1) Problem 11.2 "Sources of Tropospheric O_3" in Jacob textbook

2) Chemical regimes in the upper troposphere.

Aircraft emissions of NO_x may increase ozone concentrations in the upper troposphere where it is an efficient greenhouse gas. We examine here the sensitivity of ozone to NO_x in the upper troposphere under different conditions. The NO_x radicals ($NO_x \equiv NO + NO_2$) cycle through the reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3 \qquad (2)$$

Assume that the [NO]/[NO_2] ratio is determined solely by reactions (1)-(2) (a reasonable approximation in the upper troposphere). For the rest of this problem, write $[NO] = \alpha[NO_x]$ and $[NO_2] = (1-\alpha)[NO_x]$ where α is a coefficient assumed constant.

The HO_x radicals ($HO_x \equiv OH + HO_2$) in the upper troposphere are produced at a rate $P(HO_x)$ that we assume to be constant. They cycle and are consumed principally by the following reactions:

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (3)$$

$$OH + CO \xrightarrow{O_2} HO_2 + CO_2 \qquad (4)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (5)$$

$$OH + HO_2 \rightarrow H_2O + O_2 \qquad (6)$$

$$HO_2 + NO_2 \xrightarrow{M} HNO_4 \qquad (7)$$

$$OH + NO_2 \xrightarrow{M} HNO_3 \qquad (8)$$

6.1 Identify four different HO_x sinks in the above mechanism.

6.2 We can distinguish four different chemical regimes in the upper troposphere depending on the dominant reaction for HO_x loss. Let us model each of these regimes by considering the limiting case where loss of HO_x is exclusively by the dominant reaction. Further assume that the HO_x radicals are in chemical steady state, and that HO_x cycling is efficient so that the HO_x cycling reactions are much faster than the HO_x loss reactions. For each regime, determine the dependence of the ozone production rate on [NO_x].

6.3 Which of the four regimes applies to very low NO_x concentrations? to very high NO_x concentrations? Plot qualitatively the O_3 production rate as a function of [NO_x], identifying each chemical regime in the plot. Briefly conclude as to the challenge of predicting the response of O_3 to increasing aircraft NO_x emissions.