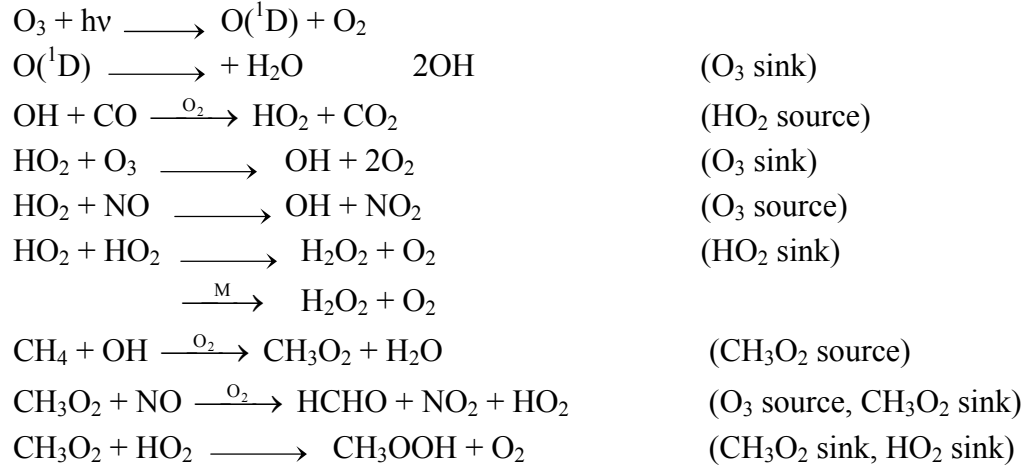6.9   Regions of the troposphere can be ozone-producing or ozone-depleting depending on the

local level of NO_x. The principal chemical sink of O_3 is O_3 photolysis followed by $O(^1D)$

+ H_2O. For example, at 10 °S at the surface, $j_{O3 \to O(1D)} \approx 7 \times 10^{-6}$ s^{-1}, leading to a photolysis

lifetime of O_3 of about 11 days. The chemical sink of O_3 next in importance to photolysis

is the reaction,

$$HO_2 + O_3 \longrightarrow OH + 2O_2.$$
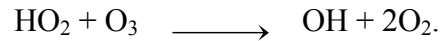
The principal chemical source of O_3 in the troposphere is production through the methane

oxidation chain. The level of NO is critical in this chain in dictating the fate of the HO_2

and CH_3O_2 radicals. The reactions HO_2 + NO and CH_3O_2 + NO lead to O_3 production,

whereas HO_2 + O_3 leads to O_3 removal.

So the reactions considered in the problem include:

$O_3 + h\nu \longrightarrow O(^1D) + O_2$
$O(^1D) \longrightarrow + H_2O \qquad 2OH$ (O_3 sink)
$OH + CO \xrightarrow{O_2} HO_2 + CO_2$ (HO_2 source)
$HO_2 + O_3 \longrightarrow OH + 2O_2$ (O_3 sink)
$HO_2 + NO \longrightarrow OH + NO_2$ (O_3 source)
$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$ (HO_2 sink)
$\xrightarrow{M} H_2O_2 + O_2$
$CH_4 + OH \xrightarrow{O_2} CH_3O_2 + H_2O$ (CH_3O_2 source)
$CH_3O_2 + NO \xrightarrow{O_2} HCHO + NO_2 + HO_2$ (O_3 source, CH_3O_2 sink)
$CH_3O_2 + HO_2 \longrightarrow CH_3OOH + O_2$ (CH_3O_2 sink, HO_2 sink)

a) Determine the mixing ratio of NO at which the rate of the HO_2 + NO reaction just

equals that of the HO_2 + O_3 reaction if O_3 = 20 ppb. Assume 298 K.

