 1-day lifetime of NOₓ against oxidation by OH.
11.9 Peroxyacetyl Nitrate (PAN) as a reservoir for NO<sub>x</sub>

1. Consider an urban atmosphere containing 100 ppbv NO<sub>x</sub> and 100 ppbv O<sub>3</sub> with \( T = 298 \) K and \( P = 1000 \) hPa. Calculate the steady-state concentrations of NO and NO<sub>2</sub> at noon based on the null cycle:

\[
NO + O_3 \rightarrow NO_2 + O_2 \quad (1)
\]

\[
NO_2 + h\nu \rightarrow NO + O_3 \quad (2)
\]

with \( k_1 = 2.2 \times 10^{-12} \exp(-1430/T) \) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, and \( k_2 = 1 \times 10^{-8} \) s<sup>-1</sup> (noon). How does the \([NO_2]/[NO_x]\) ratio vary with time of day? How would it be affected by the presence of peroxy radicals?

2. Photolysis of acetone \((CH_3C(O)CH_3)\) is an important source of PAN. In a high-NO<sub>x</sub> atmosphere, the peroxyacetyl radical \((CH_3C(O)OO)\) produced by photolysis of acetone reacts with either NO or NO<sub>2</sub>:

\[
CH_3C(O)CH_3 + h\nu \xrightarrow{2O_2} CH_3C(O)OO + CH_3O_2 \quad (3)
\]

\[
CH_3C(O)OO + NO \xrightarrow{O_2} CH_3O_2 + CO_2 + NO_2 \quad (4a)
\]

\[
CH_3C(O)OO + NO_2 + M \rightarrow PAN + M \quad (4b)
\]

\[
PAN \rightarrow CH_3C(O)OO + NO_2 \quad (5)
\]

Derive an equation showing that the steady-state concentration of PAN is independent of NO<sub>x</sub> but proportional to acetone and O<sub>3</sub>. Explain qualitatively this result.

3. Consider an air parcel ventilated from a city at time \( t = 0 \) and subsequently transported for 10 days without exchanging air with its surroundings. We wish to examine the fate of NO<sub>x</sub> as the air parcel ages. The air parcel contains initially 100 ppbv NO<sub>x</sub>, zero PAN, and zero HNO<sub>3</sub>. The lifetime of NO<sub>x</sub> against conversion to HNO<sub>3</sub> is 1 day. We assume that HNO<sub>3</sub> is removed rapidly by deposition and cannot be recycled back to NO<sub>x</sub>. We also assume \([NO] \ll [NO_2]\) in the air parcel at all times (cf. question 1).
3.1. We first ignore PAN formation. Calculate the temporal evolution of the NO\textsubscript{x} concentration in the air parcel. What is the concentration of NO\textsubscript{x} after a transport time of 10 days?

3.2. We now examine the effect of PAN formation, assuming a constant concentration \([\text{CH}_3\text{C} (\text{O})\text{OO}] = 1 \times 10^8\) molecules cm\(^{-3}\) in the air parcel. Rate constants are \(k_{4b} = 4.7 \times 10^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) and \(k_5 = 1.95 \times 10^{16}\) exp(-13,543/T).

3.2.1. What is the lifetime of NO\textsubscript{x}? What is the lifetime of PAN at 298 K? at 260 K?

3.2.2. Calculate the temporal evolution over a 10-day period of NO\textsubscript{x} and PAN concentrations for an air parcel transported in the boundary layer (\(T = 298\) K). [Hint 1: assume quasi steady-state for NO\textsubscript{x}. Why is this assumption reasonable? Hint 2: you will find it convenient to define a chemical family NO\textsubscript{x}* = NO\textsubscript{x} + PAN]. What is the concentration of NO\textsubscript{x} remaining after 10 days?

3.2.3. Repeat the same calculation as in question 3.2.2 but for an air parcel pumped to high altitude (\(T = 260\) K) at time \(t = 0\) and remaining at that temperature for the following 10 days.

3.2.4. Conclude briefly on the role of PAN formation in promoting the long-range transport of anthropogenic NO\textsubscript{x} in the atmosphere.

[To know more: Moxim, W.J., et al., Simulated global tropospheric PAN: its transport and impact on NO\textsubscript{x}, \textit{J. Geophys. Res.}, 101, 12621-12638, 1996].