Test 1 – The Atmosphere

1. During a photochemical smog episode in the coastal city of Seattle, the steady-state concentration of oxygen radicals at ground level was measured to be 0.080 ppmv at 25°C. Convert this value to:

a) partial pressure in atm

b) mol L^{-1}

c) molecules cm^{-3}

2. (a) Fill in blank:

The formation and destruction cycles in the stratosphere helps to maintain a steady concentration of ozone. The following set of 4 chemical reactions that represent steady state ozone in the troposphere.

$$O_2 + UV\text{-}\square \rightarrow 2\,O$$

$$\square + O_2 + \square \rightarrow \square + M$$

$$O_3 + UV\text{-}\square \rightarrow \square + \square$$

$$O_3 + O \rightarrow 2\,\square$$

Based on Chapman steady state analysis, the concentration of O_3 decreases as air density (M) _______________ (*Fill in the trend)* and the rate of O_2 dissociation decreases at lower altitude because the intensity of UV-C light ________________ *(Fill in the trend)*

(b) Write out a mechanism by which chlorine atom catalytically destroys ozone in the stratosphere. Indicate whether these reactions represent Mechanism I or Mechanism II type destruction?

$$Cl + O_3 \rightarrow \square + O_2$$

$$Br + O_3 \rightarrow \square + O_2$$

$$\square + \square \rightarrow Cl + Br + O_2$$

Net Reaction: $\square$

This reaction scheme represents Mechanism $\square$ type destruction of ozone.

(c) Perform a steady state analysis on the following three step reaction mechanism and derive an expression for steady state concentration of O* in terms of concentrations of other chemicals.

$$O_3 + h\nu \rightarrow O_2 + O^*$$

$$O^* + M \rightarrow O + M$$

$$O^* + H_2O \rightarrow 2\ {\bullet}OH$$

3. Stokes' Law describing partial sedimentation is given by:

$$v = \frac{g\, d^2 (\rho_s - \rho_f)}{18\, \mu}$$

where v = terminal velocity, g = 9.81 m s^{-2} is gravitational acceleration, ρ_s = density of the particle, ρ_f = density of the fluid, μ = air viscosity (1.76 x 10^{-4} g cm^{-1} s^{-1}) and d = particle diameter in centimeters.

Gas	*% Volume*
Nitrogen	78.09
Oxygen	20.95
Argon	0.934
Carbon dioxide	0.0380

Composition of dry air.

a) Show that the above expression is equal to the expression below.

$$v = \frac{2\, g\, r^2 (\rho_s - \rho_f)}{9\mu}$$

b) Use the ideal gas law to calculate the weight of one cubic centimeter of air at 1.0 atm and 15°C. Where air is a mixture of gases with molecular mass $\overline{M} = \Sigma\, r_i\, m_i$ where r_i = volume mixing ratio and m_i = molecular weight of ith gas.

c) Assume particles have a density of 2.40 g cm^{-3} and are being released by a 100 m smokestack. How long does it take a 25 μm diameter particle to settle to the ground?

4. Consider the following aqueous route to oxidize SO_2:

$$SO_2(aq) + H_2O_2(aq) \rightarrow H_2SO_4(aq) \qquad k = 1.1 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$$

a. The partial pressures and Henry's Law constants for SO_2 and H_2O_2 are 3.0 ppm (K_H = 1.2 mol L^{-1} atm^{-1}) and 4.0 ppb (K_H = 1.0 x 10^5 mol L^{-1} atm^{-1}), respectively.

a) Write down the rate expression for this reaction.

b) Calculate the partial pressure (atm) of each of the gases at ground level.

c) Calculate the concentration of each of the gases using Henry's law (mols L^{-1}).

d) Calculate the reaction rate of this process.

5. When the concentration of nitrogen oxides in a region of the air is very low, peroxy radicals combine with other species rather than oxidizing nitric oxide. Deduce the mechanism, including the overall equation, for the process by which carbon monoxide is oxidized to carbon dioxide under these conditions, assuming that the hydroperoxy radicals react with ozone.

[Note: include all radicals and bonds in your structures]

From your result, would you predict that ozone levels would be abnormally high or low in air masses having low nitrogen monoxide concentration?

BONUS:

a) Draw the complete Lewis structures for NO_2, HONO, and HNO_3, illustrating the radical nature of the first species and the nonradical nature of the last two species. (resonance structures and formal charges are not required).

b) Predict the most likely reaction (if any) that would occur between a hydroxyl radical and each of the following atmospheric gases:

i) Methane

ii) Methanol

iii) Water vapour