ATOC 3500/CHEM 3151 – Air Pollution Chemistry
Midterm Spring 2016

I. True or False (24 pts)

1. The mixing ratio "one part per billion" (or "1 ppb") can also be written as $1x10^{-9}$. T

2. 100 kilometers is an important altitude because half of the weight of the earth's atmosphere is above this altitude. F (that altitude is where pressure = 500 mbar – half the surface pressure)

3. Water vapor can never make up more than 1% of the amount of air by number because larger amounts will spontaneously condense to form precipitation. F – can be even 3-4% in warm areas

4. The largest mixing ratios of ozone are found in Earth's stratosphere. T

5. Nitrogen oxides in Earth's atmosphere can be formed by processes such as lightning and combustion. T

6. 760 torr and 1013 mbar are the same pressure, both occurring at about 2 km above sea level. F – these are equal, but they are sea level pressures

7. A reasonable average value for the scale height of Earth's atmosphere is 7 km. T

8. Most, but not all, reactions between molecules get faster with decreasing temperature. F (inverse is true)

9. One can readily calculate the mixing ratio of an atmospheric constituent X by multiplying the total number concentration, [X], by the total number density of the atmosphere, [M]. F – divide by [M]

10. A radical is an atom or molecule that has no unpaired electrons. F – has at least one unpaired spin

11. Although ozone is produced in the stratosphere by photolysis of O_2 by ultraviolet light, in the troposphere the process that produces ozone is photolysis of NO_2. T

12. OH is formed in the atmosphere primarily by direct photodissociation of water vapor (H_2O). F – from ozone photolysis followed by reaction of $O(^1D)$ with H_2O

II. Multiple Choice (24 points)

1. The "mixing ratio by volume" is identical to what quantity used commonly by chemists?
   (a) number density
   (b) number concentration
   (c) mole fraction
   (d) temperature
   (e) entropy

2. If one knows Earth's gravity, total surface area, and average pressure at the surface, what important quantity can be easily derived?
   (a) Avogadro's number
   (b) mean free path
   (c) stability
   (d) collision frequency
   (e) total mass of the atmosphere

3. Ozone in the stratosphere is important because
   (a) it absorbs virtually all the solar ultraviolet radiation between 240 and 290 nm which can be lethal to life at Earth's surface.
   (b) it greatly influences upper atmospheric meteorology due to heating caused by absorption of UV radiation.
   (c) by heating the stratosphere, it causes an inversion that results in vertically stable air.
   (d) all of the above
   (e) none of the above

4. The quantity kT/mg (which is the same as RT/g in different units), is called the "scale height", and is in units of
   (a) volume
   (b) length
   (c) mass
   (d) number
   (e) all of the above

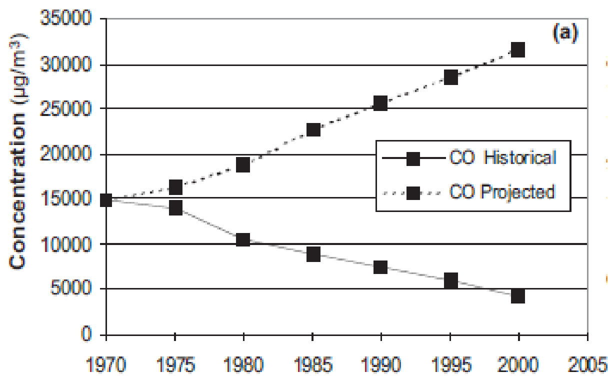
5. Which of the following statements about $O(^1D)$ (O "singlet D") is not true?
   (a) It is an oxygen atom in a highly energetic (or reactive) form.
   (b) It is formed by photolysis of ozone.
   (c) By reacting with water vapor (H_2O) it is an important source of OH.
   (d) It is found in all regions of the atmosphere at all times of day.
   (e) Because it is so reactive, the entire atmosphere contains only 1g of it at any given time.

