

**1. Greenhouse Gases (50 pts: 12, 8, 20, 10)**

a) Circle each of the following gases that absorb infrared radiation: CO<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, O<sub>3</sub>, N<sub>2</sub>O, N<sub>2</sub>

CO<sub>2</sub>, CH<sub>4</sub>, O<sub>3</sub>, N<sub>2</sub>O absorb infrared or long wave radiation, between 750 nm and 1 mm.

b) Assess the following statements about the Earth's albedo.

- i) TRUE or FALSE: The albedo is the amount of incoming solar radiation absorbed by the Earth. **F**
- ii) TRUE or FALSE: The albedo includes clouds, aerosols, and the surface. **T**
- iii) TRUE or FALSE: The current albedo is estimated to be 31% of incoming solar radiation. **T**
- iv) TRUE or FALSE: The albedo will be higher if the fraction of ice-covered earth is reduced. **F**

c) Answer the following questions about the Earth's radiation balance.

i) Give an expression for the incoming solar radiation at the top of the Earth's atmosphere in terms of the solar constant (S<sub>0</sub>) and the albedo (α<sub>p</sub>).

$0.25 \cdot S_0 (1 - \alpha_p)$

ii) Give an expression for the outgoing black body radiation of the Earth, assuming no atmosphere.

$\sigma T_e^4$

iii) Given conservation of energy, how are the quantities in (i) and (ii) related?

$0.25 \cdot S_0 (1 - \alpha_p) = \sigma T_e^4$

ii) Is the no-atmosphere Earth colder than reality or warmer? Why?

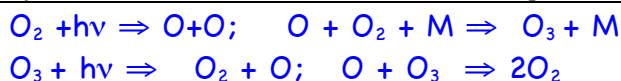
Colder by about 30C. It is too cold because it doesn't have a greenhouse effect.

d) What is the thermodynamic basis for knowing that global warming results from increased CO<sub>2</sub>?

The first law of thermodynamics tells us that energy is conserved, and this means that increased absorption by CO<sub>2</sub> will result in higher temperatures.

**2. Chapman Cycle (50 pts: 20, 12, 18)**

a) Write the four reactions of the Chapman Cycle.



b) Name the three factors needed to calculate the rate constant (j) for the photolysis reactions in part (a). Which of these factors varies the most with altitude? Why?

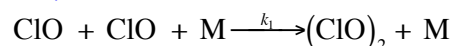
Photolysis rate constants are calculated from quantum yield, absorption cross section, and photon flux. Photon flux varies the most with altitude.

c) Assess if the following statements are true or false.

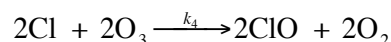
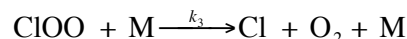
- i) TRUE or FALSE: The Chapman Cycle reactions lead to ozone production in the stratosphere. **T**
- ii) TRUE or FALSE: The Chapman Cycle reactions lead to ozone destruction in the stratosphere. **T**
- iii) TRUE or FALSE: There is not enough photon flux in the troposphere to photolyze O<sub>2</sub> to make O<sub>3</sub>. **T**
- iv) TRUE or FALSE: There are more O than O<sub>3</sub> in the stratosphere. **F**
- v) TRUE or FALSE: Both O<sub>3</sub> and O<sub>2</sub> photolyze to make O. **T**
- vi) TRUE or FALSE: The O made from photolysis of both O<sub>3</sub> and O<sub>2</sub> is largely excited state (O(1D)). **F**

**3. Ozone Hole (39 pts: 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3)**

- a) TRUE or FALSE: Polar vortex transports HCl, ClO and ClONO<sub>2</sub>. **T**
- b) TRUE or FALSE: Polar stratospheric clouds form at -80C. **T**
- c) TRUE or FALSE: HCl and ClONO<sub>2</sub> make Cl<sub>2</sub> gas by aqueous phase reactions on PSCs. **F**
- d) TRUE or FALSE: Cl<sub>2</sub> is photolyzed by spring time sunlight. **T**
- e) TRUE or FALSE: Cl catalyzes 25% of the O<sub>3</sub> destruction in the ozone hole. **T**
- f) TRUE or FALSE: Br catalyzes 75% of the O<sub>3</sub> destruction in the ozone hole. **F**
- g) TRUE or FALSE: CFCs cause the ozone hole. **T**
- h) TRUE or FALSE: CFCs are removed by rainfall in the troposphere. **F**
- i) TRUE or FALSE: ClONO<sub>2</sub> stores Cl in an unreactive state. **T**
- j) TRUE or FALSE: Destruction of O<sub>3</sub> catalyzed by ClO does not require O. **T**
- k) TRUE or FALSE: NO catalyzes O<sub>3</sub> destruction when O is present. **T**



- l) TRUE or FALSE: The net reaction of this cycle is 3O<sub>2</sub> → 2O<sub>3</sub>:  $(\text{ClO})_2 + h\nu \xrightarrow{j_2} \text{Cl} + \text{ClOO}$  **F**



- m) TRUE or FALSE: The rate expression for the first step in the cycle in 3(l) varies with pressure. **T**

**4. Atmospheric Composition (61 pts: 10, 20, 10, 10+4, 6)**

- a) For each volume composition or mixing ratio (or range) in the atmosphere listed below, pick the component that is found in that amount in the *atmosphere at the surface in 2010*:

**CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, CFC-11, O<sub>3</sub>, SF<sub>6</sub>, N<sub>2</sub>O, N<sub>2</sub>, Ar, H<sub>2</sub>O.**

**N<sub>2</sub> (78%), O<sub>2</sub> (21%), Ar (1%), H<sub>2</sub>O (0-4%), CO<sub>2</sub>(390 ppm).**

Top 5 contributions:

**78%**

**0-4%**

**21%**

**1%**

**390 ppm**

- b) From the list of components in Question 4(a), answer the following:

i) Which component(s) of the atmosphere has a distinct layer of high concentration in the stratosphere? **O<sub>3</sub>**

ii) Which component(s) can act as a greenhouse gas? **CO<sub>2</sub>, CH<sub>4</sub>, CFC-11, O<sub>3</sub>, SF<sub>6</sub>, N<sub>2</sub>O, H<sub>2</sub>O**

iii) Which component(s) are noble gases? **Ar**

iv) Which component is observed in three different phases in atmospheric conditions? **H<sub>2</sub>O**

v) Which components have no natural sources? **CFC-11**

- c) If the mass of the atmosphere is 5\*10<sup>18</sup> kg and if CFC-11 makes up 0.2x10<sup>-9</sup>%, what is the mass of CFC-11 in the atmosphere? (MW<sub>CFC-11</sub> = 137, MW<sub>air</sub> = 29 g/mole). For simplicity you may assume 137/29 ≈ 5.

**(0.2x10<sup>-9</sup> CFC-11 molecules/10<sup>2</sup> air molecules)\*(5 kg CFC-11/kg air)\*(5\*10<sup>18</sup> kg air)=5\*10<sup>7</sup> kg CFC-11**

- d) What is the (minimum) residence time for an atmospheric constituent to be called "long-lived"? **1 yr**

Which of the species listed in 4(a) are long-lived? **CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, CFC-11, SF<sub>6</sub>, N<sub>2</sub>O, N<sub>2</sub>, Ar.**

- e) Some of the "in situ" (or photochemical) atmospheric components are from natural sources and others are from man-made sources. For the in situ compounds below, specify which are mostly natural or man-made.

i) Stratospheric Ozone: **natural** ii) Tropospheric Ozone: **man-made** iii) NO<sub>2</sub>: **man-made**