_____(name)

ATOC 3500 – Midterm Exam 2
Wednesday, November 15, 2006

There are four parts to this exam, worth a total of 100 points. You should not have to use a calculator. If you are unsure of an answer, please provide additional information for possible partial credit. Open book/notes are fine.

1. (24 pts) True or False

___T__ (a) Wavelengths shorter than ~310 nm are absorbed by O_2 and O_3 before they reach the earth's surface.

___F__ (b) The inverted temperature profile (the "inversion") in the stratosphere is due to absorption of visible radiation by ozone. It's due to absorption of ultraviolet

___F__ (c) The maximum in the intensity radiated from the sun is in the ultraviolet portion of the spectrum. it's in the visible/infrared

___F__ (d) The main contributors to acid rain are phosphoric acid and hydrochloric acid. The main contributors are sulfuric and nitric acids

___T__ (e) In pure water with a pH of 7 the concentration of OH^- is the same as that of H^+.

___T__ (f) A solution with a pH of 5 is ten times more acidic than one with a pH of 6.

___T__ (g) The rate of a chemical reaction depends on the concentrations of all of the reactants.

___F__ (h) Ozone was found in the atmosphere only after oxygen was discovered to be a major component of air. Oxygen was actually discovered after ozone!

___F__ (i) Even if chlorofluorocarbons had not been regulated in the 1990s, their production rate would have soon decreased as less uses were found for them. Their uses were increasing at a very rapid pace

___T__ (j) Exposure to radon is estimated to cause fewer deaths in the United States each year than drunk driving.

___T__ (k) In November, 2006, the Bush Administration requested permission to produce thousands of tons of methyl bromide despite the fact that the chemical had already been banned because it depleted ozone.

___F__ (l) The conversion of biomass into ethanol for fuel to substantially reduce carbon emissions is likely to have little or no impact on world food supplies. The use of land for biomass reduces the availability for food crops

2. (30 pts) Nitric acid (HNO_3) forms when the gaseous pollutant nitrogen dioxide (NO_2) reacts with OH.

$$OH + NO_2 + M \rightarrow HNO_3 + M$$

(a) (3 pts) Is the reaction above an example of a bimolecular reaction or termolecular reaction?

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(b) (4pts) What information is needed to calculate the rate of this reaction?

Rate constant and concentrations of all of the reactants (OH, NO_2 and M)

(c) (3 pts) Write an expression for the equilibrium constant, K_a, for nitric acid when it dissolves in water using the equilibrium below.

$$HNO_3 \rightleftarrows H^+ + NO_3^-$$

$K_a = [H^+]\,[NO_3^-]/[HNO_3]$

(d) (3 pts) HNO_3 is called a 'strong acid' because its equilibrium constant, K_a, is very large (essentially infinity). Knowing this, determine the pH of 1000 L of water into which 1 Mole of HNO_3 was added (it's ok to set up an expression and not solve it, just so you give enough information for me to believe that you know what you are doing!).

if K_a is infinity, then $HNO_3 \Rightarrow 0$ when it is added to water. That means that all of the HNO_3 added will dissociate into H^+. So if we add 1 mole of HNO_3 to 1000 L of water, we will have 1 mole of H^+ in 1000 L of water – or 10^{-3} moles per liter. This is a pH of 3

$-\log_{10}(10^{-3}) = 3$

(e) (3 pts) Describe how one might go about using emissions data on NO_2 (for example, from cars and industry) and measurements of nitrate (NO_3^-) in water to see if there is a link between those emissions and acid rain.

Try to link the emissions of NO_2 to the appearance of HNO_3 in water (in this case, the NO_3^- that is measured in water). You might also look for trends in these two quantities, but it's better to have a quantitative link between emissions and subsequent pollution than just a trend, because trends could be due to something else.

(f) (3 pts) Carbonic acid (H_2CO_3) is called a "weak acid" because it has an equilibrium constant that is much smaller than 1. Assume that a H_2CO_3 molecule dissociates once in water to produce a single H^+. Write an expression for the equilibrium constant for

carbonic acid and describe how you would calculate the pH of 1000 L of water into which 1 mole of carbonic acid was added if you knew the equilibrium constant, K_{eq}.

$$H_2CO_3 = H^+ + HCO_3^-$$

$$K_{eq} = [H^+]\,[HCO_3^-]/[H_2CO_3]$$

First, you'd assume that $[H^+]$ and $[HCO_3^-]$ are equal, then note that if you produce x moles of H^+ you lose x moles of H_2CO_3, so you can write an algebraic expression for Keq that looks like this:

$$K_{eq} = x^2/(1/1000\text{-}x)$$

Then, you'd either solve this with the quadratic equation, or you would assume $x << 1$ and just say that $x^2 = (1000\ Keq)$ – then check to make sure that the condition $x << 1$ holds, and if not, adjust your demoninator a bit and repeat

(g) (3 pts) Will the pH of the solution of carbonic acid in part (e) be the same, higher, or lower than that for the solution of nitric acid in part (d)?

pH of carbonic acid will be higher, because less of it dissociates than nitric acid.