6. Hydroxyl radicals (OH) are important in the atmosphere because
   (a) They convert SO_2 (sulfur dioxide) into H_2SO_4 (sulfuric acid).
   (b) They convert NO (nitric oxide) and NO_2 (nitrogen dioxide) into HNO_3 (nitric acid).
   (c) They react with CH_4 (methane).
   (d) They react with CO (carbon monoxide).
   (e) All of the above.

7. The adiabatic lapse rate, which represents the change in temperature of parcel of air as rises or descends in the atmosphere, has what value in Earth's atmosphere near the surface?
   (a) 6 ^{o}C km^{-1} for a "dry" parcel and 10 C km^{-1} for a "wet" parcel
   (b) 10 ^{o}C km^{-1} for a "dry" parcel and 6 C km^{-1} for a "wet" parcel
   (c) 6 ^{o}C km^{-1} for a "dry" parcel and 6 C km^{-1} for a "wet" parcel
   (d) 10 ^{o}C km^{-1} for a "dry" parcel and 10 C km^{-1} for a "wet" parcel
   (e) all the above, depending on the time of day.

8. The equation [M] = 7.25 x 10^{18} P / T (where P is in mbar and T is in Kelvin and [M] is in molecules cm^{-3}) was derived from what relationship?
   (a) The barometric (hydrostatic) equation.
   (b) The ideal gas law
   (c) Radiative balance
   (d) The adiabatic lapse rate
   (e) All of the above

III. (28 pts) Carbon monoxide (CO) is a toxic compound that is produced by incomplete combustion of hydrocarbons and by photochemical reactions in the atmosphere. Since the United States enacted the Clean Air Act in 1970, abundances of CO in US cities have steadily declined thanks to regulations that have limited emissions (for example, catalytic converters on automobiles). The figure below shows an example of the change in CO over time in a moderately polluted US city compared to projected increases had there been no regulations.



(a) (3 pts) "Micrograms per meter cubed" (µg m^{-3}) is yet another way to express an atmospheric concentration. It is relatively straightforward to show that 15,000 µg m^{-3} equivalent to about 3×10^{14} molecules cm^{-3}. What three quantities would you use to make this conversion (note, you don't need to do the calculation!)?

I was looking for (1) molecular weight (can be grams per mole, as long as you remember to convert to micrograms), (2) Avogadro's number (molecules to moles) and (3) conversion from m^3 to cm^3.

The following set of reactions describes the oxidation of carbon monoxide in Earth's atmosphere near the surface.

$$CO + OH \rightarrow CO_2 + H \qquad k_1 = 1\times10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$H + O_2 \rightarrow HO_2 \qquad k_2 = 1\times10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad k_3 = 1\times10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$$

Net: $CO + O_2 + NO \rightarrow CO_2 + NO_2$

(b) (3 pts) Explain why we refer to OH as a 'catalyst' in the oxidation of carbon monoxide.

It is needed for the reactions to proceed, but it isn't consumed in the overall process.

(c) (3 pts) Based on the cycle above, describe why the oxidation of CO in the troposphere can leads to formation of ozone, and why this formation only occurs during daytime.

The cycle produces NO_2, which photolyzes to form O atoms. O atoms quickly combine with O_2 to form ozone.

(d) (4 pts) Complete the expression below for the rate of change of CO.

$$-d[CO]/dt = \text{Rate of reaction (1)} = \_\_k_1 [CO] [OH]\_\_\_\_\_\_\_$$

(e) (5 points) Using reactions (1) and (2), derive an expression for the ratio of [H] to [OH] in terms of k_1 and k_2 and [CO] and [O2]. (Hint - assume that the concentration of [H] is in steady state.