$$k_{HO_2+O_3}[HO_2][O_3] = k_{HO_2+NO}[HO_2][NO]$$

$$\rightarrow [NO] = f_{NO}\,[M] = \frac{k_{HO_2+O_3}[HO_2][O_3]}{k_{HO_2+NO}[HO_2]} = \frac{k_{HO_2+O_3}f_{O_3}[M]}{k_{HO_2+NO}}$$

$$\rightarrow f_{NO} = \frac{k_{HO_2+O_3}f_{O_3}}{k_{HO_2+NO}} = \frac{1.9\times10^{-15}\times20\times10^{-9}}{8.1\times10^{-12}} = 4.69\times10^{-12} = \underline{\textbf{4.69 ppt}}$$

Assume O_3 is at photostationary state, so we have that

b) To what level of NOx does the NO level determined in (a) correspond under noontime conditions? Assume jNO2 = 0.015 s-1.

$$[O_3] = \frac{j_{NO_2}[NO_2]}{k_{NO+O_3}[NO]}$$

$$\rightarrow [NO_2] = f_{NO2}\,[M] = \frac{k_{NO+O_3}[NO][O_3]}{j_{NO_2}} = \frac{k_{NO+O_3}f_{NO}f_{O_3}[M]^2}{j_{NO_2}}$$

$$\rightarrow f_{NO_2} = \frac{k_{NO+O_3}f_{NO}f_{O_3}[M]}{j_{NO_2}} = \frac{1.9\times10^{-14}\times4.69\times10^{-12}\times20\times10^{-9}\times2.46\times10^{19}}{0.015} = 2.92\times10^{-12}$$

$$= 2.92 \text{ ppt}$$

$$\rightarrow f_{NO_x} = f_{NO} + f_{NO_2} = 4.69 + 2.92 = \underline{\textbf{7.61 ppt}}$$

c) A competition also exists between NO and HO2 for the CH3O2 radical, and the path depends on the concentrations of HO2 and NO. Assume that the local OH concentration is 106 molecules cm-3. Compute the local HO2 concentration assuming that reaction with CO is the main sink of OH and HO2-HO2 self-reaction is the main sink of HO2. Assume a CO mixing ratio of 100 ppb.
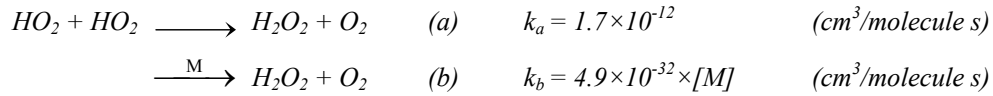
Assume steady-state of HO_2, so the source of HO_2, the reaction of OH + CO, is balanced by the sink of HO_2, here only the HO_2-HO_2 slef-reaction:

$$k_{OH+CO}[OH][CO] = 2k_{HO_2+HO_2}[HO_2]^2$$

$$\rightarrow [HO_2] = f_{HO_2}[M] = \sqrt{\frac{k_{OH+CO}[OH][CO]}{2k_{HO_2+HO_2}}} = \sqrt{\frac{k_{OH+CO}[OH]f_{CO}[M]}{2k_{HO_2+HO_2}}}$$

$$\rightarrow f_{HO_2} = \sqrt{\frac{k_{OH+CO}[OH]f_{CO}}{2k_{HO_2+HO_2}[M]}} = \sqrt{\frac{2.4\times10^{-13}\times10^6\times100\times10^{-9}}{2\times2.9\times10^{-12}\times2.46\times10^{19}}} = 1.30\times10^{-11} = \underline{\textbf{13.0 ppt}}$$

Note: *The HO_2+HO_2 reaction has two channels:*

$HO_2 + HO_2 \xrightarrow{} H_2O_2 + O_2$ (a) $k_a = 1.7\times10^{-12}$		*(cm³/molecule s)*
$\xrightarrow{M} H_2O_2 + O_2$ (b) $k_b = 4.9\times10^{-32}\times[M]$		*(cm³/molecule s)*

