ATS 621, Fall 2011

HOMEWORK #7: due Thursday, November 3, 2011

Please provide solutions with complete calculations for full credit. Use SI units.
Point values listed in brackets for each question.

Q1 (30): Ozone Production Efficiency

When ozone production is in the NOx-limited regime, an important quantity used to project the benefit of NOx emission controls is the ozone production efficiency per unit NOx oxidized (OPE). Consider the following simplified mechanism for ozone smog production involving the oxidation of a hydrocarbon (RH) in the presence of NOx:

$$RH + OH \xrightarrow{O_2} RO_2 + H_2O \quad (1)$$
$$RO_2 + NO \rightarrow OH + NO_2 + \text{products} \quad (2)$$
$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3 \quad (3)$$
$$NO + O_3 \rightarrow NO_2 + O_2 \quad (4)$$
$$NO_2 + OH \xrightarrow{M} HNO_3 \quad (5)$$

Assume in what follows that (4) is much faster than (2), and that (5) is much slower than (1) and (3). Assume also that all radicals are in steady state. Denote *ki* the rate constant of reaction (i)

1.1 Show that OPE = $k_1[RH]/(k_5[NO_2])$.

1.2 It is more useful to express the OPE as a function of $[NO_x]$ rather than as a function of $[NO_2]$ because of the rapid cycling between NO and NO_2. Derive an expression for the $[NO_2]/[NO_x]$ ratio as a function of $[O_3]$ only. Replace into your OPE equation. What do you conclude as to the dependence of OPE on the ozone concentration? Explain qualitatively your result. Does this dependence hinder or enhance the effectiveness of NO_x emission controls for reducing ozone levels?

1.3 An alternate branch for reaction (2) produces a stable organic nitrate $RONO_2$ which is eventually removed by deposition:

$$RO_2 + NO \xrightarrow{M} RONO_2 \quad (2')$$

Show that if this reaction dominates NOx loss (that is, if (2') is much faster than (5)), then the OPE is a constant.

Problems from Jacob:

Q2 (40): 12.1

Q3 (30): 8.1