[H]/[OH] =

Formation of H: rate = k_1 [CO] [OH]
Loss of H: rate = k_2 [H][O_2]

Set equal to each other for steady state: k_1 [CO] [OH] = k_2 [H][O_2]
Solve for [H]/[OH] = k_1 [CO] / k_2 [O_2]

(f) (3 pts) Based on what you know about the mixing ratios of O_2 and CO in the atmosphere, do you expect the concentration of H to be larger or smaller than the concentration of [OH]? Explain your answer.

O_2 is 21% of the atmosphere. Argon is 1%, anything else (other than N_2) is much smaller still. Since $k_1 = k_2$, [H]/[OH] << 1 since [CO] / [O_2] << 1.

(g) (3 pts) Reaction (2) actually requires a third-body to proceed. That is, it should be written as $H + O_2 + M \rightarrow HO_2 + M$. Describe how your result from Part (e) might differ if you were examining this balance at higher altitudes – that is, what do you expect will happen to the [H]/[OH] ratio as altitude increases because of this three-body reaction?

Since we haven't gone too deep into termolecular reactions, I decided to write the second reaction as bimolecular. That's ok as long as we use the appropriate pressure to determine the value for k_2. I gave this for sea level. But as we go up in altitude, the rate of a termolecular reaction will get smaller because [M] is decreasing rapidly with height. So if k_2 drops, the ratio [H] / [OH] will increase.

(h) (4 pts) One of the caveats of the oxidation of carbon monoxide is that OH initially needs to be present for the reaction sequence to start (that is, even though it is a catalyst, there must be some way to produce it that doesn't rely on the presence of CO). Where does this OH come from (i.e, from what set of reactions)?

Ah, my favorite question! It will be on the final too!

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \rightarrow OH + OH$$

IV. (24pts) "In your own words" - Give a very short definition or description of each of the following, something that a person who is unfamiliar with atmospheric chemistry might understand.

(a) Mixing ratio

Mole fraction of compound X in atmosphere – or ratio of [X] / [M]. Anything correct and understandable worked, even mass, although we often call that the mass mixing ratio.

(b) [M]

Concentration (or number density) of total air molecules.

(c) Atmospheric 'lifetime'

The ratio of the concentration of a compound to the rate of loss of that compound. Sometimes we consider this like the "half-life", although it's really called the "e-folding time" since it's usually an exponential function. Note that is isn't the time that it takes for the material to completely disappear (or return to natural abundance). But I didn't count off for those. After one lifetime, there is still excess stuff around. It's really only after many lifetimes that a perturbation returns to a steady state. And, when something is in steady state, we still define the "lifetime" as the concentration divided by the rate of loss, even though the concentration isn't changing!

(d) "aerosol"

A suspension of solid or liquid particles in a gas (air, in the case of the atmosphere).

(e) Photochemical 'smog'

Pollutants, usually things like O_3, CO, NOx, and particulate matter that form from the action of sunlight on emissions in the atmosphere. Note – many of you didn't mention sunlight, but talked about haze. Haze is often associated with photochemical smog, but some smogs can have low levels of haze. What is critical, though, is the presence of sunlight. Without that, photochemical smog can't form. The word "photochemical" distinguishes the compounds formed in sunlight from things like sulfate and nitrate that can form in darkness.

(f) Why the temperature of air typically decreases with increasing altitude.

The surface of the earth is usually heated, which causes air to rise because it becomes buoyant. As air rises, the pressure drops, so it expands and cools

(g) Why the mixing ratios of atmospheric constituents with long lifetimes are relatively constant (e.g., O_2 is 21%) throughout the atmosphere, whereas constituents with short lifetimes tend to have highly variable mixing ratios.

When a compound has a long lifetime, it can mix due to weather, transport, etc. This reduces gradients. A short lifetime means that there are loss processes that remove the constituent from the atmosphere, so this produces bigger gradients (i.e., variability) between the sources and the sinks.

(g) Chapman chemistry

Four reactions involving oxygen species (O_3, O and O_2) that explain the presence of the ozone layer in the stratosphere.