So the overall rate constant for the HO_2+HO_2 reaction is the sum of the rate constants of the two channels,

$$k_{HO_2+HO_2} = k_a+k_b = 1.7\times10^{-12} + 4.9\times10^{-32}\times2.46\times10^{19} = 2.9\times10^{-12} \; \textit{(cm³/molecule s)}$$

d) Determine the NO mixing ratio for the conditions of 2(c) at which the reaction of CH3O2 with NO just equals that with HO2. To what NOx level does this NO value correspond?

$$k_{CH_3O_2+NO}[CH_3O_2][NO] = k_{CH_3O_2+HO_2}[CH_3O_2][HO_2]$$

$$\rightarrow [NO] = f_{NO}[M] = \frac{k_{CH_3O_2+HO_2}[HO_2]}{k_{CH_3O_2+NO}} = \frac{k_{CH_3O_2+HO_2}f_{HO_2}[M]}{k_{CH_3O_2+NO}}$$

$$\rightarrow f_{NO} = \frac{k_{CH_3O_2+HO_2}f_{HO_2}}{k_{CH_3O_2+NO}} = \frac{5.2\times10^{-12}\times1.30\times10^{-11}}{7.7\times10^{-12}} = 8.75\times10^{-12} = \underline{\textbf{8.75 ppt}}$$

$$\rightarrow f_{NO_2} = \frac{k_{NO+O_3}f_{NO}f_{O_3}[M]}{j_{NO_2}} = \frac{1.9\times10^{-14}\times8.75\times10^{-12}\times20\times10^{-9}\times2.46\times10^{19}}{0.015}$$

$$= 5.43\times10^{-12} = 5.45 \; ppt$$

$$\rightarrow f_{NO_x} = f_{NO} + f_{NO_2} = 8.75 + 5.45 = \underline{\textbf{14.2 ppt}}$$

e) It is desired to prepare a plot of the rates of both O3 production, PO3, and loss, LO3, (molecules cm-3s-1) as a function of NO. Consider NO mixing ratios from 1 to 100 ppt. Ozone production occurs as a result of HO2 and CH3O2 reacting with NO, whereas O3 loss occurs by photolysis and reaction with HO2. Plot PO3 and LO3 as a function of NO. Recall that the results of Admission Ticket #15 can be used to estimate the photolysis term in LO3. For this, assume 50% RH. Assume a local O3 mixing ratio of 20 ppb. Note any assumptions you make in estimating [CH3O2].

$$P_{O_3} = k_{HO_2+NO}[HO_2][NO] + k_{CH_3O_2+NO}[CH_3O_2][NO]$$

$$= \left(k_{HO_2+NO} f_{HO_2} + k_{CH_3O_2+NO} f_{CH_3O_2} \right) f_{NO}[M]^2$$

$$= \left(8.1\times10^{-12} \times 1.3\times10^{-11} + 7.7\times10^{-12} f_{CH_3O_2} \right) \times f_{NO} \times \left(2.46\times10^{19}\right)^2 \qquad (1)$$

$$L_{O_3} = k_{O(^1D)+H_2O}[O(^1D)][H_2O] + k_{HO_2+O_3}[HO_2][O_3]$$

$$= k_{O(^1D)+H_2O}[O(^1D)]f_{H_2O}[M] + k_{HO_2+O_3} f_{HO_2} f_{O_3}[M]^2$$

$$= 2.2\times10^{-10}[O(^1D)]f_{H_2O} \times 2.46\times10^{19} + 1.9\times10^{-15} \times 1.3\times10^{-11} \times 20\times10^{-9} \times \left(2.46\times10^{19}\right)^2 \ (2)$$

Assume f_{HO2} the same as in 2(c):

$$f_{HO_2} = \sqrt{\frac{k_{OH+CO}[OH]f_{CO}}{2k_{HO_2+HO_2}[M]}} = \sqrt{\frac{2.4\times10^{-13} \times 10^6 \times 100\times10^{-9}}{2\times 2.9\times10^{-12} \times 2.46\times10^{19}}} = 1.30\times10^{-11}$$

