Problem 1: Nighttime loss of NOx in the lower troposphere proceeds by:

\[\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2,\]  \hspace{1cm} (1)

\[\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2,\]  \hspace{1cm} (2)

\[\text{NO}_2 + \text{NO}_3 + M \leftrightarrow \text{N}_2\text{O}_5 + M,\]  \hspace{1cm} (3)

\[\text{N}_2\text{O}_5 \xrightarrow{\text{aerosol,} \ H_2\text{O}} 2\text{HNO}_3.\]  \hspace{1cm} (4)

Reaction (3) is viewed as an equilibrium process with constant \(K_3 = [\text{N}_2\text{O}_5]/([\text{NO}_3][\text{NO}_2]) = 3.6 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\). 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 O\(_3\) 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 NO\(_2\) (the NO/NO\(_x\) concentration ratio is negligibly small). Explain why.

3. Let NO\(_x^*\) represent the chemical family composed of NO\(_3\) and N\(_2\)O\(_5\), that is, \([\text{NO}_x^*] = [\text{NO}_3] + [\text{N}_2\text{O}_5]\). Calculate the lifetime of NO\(_x^*\) at night.

4. Assuming that NO\(_x^*\) 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 HNO\(_3\) by the above mechanism. Compare to the typical 1-day lifetime of NO\(_x\) against oxidation by OH.
Problem 2:

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

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2, \quad (1)
\]

\[
\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}_3, \quad (2)
\]

with \( k_1 = 2.2 \times 10^{-12}\exp(-1430/T) \) cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} and \( k_2 = 1 \times 10^{-2} \) s\textsuperscript{-1} (noon). How does the \([\text{NO}_2]/[\text{NO}_x]\) ratio vary with time of day? How would it be affected by the presence of peroxy radicals?

2. Consider an air parcel ventilated from a city at time \( t = 0 \) and subsequently transported 10 days without exchanging air with its surroundings. We wish to examine the fate of the NO\textsubscript{x} as the parcel ages. The air parcel initially contains 100 ppbv NO\textsubscript{x} and zero PAN, and zero HNO\textsubscript{3}. The lifetime of NO\textsubscript{x} against conversion to HNO\textsubscript{3} is 1 day. Assume that HNO\textsubscript{3} is removed rapidly by deposition and cannot be recycled back to NO\textsubscript{x}. Also assume that at all times \([\text{NO}] \ll [\text{NO}_2]\) in the air parcel.

2.1 Ignoring 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 of 10 days.

Make use of the schematic reaction: \( \text{NO}_x \rightarrow \text{HNO}_3 \)  \( (6) \)

Recalling that \([\text{NO}] \ll [\text{NO}_2]\).

2.2 Now consider the effect of PAN formation, assuming a constant concentration of \([\text{CH}_3\text{C(O)OO}] = 1 \times 10^8\) molecules cm\textsuperscript{-3} in the air parcel. Rate constants for the PAN reactions below are \( k_{sb} = 4.7 \times 10^{12} \) cm\textsuperscript{3} molecules\textsuperscript{-1} s\textsuperscript{-1} and \( k_5 = 1.95 \times 10^{16} \exp(-13,543/T) \) s\textsuperscript{-1}. What is the lifetime of NO\textsubscript{x}? What is the lifetime of PAN at 298 K and 260 K? (For NO\textsubscript{x} consider both HNO\textsubscript{3} and PAN formation)

\[
\text{CH}_3\text{C(O)OO} + \text{NO}_2 + M \rightarrow \text{PAN} + M, \quad (4b)
\]

\[
\text{PAN} \rightarrow \text{CH}_3\text{C(O)OO} + \text{NO}_2. \quad (5)
\]