## PHYS/OCEA 4595 Atmospheric Chemistry Exam, December 17 2020

## Helpful Constants:

pptv = part per trillion ppbv = part per billion ppmv = part per million 1 hPa = 100 Pa = 100 N/m<sup>2</sup> average surface pressure  $p_0 = 1000$  hPa gravitational acceleration g = 9.80 m/sec<sup>2</sup> radius of the earth R = 6400 km mean molecular mass of dry air M<sub>a</sub> = 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:  $[X] = K_H P_X$ . pH =  $-\log[H^+]$  (where  $[H^+]$  is in moles/l) Transmission  $T = e^{-\delta/cos\theta}$ optical depth:  $\delta = n\sigma L = N\sigma$  (N in molecules/area, n in molecules/volume,  $\sigma$  the cross-section.)

Ideal Gas Law: PV = NRT, with V in  $m^3$ , P in Pa, N in number of moles, the Ideal Gas Constant R = 8.31 J/(mol K), and T in K.

The Ideal Gas Law can also be written:  $n_a = 7.25 \times 10^{18} P/T$ , where P is in hPa, and T is in K. This gives  $n_a$  in molec/cm3.

**1.** Is  $O_2$  a greenhouse gas? Why or why not? (1 point)

**2.** Does the amount of surface biomass exert a strong controlling influence on atmospheric levels of  $O_2$  on long timescales? Explain. (1 point)

**3.** What is the main reason an ozone hole does not form in the Arctic? (1 point)

4. Suppose molecule A is dissociated by light with wavelengths less than 250 nm, while molecule B is dissociated by visible light. Roughly plot how the photolysis rates of A and B would depend on altitude, and indicate their relative magnitude. (2 points)

5. The input of  $NO_x$  and CO into the troposphere is many times larger now than it was one hundred years ago. The oxidation of each of these species (to  $HNO_3$  and  $CO_2$  respectively) results in the loss of one OH. But the concentration of OH has probably remained stable, or in some areas increased, over the past one hundred years. What is the main reason why OH has not gone down as much as you might expect? (1 point)

6. Number correctly the sequence of events in the formation of the Antarctic ozone hole, from 1 the earliest to 8 the latest. (4 points)

Rapid ozone destruction Formation of PSC's (Polar Stratospheric Clouds) Polar vortex temperatures get colder Formation of Antarctic polar night Conversion of chlorine reservoirs to Cl<sub>2</sub> Sunlight returns to the Antarctic Cl<sub>2</sub> photolyzes Recovery of HCl and ClONO<sub>2</sub> concentrations 7. What are the two most important properties of a gas that determine its Greenhouse Warming Potential (GWP)? (2 points)

8. The effectiveness of a molecule as a greenhouse gas (its radiative forcing) depends partly on its altitude. Compare a water molecule near the surface and one near the tropopause. Which would have a stronger radiative forcing? Explain. (2 points)

**9.** 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  $N_2$  to a form that plants can more readily assimilate? (2 points)

10. The growth of corals can be represented by the formula:

 $Ca^{2+} + CO_3^{2-} \Rightarrow CaCO_3(s)$ 

(i) Assume coral growth occurs under the condition that the pH of the ocean is fixed, and that atmospheric  $CO_2$  is in equilibrium with dissolved  $CO_2$  in the ocean. Would coral growth result in an increase or decrease of atmospheric  $CO_2$ ? Explain. (2 points)

(ii) On the other hand, assume that coral growth occurs under the condition that the total amount of dissolved inorganic carbon in the ocean is fixed. Dissolved inorganic carbon is defined as:

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

In this case, how would coral growth affect ocean pH? Explain. (2 points)

(iii) Suppose it was possible to inject  $NH_3$  into the ocean. Would this increase or decrease the flux of  $CO_2$  into the ocean? Explain. Showing relevant reactions would be helpful. (2 points)

11. Species X has a constant mixing ratio of 100 ppbv in the atmosphere, i.e.  $C_x = 1.0 \times 10^{-7}$ . The absorption cross-section of X at 300 nm is  $1.0 \times 10^{-18}$  cm<sup>2</sup>/molecule. The pressure at the surface is 1000 hPa (i.e.  $1.0 \times 10^5$  N/m<sup>2</sup>).

(i) What is the atmospheric column of X in molec/ $cm^2$ ? (4 points)

(ii) What is the optical depth  $\delta$  of X in the atmosphere at 300 nm? (2 points)

(iii) If there are no other absorbers in the atmosphere at 300 nm, and the sun is 30 degrees from the vertical, what fraction of the incoming solar radiation at 300 nm reaches the surface? (4 points)

12. (i) The global average  $CO_2$  mixing ratio is 410 ppmv. The global average surface pressure is 1000 hPa. Assume that the mean molecular weight of the atmosphere is the same as that for dry air. The molecular weight of  $CO_2$  is 44 g/mole How many kg of  $CO_2$  are in the atmosphere? (4 points)

(ii) Carbon dioxide dissolves in water with a Henry's Law constant of  $K_H$ .