Assume steady-state of CH_3O_2:

$$k_{CH_4+OH}[CH_4][OH] = k_{CH_3O_2+NO}[CH_3O_2] + [NO] + k_{CH_3O_2+HO_2}[CH_3O_2][HO_2]$$

$$\rightarrow [CH_3O_2] = f_{CH_3O_2}[M] = \frac{k_{CH_4+OH} f_{CH_4}[M][OH]}{\left(k_{CH_3O_2} f_{NO} + k_{CH_3O_2+HO_2} f_{HO_2} \right)[M]}$$

$$\rightarrow f_{CH_3O_2} = \frac{k_{CH_4+OH} f_{CH_4}[OH]}{\left(k_{CH_3O_2} f_{NO} + k_{CH_3O_2+HO_2} f_{HO_2}\right)[M]}$$ (assume f_{CH4} = 1700ppb)

$$= \frac{6.3\times10^{-15}\times1700\times10^{-9}\times10^6}{\left(7.7\times10^{-12}\times f_{NO} + 5.2\times10^{-12}\times1.30\times10^{-11}\right)\times2.46\times10^{19}}$$ (3)

Derive f_{H2O} and $[O(^1D)]$ as in Ticket # 15 at T = 298 K and RH = 50 % (use j_{O3} = $7\times10^{-6}s^{-1}$):

$a = (1\text{-}373.15/T) = (1\text{-}373.15/298)$,

$f_{H2O} = RH \times P_{H2O,S}/P_s = RH \times exp(13.3185a\text{-}1.976a^2\text{-}0.6445a^3\text{-}0.1299a^4) = 0.015$

$$[O(^1D)] = \frac{j_{O_3}[O_3]}{k_{O(^1D)+M}[M] + k_{O(^1D)+H_2O}[H_2O]} = \frac{j_{O_3} f_{O_3}}{k_{O(^1D)+M} + k_{O(^1D)+H_2O} f_{H_2O}}$$

$$= \frac{7\times10^{-6}\times20\times10^{-9}}{2.9\times10^{-11} + \times2.2\times10^{-10}\times0.015} = 4.32\times10^{-3} \text{ (molecule/cm}^3).$$

Substitute Eq.(3) into Eq.(1) and derive P_{O3} as a function of f_{NO}. Use the above f_{H2O} and $[O(^1D)]$ values to calculate L_{O3}. The figure below is the plot of P_{O3} and L_{O3} at f_{NO} from 1 to 100 ppt. P_{O3} increases with increasing NO level while L_{O3} is at constant of 6.6×10^5 molecule/cm^{3}s. **The two curves cross each other at f_{NO} = 8.4 ppt**.
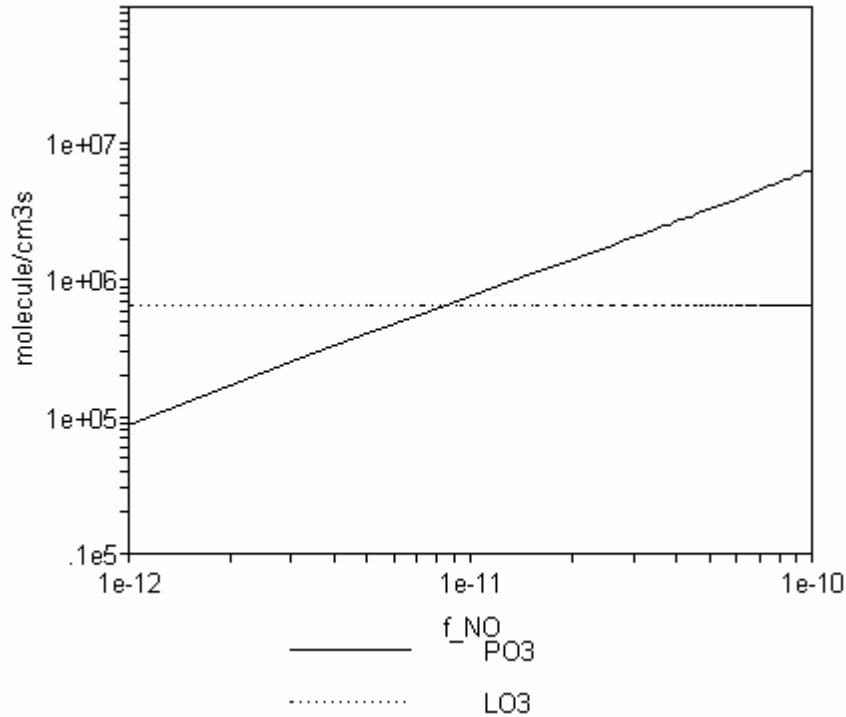
We can judge whether a region is O_3-producing or O_3-destroying by comparing the local

