

PROBLEMS

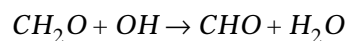
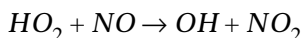
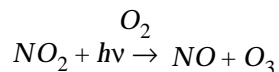
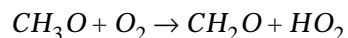
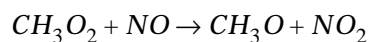
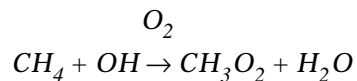
11. 1 Sources of CO

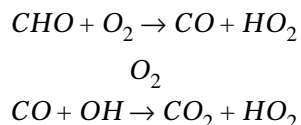
The two principal sources of CO to the atmosphere are oxidation of CH₄ and combustion. Mean rate constants for oxidation of CH₄ and CO by OH in the troposphere are $k_1 = 2.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_2 = 1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, 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 5×10^{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 NO_x. 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-NO_x conditions:





2.1 Write a net reaction for the oxidation of CO to CO₂ by the above mechanism. Do the same for the oxidation of CH₄ to CO₂ (some of the reactions may proceed more than once). How many O₃ molecules are produced per molecule of CO oxidized? per molecule of CH₄ oxidized?

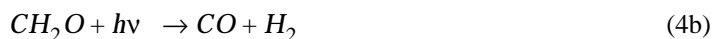
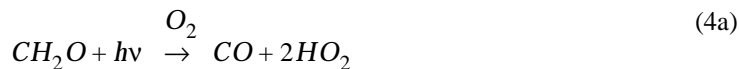
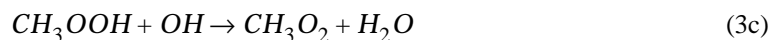
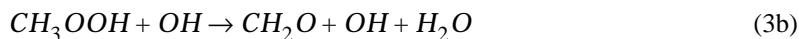
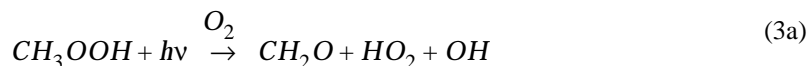
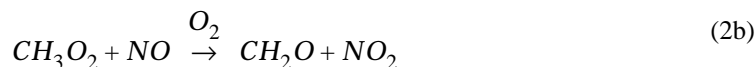
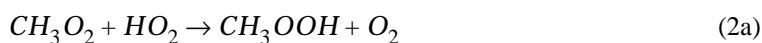
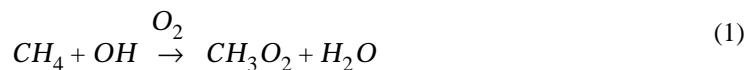
2.2 Present-day global emission estimates are 3x10¹³ moles yr⁻¹ for CH₄ and 4x10¹³ moles yr⁻¹ for CO. Using your results from question 2.1, estimate the global production rate of ozone in the troposphere.

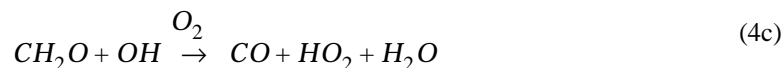
2.3 The range of estimates for the global chemical production rate of ozone in the troposphere, as derived from 3-dimensional models of tropospheric chemistry, is 6-10x10¹³ moles yr⁻¹. Explain how the approach you used in question 2.2 might be expected to overestimate the production rate of ozone.

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 CH₄ to CO₂:





Assume the following branching ratios: (2:1) for loss of CH_3O_2 by (2a:2b), (1:1:1) for loss of CH_3OOH by (3a:3b:3c), (2:1:1) for loss of CH_2O by (4a:4b:4c). These ratios are typical of lower tropospheric air in the tropics.

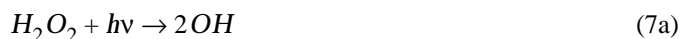
1.1 Show that $9/7 = 1.29$ molecules of CH_3O_2 are produced in the oxidation of one molecule of methane to CO_2 . (1st hint: Reaction (3c) recycles CH_3O_2 . 2nd hint: $1/(1-x) = 1 + x + x^2 + \dots$).