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

$$K_H = [CO_2 \cdot H_2O]/P_{CO_2} = 3 \times 10^{-2} M/atm$$

The volume of the ocean is  $1.35 \times 10^{18}$  m<sup>3</sup>. Assume atmospheric CO<sub>2</sub> is in equilibrium with dissolved CO<sub>2</sub> in the ocean. What is the mass of dissolved CO<sub>2</sub> in the ocean? Note: not looking for Dissolved Inorganic Carbon here, dissolved CO<sub>2</sub> only. Note that 1 atm = 1000 hPa. From this you can determine  $P_{CO_2}$ . There are 1000 *l* in one m<sup>3</sup>. (4 points)

13. 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<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> respectively, which are then scavenged by rain. (i) Estimate the mean concentrations (M) of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> in rain, assuming a global mean precipitation rate over the earth of 2 mm/day. (6 points)

<sup>(</sup>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)

14. A gas X is emitted in the Northern Hemisphere only, with an emission rate E. Let  $M_n$  refer to the mass of X in the Northern Hemisphere and  $M_s$  to the mass of X in the Southern Hemisphere. The first order exchange constant for the exchange of mass between the two hemispheres is  $k = 0.9 \text{ year}^{-1}$ . I.e. this refers to a first order dynamical loss rate from each hemisphere to the other hemisphere. Gas X has a first order atmospheric loss rate of  $k_l = 0.8(yr)^{-1}$  in both hemispheres. Ignore transport with the stratosphere.

(i) Write down a box model equation for  $M_n$ . Hint:  $dM_n/dt$  should equal a sum of four terms. (4 points)

(ii) Write down a box model equation for  $M_s$ . Hint:  $dM_n/dt$  should equal a sum of three terms. (3 points)

(iii) Assume X is in steady state in both hemispheres. Calculate the  $M_s/M_n$  ratio. (3 points)

(iv) Express  $M_n$  in terms of E. (2 points)

15. Assume that every CO reacts with OH to produce HO<sub>2</sub>.  $CO + OH(+O_2) \rightarrow CO_2 + HO_2$   $k_1 = 2.4 \times 10^{-13} \text{ cm}^3/\text{molec} - \text{sec}$ The HO<sub>2</sub> that is produced can then react with either NO or O<sub>3</sub>.  $HO_2 + O_3 \rightarrow OH + 2O_2$   $k_2 = 1.6 \times 10^{-15} \text{ cm}^3/\text{molec} - \text{sec}$   $HO_2 + NO \rightarrow OH + NO_2$   $k_3 = 9.3 \times 10^{-12} \text{ cm}^3/\text{molec} - \text{sec}$   $[M] = 2 \times 10^{19} \text{ molec/cm}^3$   $O_3 = 50 \text{ ppbv}$ CO = 80 ppbv NO = 100 pptv  $HO_x = 3 \text{ pptv}$ 

Every NO<sub>2</sub> that is produced subsequently photolyzes to produce an O, which then reacts with  $O_2$  to produce  $O_3$ .

(i) 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. (4 points)

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

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

(iv) For every  $HO_2$  that is produced, what fraction reacts with NO to produce an ozone? (4 points)

(v) What is the NET number of ozones produced (i.e. both produced and destroyed) for every CO oxidized. (2 points)

16. The southern San Joaquin Valley of California experiences extended stagnation episodes in winter due to strong and persistent subsidence inversions. These stagnation episodes are often accompanied by thick valley fogs. Use a box model to describe the valley air during a foggy stagnation episode. The top of the box is defined by the base of the inversion, 400 m above the valley floor. There is no ventilation out of the box. The temperature in the box is 273 K.

(i) Assume the Valley has an area of  $2.0 \times 10^{10}$  m<sup>2</sup>. The average pressure at the surface of the Valley is 1000 hPa. The pressure at 400 m is 950 hPa. Estimate the number of moles of air in the Valley (i.e. below 400 m). (2 points)

(ii) Steam generators emit SO<sub>2</sub> with a mean flux  $E = 4.0 \times 10^2$  moles per km<sup>2</sup> per day. This SO<sub>2</sub> is removed from the valley air either by deposition to the surface (first-order rate constant  $k_d = 0.5 \, day^{-1}$ ), or by oxidation to H<sub>2</sub>SO<sub>4</sub> (sulfuric acid) with a first-order rate constant  $k_o = 1.0 \, day^{-1}$ . Use S to refer to the number of moles of SO<sub>2</sub> in the Valley. Calculate S at steady state. (6 points)

(iii) Calculate the steady state  $SO_2$  concentration in the valley in units of ppbv. (2 points)

(iv) Sulfuric acid produced from SO<sub>2</sub> oxidation in the valley air is incorporated immediately into the fog droplets. These fog droplets are then removed from the valley air by deposition with a first-order rate constant  $k_{dep} = 2.0 \, day^{-1}$ . Let SA refer to the number of moles of H<sub>2</sub>SO<sub>4</sub> in the valley. Write a box model equation for SA incorporating these processes (i.e. one source and one sink). You can assume SA is in steady state. (4 points)

(v) Use this equation to solve for SA. (2 points)

(vi) Within the valley the liquid water fog content is  $1.0 \times 10^{-4}$  l water per m<sup>3</sup> of air. How many litres of fog water are in the valley? (2 points)

(vii) What is the pH of this fog water? You can assume sulfuric acid is the only substance dissolved in the fog droplets. (2 points)

(viii) The Valley also contains large sources of ammonia from livestock and fertilized agriculture. The  $NH_3$  emission flux is  $5.6 \times 10^2$  moles per km<sup>2</sup> per day. Assume that  $NH_3$  instantly dissolves in fog, converts to ammonium with 100 percent efficiency (if protons available), and that ammonium and sulfuric acid titrate each other. What is the resulting pH of the fog water? (6 points)