f) Based on the NO mixing ratio at which PO3 = LO3, would you judge the following

regions of the troposphere to be O3-producing or O3-destroying?

Remote Pacific Ocean marine boundary layer

Downtown Los Angeles

Rural Southeastern U.S.

[NO] with the value of [NO] at the cross point of PO3 and LO3, which is around fNO = 8.4

ppt as derived in 2 (d). (Assume the regions have the same local $[O_3]$, $[OH]$, $[CO]$ and $[CH_4]$

levels and the same j_{O3} as in our calculations). If the NO mixing ratio is higher than 8.4 ppt, the

region is O_3-producing since P_{O3} is larger than L_{O3} at the right hand side of the cross point, and

contrarily if f_{NO} is lower than 8.4 ppt, the region is O_3-destroying.

Table 2.6 in Seinfeld and Pandis provides typical NO_x mixing ratios at different regions, which can be converted to NO mixing ratio by assuming photostationary state:

$$f_{NO_x} = f_{NO} + f_{NO_2} = \left(1 + \frac{k_{NO+O_3} f_{O_3}[M]}{j_{NO_2}}\right) f_{NO} = \left(1 + \frac{1.9 \times 10^{-14} \times 20 \times 10^{-9} \times 2.46 \times 10^{19}}{0.015}\right) f_{NO}$$

$$\rightarrow f_{NO} = 0.6 f_{NOx}$$

Regions	f_{NOx} (ppt)	f_{NO} (ppt)	O_3-producing/destroying
Remote Pacific Ocean MBL	20-40	12-24	**slightly O$_3$-producing**
Downtown Los Angeles	10^4-10^6	10^4-10^6	**highly O$_3$-producing**
Rural Southeastern U.S.	200-10^4	100-10^4	**moderately O$_3$-producing**

Note:

1. The NO level at the cross point varies with local conditions. For example, a higher j_{O3} value can shift the cross point to higher f_{NO} to around 50 ppt. In this case the region of remote Pacific Ocean can become ozone-destroying. So the remote regions is actually at a place where the ozone production and loss are about at balance.

2. In 2 (c) we assumed that the HO_2+HO_2 reaction is the main sink for HO_2 and ignored the other HO_2 loss reaction to derive the HO_2 level. This is only true under low NO_x condition. In regions with high NO_x level, such as LA downtown, the HO_2+NO can become the dominant HO_2 sink, and the way to evaluate local HO_2 level has to be modified. The rigorous solution is to consider the full balance of HO_2, i.e.

$$k_{OH+CO}[OH][CO] =$$
$$2k_{HO_2+HO_2}[HO_2]^2 + k_{HO_2+NO}[HO_2][NO] + k_{CH_3O_2+HO_2}[CH_3O_2][HO_2] + k_{HO_2+O_3}[HO_2][O_3]$$

Substitute the steady-state approximation of CH_3O_2 from 2 (d) into the above equation and solve for f_{HO2} as a function of f_{NO}. Use this solution of f_{HO2} in calculating P_{O3} and L_{O3}, the plot shows that the two curve cross at a slightly higher NO level (around 12 ppt), and the magnitudes of both P_{O3} and L_{O3} are smaller than the results from using just low-NOx limit for HO_2.