Chemistry 471/671

Problem Set #2: Atmospheric Chemistry I (12 points)
Due Tuesday, September 18, 2007

1) Given: standard atmospheric pressure at sea level is 760 torr, and at 100 km of altitude is $4.2*10^{-4}$ torr. Assume an average tropopause height of approximately 15 km, and assume that the falloff of pressure with altitude is a simple exponential. What proportion by mass of the earth's atmosphere is contained within the troposphere?

2) Given two reactions, A + B → products. Assume that the concentrations of reagents are constant, and that each reaction has the same A-factor. One of these reactions has an activation energy of 25 kJ/mol, while the other has an activation energy of 18 kJ/mol. Calculate the relative rates of these two reactions a) at 298 K and b) at 243 K. Why those two temperatures? What are the implications?

3) Consider the reaction $NO + O_3 \rightarrow NO_2 + O_2$, which has a rate constant given by $k = 1.8 * 10^{-12} e^{-1370/T}$ cm^3 $molecules^{-1} s^{-1}$. Use the following standard heats of formation.

Substance	ΔH_f^o (kJ mol^{-1})
NO	90.25
NO_2	33.18
O_3	142.7

a. What is the activation energy of this reaction?
b. What is the standard enthalpy of this reaction? Is it exothermic or endothermic?
c. Draw the potential energy profile of this reaction.
d. From the energy profile can you predict if the reverse reaction will have a larger or smaller rate constant?

4) Peroxyacetylnitrate (PAN) is formed by addition of NO_2 to the corresponding peroxyacetyl radical. PAN is considered to by a sink for NO_2 in the afternoon during smog incident.

$CH_3C(=O)O_2 + NO_2 \leftrightarrow CH_3C(=O)O_2NO_2$

$k(reverse) = 1.86 \times 10^{16} e^{-13500/T}$

a) Calculate the half-life of PAN as it releases NO_2 at 5 and 35°C.
b) Based on these calculated half-lives, what would favor PAN as a sink for NO_2?

5 (4 points) Consider the atmospheric oxidation sequence for propene, $CH_3\text{-}CH\text{=}CH_2$. Determine the terminal products of this oxidation. Note that there are several possible sites for the initial attack by OH, and again at each subsequent point in the chain. Specify which initial addition channel you expect to dominate, and why, **and** which initial abstraction site you expect to dominate and why. Draw all of the possible first-step products, and then follow each of your "dominant" product channels to their logical conclusion. Each time you must choose between two ore more possible pathways, select the one you expect to be dominant, explain why, and ignore the less likely pathway. For this problem, consider aldehydes to be terminal products – that is, do not consider photodissociation in your mechanism.