(h) (3 pts) Will the pH of water in contact with atmospheric CO_2 increase or decrease as the amount of CO_2 in the atmosphere increases?

pH will decrease as CO_2 in the atmosphere increases, as more carbonic acid will be produced by the dissolved CO_2.

(a) (5 pts) Describe some of the effects of acid precipitation on the environment.

Many answers were – fish and other aquatic life killed, erosion of limestone, statues eroded, etc. etc.

3. (25 pts) Aerosols absorb and scatter light, thereby affecting visibility. In class, we learned that the Koschmieder equation below can be used to estimate the amount of particulate material in the air.

$$V_r = 3.92/Be = 1000/TSP$$

where V_r is the visual range in km, Be is the extinction coefficient, and TSP is total suspended particulate in $\mu g\ m^{-3}$.

(a)(5 pts) On a clear day in Boulder, one can often see the tops of large thunderstorms on the eastern plains over 250 km away, whereas on a hazy day, it may not be possible to see Longs Peak, which is less than 50 km away. Use this information to estimate the amount of TSP in each of these cases.

Vr = 1000/TSP, so if Vr is greater than 250 km, then TSP must be less than 4 $\mu g\ m^{-3}$
If Vr is less than 50 km, then TSP must be greater than 20 $\mu g\ m^{-3}$

(b)(5 pts) In class it was noted that the criterion for visibility (or "visual range") is a transmission through the atmosphere of 0.02 (or 2%). This was also called the "threshold of perception" on page 98 of the book. Transmission refers to the amount of light that is transmitted along of path of air over a distance "d" using Beer's Law:

$$\text{Transmission} = I/I_o = \exp\{-\sigma \times N \times d\}$$

What do the terms σ and N refer to in Beer's Law? (note that the product σ x N is the extinction coefficient, Be, in the Koschmieder equation).

σ refers to the absorption cross section (how effectively something absorbs) and N is the amount of stuff that is absorbing (the concentration)

(c) (5 pts) In one of the homework problems, we determined Be (and ultimately the transmission) for an aerosol. We assumed that the particles were spherical. What two properties of the aerosol did we need to know in order to determine this extinction coefficient?

The radius (or diameter) in order to get the absorption coefficient (or shadow area) and the abundance (or concentration) in the atmosphere.

(d) (5 pts) The heavily forested areas of the Great Smoky Mountains are relatively free of human sources of air pollution, yet they are known to have very low visibility during some times of year. What is the source of particles that form the haze over the Great Smoky Mountains?

Emissions of hydrocarbons from the trees – these compounds react with OH in the atmosphere to make other compounds that condense to make tiny particles.

(e) (5 pts) What are some of the main sources of human-caused particulates found in the most polluted regions of the earth?

Sulfate and organic compounds emitted from fossil fuel combustion. Also some building practices that make dust.

Extra credit – Why is the haze that often forms over forested areas blue in tint?

Small particles produced by the organic compounds scatter blue light more effectively than other colors (called "Rayleigh scatter") so they make a blueish colored haze.

4. (21 pts) Provide short answers for seven of the following questions

(a) What are the main characteristics of a London-type smog?

Damp – foggy, smoke and fog combine to make smog. Sulfur as well makes the fog caustic.

(b) What is meant by the term steady state?

Rate of production equals rate of loss – so concentration stays constant.

(c) What did Sidney Chapman contribute to the understanding of stratospheric ozone?

He determined what reactions of oxygen could produce an ozone layer, and estimated the amount of ozone that would be present. The true amount was less than this, due to other reactions that he neglected, like catalytic reactions with NO and chlorine, but he came pretty close! Not bad for someone working with limited information in the 1930s!

(d) Who said "It may mean the end of the world" when in 1974 his wife asked how his research work was going?

F. Sherwood Rowland – UC Irvine professor who postulated that CFCs would destroy stratospheric ozone and eventually won a Nobel Prize in 1995. Interestingly, his own thesis advisor won a Nobel Prize many years earlier for work in chemistry.

(e) Why don't particles with diameters larger than ~10 μm end up in one's lungs?

They are lodged in the linings of the upper respiratory tract because they can't bend corners as well as small particles (called inertial impaction)

(f) Why are oxygenated fuels, like ethanol, added to gasoline?

To increase octane (fuel burning efficiency) and to reduce emissions of CO and NOx.

(g) What is meant by confounding factors in epidemiological studies of air pollution?

Factors that make it difficult to isolate a single cause for a problem.

(h) How can one use a box-model to estimate a lifetime of a species in the atmosphere?

Take the concentration of the species in the box and divide it by the total loss rate of the species from the box.