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:



Assume branching ratios (1:1:2) for loss of HO_2 by (6a:6b:6c) and (1:1) for loss of H_2O_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

$$[CH_2O] = \frac{k'}{k}[CH_4][OH]$$

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.).

| | [CH ₄] | [CH ₂ O] | T, K |
|---------------|--------------------|---------------------|------|
| Present | 1700 | 0.10 | 260 |
| Preindustrial | 740 | 0.050 | 260 |
| Glacial | 410 | 0.010 | 250 |

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

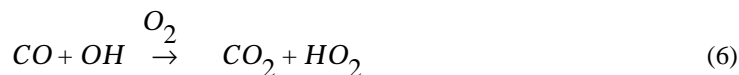
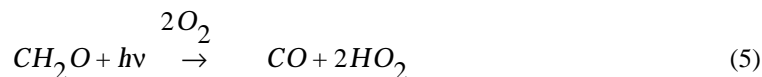
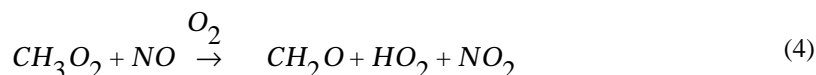
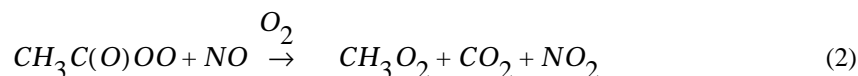
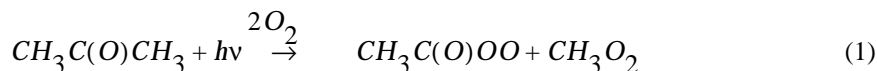
2.2. How do you interpret the difference in OH concentrations between pre-industrial times and today?

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?

[Source: Staffelbach, T., et al., Formaldehyde in polar ice cores: a possibility to characterize the atmospheric sink of methane in the past?, *Nature*, 349, 603-605, 1991.]

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 O_3 . Acetone is emitted to the atmosphere by both biogenic and anthropogenic sources, and is removed from the atmosphere mainly by photolysis ($\lambda < 360$ nm). Consider the following mechanism for complete oxidation of acetone to CO_2 in the atmosphere:



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 O_3 molecules and how many HO_x molecules are produced in the complete oxidation of one molecule of acetone to CO_2 by reactions (1)-(7)? (note that some of the reactions may proceed more than once)

2. The source of HO_x from photolysis of acetone can be compared to the source from photolysis of O_3 :



with rate constants $k_8 = 1.0 \times 10^{-5} \text{ s}^{-1}$, $k_9 = 3.6 \times 10^{-11} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{10} = 2.2 \times 10^{-10} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$. For typical conditions at 10 km altitude with 67 ppmv H_2O , 50 ppbv O_3 , 0.5 ppbv acetone, and an air density $[\text{M}] = 8 \times 10^{18} \text{ molecules cm}^{-3}$, compare the source of HO_x from reaction (10) to that from conversion of acetone to CO_2 .

3. You should have found in question 2 that photolysis of acetone is an important source of HO_x in the upper troposphere. One finds by contrast that it is a negligible source of HO_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.

