AT 621, Fall 2012

Homework #1

Due Wednesday, 29 August

Problem 1. *[structures and oxidation states]*

(a) Identify whether each of the following is a stable molecule or a radical:

$HCHO$

$HCOOH$

HO_2

CH_3O_2

CO_2

CH_4

CO

CH_3

(b) For the stable molecules from part (a), deduce a likely chemical reaction sequence for the troposphere (i.e., order the stable species from less to more oxidized).

(c) Similar to (b), give a likely sequence for the following sulfur compounds:
SO_2, H_2SO_4, H_2S

(d) Identify the oxidation state of nitrogen in each of the following.

N_2O
N_2
HNO_3
NH_3
NO
NO_2

Problem 2. *[Balancing equations]*

Biological **nitrogen fixation**, the binding of atmospheric nitrogen in a chemically combined form, is a key biochemical process in the environment and is essential for plant growth in the absence of synthetic fertilizers. The process is complicated and not fully understood, but the overall microbial process for nitrogen fixation is

$$\_\{\ H_2O\} + \_N_2 + \_H_2O \rightarrow \_CO_2 + \_NH_3$$

In this equation, $\{CH_2O\}$ represents a unit of carbohydrate. For this problem, let $\{CH_2O\}$ be acetic acid, so that

$$aC_2H_4O_2 + bN_2 + cH_2O \rightarrow dCO_2 + eNH_3 \qquad (1)$$

(a) Balance the equation (1) to find values for *b,c,d,e*; let *a=1*.

(b) Compute the molecular weights of all the species in equation (1).

Problem 3. *[unit conversions; typical atmospheric concentrations]*

(a) How many molecules constitute 1 ppmv in the atmosphere at the surface (T=283 K, P = 1 atm)?

(b) The proposed new USEPA criteria pollutant standard for ozone concentrations is 80 ppbv averaged over 8 hours. Calculate the equivalent concentration of ozone in $\mu g\ m^{-3}$ for Denver and for Los Angeles.

Problem 4. *[equilibrium constants]*

Write expressions for the equilibrium constants for both the forward and reverse reactions of the following chemical equations:

(a) $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$

(b) $N_2O(g) + \frac{1}{2}O_2(g) \Leftrightarrow 2NO(g)$

(c) $4NH_3(g) + 3O_2(g) \Leftrightarrow 2N_2(g) + 6H_20(g)$

(d) $NH_4Cl(s) \Leftrightarrow NH_3(g) + HCl(g)$

Problem 5. *[Chemical kinetics; PSSA approximation]*

Consider the following sequence of elementary reactions:

$$CO + OH \longrightarrow CO_2 + H$$
$$SO_2 + OH \longrightarrow H_2SO_4$$
$$O_3 + h\nu \longrightarrow O_2 + O(^1D)$$
$$O(^1D) + H_2O \longrightarrow 2OH$$

(a) Write an equation for the time rate of change of [OH], based on reactions 1–4.

(b) Assume that OH is a very reactive species (it is), and that we can apply the PSSA to obtain its concentration. Derive an algebraic equation for the pseudo-steady-state concentration of OH.

(c) Apply the PSSA to $O(^1D)$, and use the results in your expression for [OH] from part (b) to get the concentration of OH in terms of concentrations of stable species.

(d) The rate constants for reactions 1 and 2 are

$k_1 = 2.2 \times 10^{-13}$
$k_2 = 1.1 \times 10^{-12}$

Use these constants, plus reasonable values for the atmospheric concentrations of CO and SO_2 that you find in the notes or in a text, to evaluate which species is the more important sink for OH in the atmosphere.