# PHYS/OCEA 4595 Atmospheric Chemistry Exam, December 7 2019

**Helpful Constants:**

pptv = part per trillion
ppbv = part per billion
ppmv = part per million
1 hPa = 100 Pa = 100 N/$m^2$
average surface pressure $p_0$ = 1000 hPa
gravitational acceleration g = 9.80 m/$sec^2$
radius of the earth R = 6400 km
mean molecular mass of dry air $M_a$ = 28.96 g/mole
Avogadro's Number = $6.02 \times 10^{23}$ molecules/mole
Henry's Law where [X] is the molar concentration in water and $P_X$ is pressure: $[X] = K_H P_X$.
Transmission $T = e^{-\delta/cos\theta}$
$\delta = n\sigma L = N\sigma$ (N in molecules/area, n in molecules/volume)

**1.** The concentrations of $SO_4^{2-}$ and $NO_3^{-1}$ in rainfall in Minnesota and New York are similar. However, the pH of rain in New York is substantially lower than the pH of rain in Minnesota. Specify the two main chemical species responsible for this pH difference, and briefly describe the chemical mechanism by which these two chemical species increase rainwater pH. (3 points)

**2.** What is the main reason ozone columns are higher in mid-latitudes than the tropics? (1 point)

**3.** There are two main distinct ways of generating aerosol particles. Specify these two ways and given an example of an aerosol chemical type in each category. (2 points)

**4.** There are three aerosol regimes depending on the relative magnitudes of total sulphate, total ammonia, and total nitrate. Specify how the three regimes are defined, and the fraction of total ammonia and nitrate that is typically in the aerosol form for each. (3 points)

**5.** The relative strengths of various greenhouse house gases are usually compared by a quantity called the "radiative forcing".

(i) Define the radiative forcing of a greenhouse gas. (1 point)

(ii) Why is the radiative forcing a gas a more objective way of comparing the strength of various greenhouse gases than, for example, the effect of a greenhouse gas on surface temperature in a climate model. (1 point)

(iii) The Greenhouse Warming Potential (GWP) of a particular greenhouse gas takes into account not only its instantaneous radiative forcing but another feature of a greenhouse gas that has a strong influence on its climate impact. What is this other feature? (1 point)

**6.** Number correctly the sequence of events in the formation of the Antarctic ozone hole, from 1 the earliest to 5 the latest. (2 points)

ozone destruction
Formation of PSC's (Polar Stratospheric Clouds)
cold temperatures
conversion of chlorine reservoirs to $Cl_2$
sunlight returns

**7.** (i) What is the main oxidizing agent of $SO_2$ in the troposphere? (1 point)

(ii) What is a key observation that this chemical species does indeed play an important role in oxidizing $SO_2$? (1 point)

**8.** The figure below shows the variation in top of the atmosphere radiation with wavelength as measured by a satellite above a location with clear skies, and above a location with a cloud.

(i) In the figure, label which curve corresponds to the clear and cloudy cases. (2 point)

(ii) Estimate the surface temperature in the clear sky case and the cloud top temperature in the cloudy case. (2 point)

(iii) In the cloudy case, does the presence of $CO_2$ increase or decrease the top of the atmosphere (TOA) longwave emission to space. Explain. (2 point)

**9.** The intensity of UV radiation at the surface, under clear sky conditions, is dependent on what two main variables? (2 points)

**10.** Unlike some planets, the earth has retained most of its hydrogen. What is one factor which as limited the loss of hydrogen to space on earth? (1 point)

**11.** What is the most important physical quantity that determines whether a particular molecule is a greenhouse gas or not? (1 point)

**12.** Plants need nitrogen to produce amino acids. However, they themselves can not break the $N_2$ triple bond. What are two natural nitrification mechanisms that convert $\mathrm{N_2}$ to a form that plants can more readily assimilate? (2 point)

**13.** (i) The approximate ratio of carbon, oxygen, and hydrogen present in biomass is represented as $CH_2O$. Biomass is produced during photosynthesis. Write down an approximate formula representing the production of biomass during photosynthesis. (1 point)

(ii) If photosynthesis on earth were to stop, would this result in a drastic reduction in atmospheric $O_2$? Explain why or why not. (1 point)

**14.** The mixing ratio of oxygen has been measured at several locations around the globe since about 1990. In combination with carbon dioxide measurements, they can be used to estimate the net global uptake of carbon dioxide over the land. This argument can be made using a diagram. In this diagram, let the vertical axis refer to the mixing ratio of oxygen and the horizontal axis refer to the mixing ratio of carbon dioxide. A line in the diagram can then refer to the evolution of ($CO_2$,$O_2$) over time. The diagram should include the following:

(i) An arrow roughly representing the net change in ($CO_2$,$O_2$) over the past 30 years. (1 points)

(ii) Three arrows representing the main processes affecting the evolution of ($CO_2$,$O_2$) over the past 30 years. Label each of these three arrows. The slopes of the arrows should be roughly consistent with the stoichiometry of the process in terms of how it affects $O_2$ and $CO_2$. You can assume that the vector sum of these three processes is equal to the net observed change. (3 points)

**15.** Assume that 1 percent of the incident top of the atmosphere solar flux at 300 nm reaches the surface, that the only significant absorber in the atmosphere at this wavelength is ozone, and that scattering can be neglected. The ozone absorption cross section at 300 nm is $34.3 \times 10^{-20}$ cm$^2$ per molecule. The sun is directly overhead.

(i) What is the optical depth of the atmosphere at this wavelength? (2 points)

(iii) What is the column ozone amount in molecules per cm$^2$? (2 points)

**16.** Solve for the number of moles of $CO_2$ in the earth's atmosphere if the $CO_2$ mixing ratio is 400 ppmv, and the average surface pressure is 1000 hPa. Assume that the mean molecular weight of the atmosphere is the same as that for dry air. (4 points)

**17.** Carbon dioxide dissolves in water with a Henry's Law constant of $K_H$.

$CO_2(g) + H_2O \Leftrightarrow CO_2 \cdot H_2O$

Dissolved carbon dioxide $CO_2 \cdot H_2O$ subsequently dissociates into $HCO_3^-$ (bicarbonate) and $CO_3^{2-}$ (carbonate) as follows.

$CO_2 \cdot H_2O \Leftrightarrow HCO_3^- + H^+$

$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$

with

$$K_1 = \frac{[HCO_3^-][H^+]}{[CO_2 \cdot H_2O]}$$

$$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$$

Dissolved inorganic carbon is defined as:

$$[CO_2(aq)] = [CO_2 \cdot H_2O] + [HCO_3^-] + [CO_3^{2-}].$$

Derive an expression for $[CO_2(aq)]$ in the ocean in terms of $K_H$, $P_{CO_2}$, $K_1$, $K_2$, and $[H^+]$, assuming that all of these reactions are at equilibrium. (4 points)

**18.** Suppose that a large amount of $CaCO_3$ were dumped into the ocean. Explain with respect to your answer in the previous question whether this would increase or decrease $[CO_2(aq)]$ in the ocean. Give specific reactions if possible. (2 points)

**19.** Consider the following reactions only:

$OH + O_3 \rightarrow HO_2 + O_2 \qquad k_1 = 2.0 \times 10^{-14}\, cm^3/molec - sec$

$HO_2 + O_3 \rightarrow OH + 2\,O_2 \qquad k_2 = 1.0 \times 10^{-15}\, cm^3/molec - sec$

$OH + HO_2 \rightarrow H_2O + O_2 \qquad k_3 = 1.5 \times 10^{-10}\, cm^3/molec - sec$

$O^1D + H_2O \rightarrow 2\,OH \qquad k_4 = 2.2 \times 10^{-10}\, cm^3/molec - sec$

$O^1D + N_2 \rightarrow O + N_2 \qquad k_5 = 3.0 \times 10^{-11}\, cm^3/molec - sec$

$O_3 + h\nu \rightarrow O^1D + O_2 \qquad J_{O_3} = 2.0 \times 10^{-5} sec^{-1}$

$[M] = 2 \times 10^{18}\, molec/cm^3$.

$[N_2] = 0.8[M]$.

$O_3$ = 4 ppmv

$H_2O$ = 5 ppmv

(i) What is the fraction $f$ of $O^1D$ that reacts with water vapor to produce OH, as opposed to being converted back to O. (4 points)

(ii) $HO_x$ destroys $O_x$ in the stratosphere via a catalytic cycle. What is the sequence of reactions in this cycle? (2 points)

(iii) Use family style approximations to estimate the $HO_2$/OH ratio. (4 points)

(iv) Use family style approximations, including the assumption that $HO_x$ is in steady state, to estimate [OH]. (4 points)

**20.** The preindustrial atmosphere contained sulfur compounds emitted by marine phytoplankton and volcanoes, and $NO_x$ emitted by soils and lightning. These sources accounted globally to $1 \times 10^{12}$ moles S/year and $1 \times 10^{12}$ moles N/year, respectively. Assume that all the emitted sulfur and $NO_x$ are oxidized in the atmosphere to $H_2SO_4$ and $HNO_3$ respectively, which are then scavenged by rain.