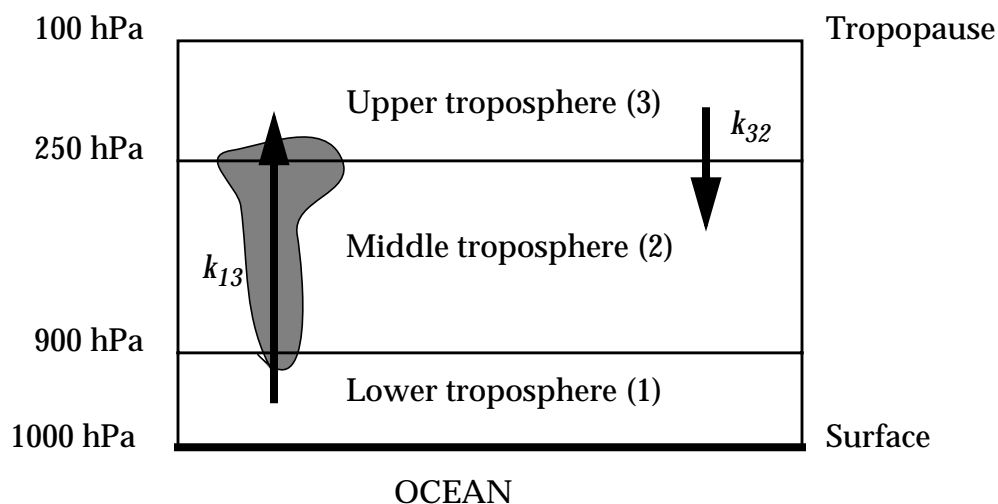
4.1. How many molecules of O_3 and of HO_x are produced in the oxidation of one molecule of CO to CO_2 ?

4.2. Compare the O_3 production rates resulting from the oxidation of CO and from the photolysis of acetone. Do you conclude that O_3 production in the upper troposphere is insensitive to changes in the concentration of acetone? Briefly explain.

[To know more: McKeen, S.A., et al., The photochemistry of acetone in the upper troposphere: a source of odd-hydrogen radicals, *Geophys. Res. Lett.*, 24, 3177-3180, 1997.]

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_3I) as a tracer of transport. Methyl iodide is emitted from the oceans and has a lifetime of 4 days against photolysis. Mean CH_3I concentrations are 0.36 pptv in the lower troposphere and 0.10 pptv in the upper troposphere. Assuming steady state for CH_3I 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

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

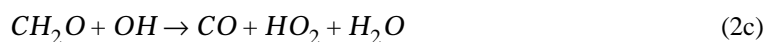
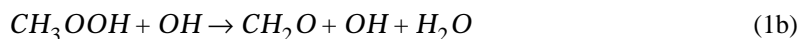
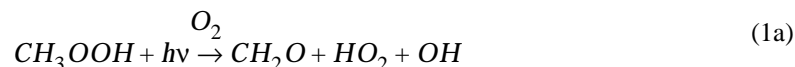
where the concentrations $[\]$ are moles per unit volume of air, R is the gas constant, and T is temperature.

3. Calculate f for the peroxides H_2O_2 ($K_{\text{H}_2\text{O}_2} = 2 \times 10^5 \text{ M atm}^{-1}$) and CH_3OOH ($K_{\text{CH}_3\text{OOH}} = 3 \times 10^3 \text{ M atm}^{-1}$) for a typical cloud liquid water content $L = 1 \times 10^{-6} \text{ m}^3 \text{ water/m}^3 \text{ air}$ and temperature $T = 250 \text{ K}$ (be careful with units!). Your results should show that H_2O_2 but not CH_3OOH is efficiently scavenged in deep convection.

4. Observed mean concentrations of CH_3OOH are 1100 pptv in the lower

troposphere and 80 pptv in the upper troposphere. Calculate the net source of CH_3OOH (molecules $\text{cm}^{-3} \text{s}^{-1}$) 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_3OOH photolyzes or reacts with OH, and the resulting CH_2O also photolyzes or reacts with OH:



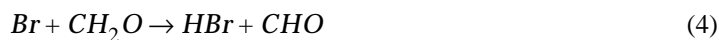
Branching ratios are (1:1) for (1a:1b) and (1:1:1) for (2a:2b:2c). Calculate the yield of HO_x per molecule of CH_3OOH injected to the upper troposphere, and from there the total HO_x source in the upper troposphere resulting from deep convective injection of CH_3OOH . Compare to a typical HO_x source of 1×10^4 molecules $\text{cm}^{-3} \text{s}^{-1}$ in the upper troposphere from the $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ reaction. Is convective injection of CH_3OOH 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, HOBr, and HBr), 10 pptv CH_2O , 3×10^7 molecules cm^{-3} HO_2 , and 1×10^5 molecules cm^{-3} OH. The air density in the parcel is 3×10^{19} molecules

cm^{-3} . Bromine chemistry is described by the reactions:



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

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.