(i) Estimate the mean concentrations (M) of ${SO_4}^{2-}$ and ${NO_3}^{-}$ in rain, assuming a global mean precipitation rate over the earth of 2 mm/day. (6 points)

(ii) Assuming there was nothing else present to influence the acidity of rainfall, and that $H_2SO_4$ and $HNO_3$ are extremely strong acids, estimate the mean pH of rain in the preindustrial atmosphere. (2 points)

**21.** Measurements indicate that $N_2O$ is increasing at a rate of 0.3 % per year. Its current mixing ratio is 315 ppbv. Its mixing ratio in the preindustrial atmosphere was 285 ppbv. It is destroyed (mostly in the stratosphere) with an overall first order loss rate $k = 0.004$ (year)$^{-1}$. Assume that this first loss rate $k$ is constant. There are $1.8 \times 10^{20}$ moles of air in the atmosphere.

(i) Estimate the number of moles of $N_2O$ emitted per year from the surface in the preindustrial atmosphere. Assume that $N_2O$ sources and sinks were in balance. (4 points)

(ii) Estimate the current emission of $N_2O$ from the surface in moles per year. (4 points)

(iii) If the current production were to stay constant, what would be the new steady state $N_2O$ mixing ratio. (2 points)

**22.** This question involves estimating the number of molecules of ozone produced per CO oxidation. Assume every CO reacts with OH to produce $HO_2$.

$CO + OH(+O_2) \rightarrow CO_2 + HO_2 \qquad k_1 = 2.4 \times 10^{-13}\, cm^3/molec - sec$

The $HO_x$ that is produced can then react with either NO or $O_3$.

$HO_2 + O_3 \rightarrow OH + 2\,O_2 \qquad k_2 = 1.6 \times 10^{-15}\, cm^3/molec - sec$

$HO_2 + NO \rightarrow OH + NO_2 \qquad k_3 = 9.3 \times 10^{-12}\, cm^3/molec - sec$

$[M] = 2 \times 10^{19}\, molec/cm^3$

$O_3$ = 50 ppbv

CO = 80 ppbv

NO = 100 pptv

$HO_x$ = 3 pptv

Assume that every $NO_2$ produced in the second reaction subsequently photolyzes to produce O, which then reacts with $O_2$ to produce $O_3$.

(i) Write down an expression the net rate of ozone production (i.e. production and destruction) associated with these reactions. (3 points)

(ii) Assume that $HO_x$ can be treated as a family with the three cycling reactions between $HO_2$ and OH as shown above. Write down an expression for the [OH]/[$HO_2$] ratio. (3 points)

(iii) Calculate the [OH]/[$HO_2$] ratio using the assigned mixing ratios and reaction constants. (2 points)

(iv) What is the mixing ratio of $HO_2$? (2 points)

(iv) Calculate the net ozone production rate in ppbv/day. (2 points)

**23.** The average emission of $NO_x$ over the continental United States is $2 \times 10^{11}$ molecules cm$^{-2}$ s$^{-1}$. Assume that all of this $NO_x$ is oxidized and rains out over the United States. The average rate of $HO_x$ production $P_{HO_x}$ at all altitudes is $4 \times 10^6$ molecules cm$^{-3}$ s$^{-1}$.

The only two sinks of $HO_x$ are:

1.$HO_2 + HO_2 \rightarrow H_2O_2 \quad k_1 = 3.0 \times 10^{-12}\, cm^3/molec - sec$
2.$NO_2 + OH + M \rightarrow HNO_3 + M \quad k_2 = 1.0 \times 10^{-11}\, cm^3/molec - sec$

The [M] dependence has already been included in $k_2$ (i.e. do not need [M] in the reaction rate.)

Model the United States as a well mixed box with a depth of 10 km. Treat all quantities as independent of height. You can assume that $HO_x$ is in steady state.

(i) What is the rate of $HO_x$ destruction via reaction (2) if $NO_2$ oxidation occurs uniformally in the box at all altitudes? (3 points)

(ii) What is the rate of $HO_x$ destruction via reaction (1)? (3 points)

(iii) Would you expect ozone production over the United States to be limited by the availability of $NO_x$ or hydrocarbons? Explain. (2 points)