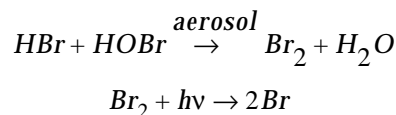
3. Write an equation for the O_3 loss rate ($-\text{d}[\text{O}_3]/\text{dt}$) in the catalytic mechanism as a function of [BrO]. What would the O_3 loss rate be if BrO were the main contributor to total bromine (that is, if $[\text{BrO}] \approx 50 \text{ ppt}$)? Would you predict near-total ozone depletion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



How would these two reactions help to explain the observed O₃ depletion? Draw a parallel to similar reactions occurring in the stratosphere.

[To know more: Haussmann, M., and U. Platt, Spectroscopic measurement of bromine oxide and ozone in the high Arctic during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, 99, 25399-25413, 1994]

11. 8 Nighttime oxidation of NO_x

Nighttime loss of NO_x in the lower troposphere proceeds by:



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 NO_x.

1. The above mechanism for NO_x loss operates only at night. Explain why.
2. At night, almost all of NO_x is present as NO₂ (the NO/NO_x 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 NO_x against oxidation to HNO₃ by the above mechanism. Compare to the typical 1-day lifetime of NO_x against oxidation by OH.

[To know more: Dentener, F.J., and P.J. Crutzen, Reaction of N_2O_5 on tropospheric aerosols: impact on the global distributions of NO_x , O_3 , and OH, *J. Geophys. Res.*, 98, 7149-

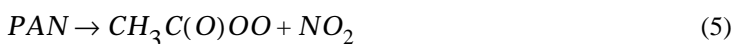
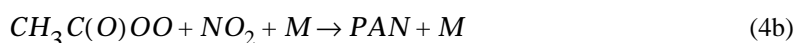
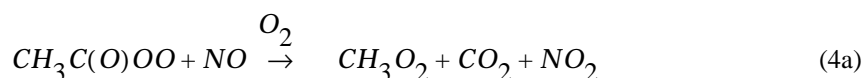
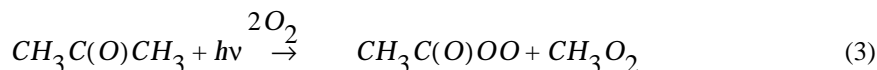
11. 9 Peroxyacetylnitrate (PAN) as a reservoir for NO_x

1. Consider an urban atmosphere containing 100 ppbv NO_x and 100 ppbv O_3 with $T = 298$ K and $P = 1000$ hPa. Calculate the steady-state concentrations of NO and NO_2 at noon based on the null cycle:



with $k_1 = 2.2 \times 10^{-12} \exp(-1430/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and $k_2 = 1 \times 10^{-2} \text{ s}^{-1}$ (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_x atmosphere, the peroxyacetyl radical ($CH_3C(O)OO$) produced by photolysis of acetone reacts with either NO or NO_2 :



Derive an equation showing that the steady-state concentration of PAN is independent of NO_x but proportional to acetone and O_3 . 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_x as the air parcel ages. The air parcel contains initially 100 ppbv NO_x , zero PAN, and zero HNO_3 . The lifetime of NO_x against conversion to HNO_3 is 1 day. We assume that HNO_3 is removed rapidly by deposition and cannot be recycled back to NO_x . 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_x concentration in the air parcel. What is the concentration of NO_x after a transport time of 10 days?

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

3.2.1. What is the lifetime of NO_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_x and PAN concentrations for an air parcel transported in the boundary layer ($T = 298 \text{ K}$). [Hint 1: assume quasi steady-state for NO_x . Why is this assumption reasonable? Hint 2: you will find it convenient to define a chemical family $\text{NO}_x^* = \text{NO}_x + \text{PAN}$]. What is the concentration of NO_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 ($T = 260 \text{ K}$) 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_x in the atmosphere.

[To know more: Moxim, W.J., et al., Simulated global tropospheric PAN: its transport and impact on NO_x , *J. Geophys. Res.*, 101, 12621-12638, 1996].