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

a) Name three anthropogenic greenhouse gases. Give the type of radiation and approximate wavelength that greenhouse gases absorb (not each one specifically, just the approximate wavelength in general).

CO_2, CH_4, CFCs, O_3, SF_6, N_2O. A greenhouse gas absorbs infrared or long wave radiation, between 750 nm and 1 mm.

b) What is the albedo of the earth? Give a description and an approximate value. How will reducing the fraction of the ocean covered by ice affect the albedo?

The albedo is the amount of incoming solar radiation that is reflected by the Earth, including by clouds, aerosols, and the surface. The current value is estimated to be 31% of incoming solar radiation. It will lower if the fraction of ice-covered earth is reduced.

c) i) Given incoming solar radiation ($S_0(1-\alpha_p)*0.25$) and outgoing black body radiation (σT_e^4) and assuming no atmosphere, what is the equation (balance) used to calculate the temperature of the Earth? What, approximately, is that temperature?

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

$T_e = [0.25*S_0(1-\alpha_p)/ \sigma]^{0.25} \sim 255K$

ii) Given the above values, and assuming there is an atmosphere that acts as a perfect black body, what is the equation (balance) of energy at the Earth's surface? Be sure to distinguish the atmosphere's temperature (T_{atm}) from the surface temperature (T_{surf}). In this model is the Earth's temperature warmer or cooler than in part (i)?

$0.25*S_0(1-\alpha_p) + \sigma T_{atm}^4 = \sigma T_{surf}^4$

warmer

d) Name two assumptions in parts c)i or c)ii that are incorrect.

The atmosphere is not one layer.
The atmosphere is not transparent to incoming solar radiation.
The atmosphere is not a perfect black body.
The Earth is not a perfect black body.
The Earth is not in perfect radiative equilibrium with the atmosphere (latent and sensible heat exchange exist.)

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2. Stratospheric Ozone (50 pts: 10, 20, 10, 10)

a) What is the name of the set of reactions that control O3 formation and destruction in the stratosphere?

The Chapman Cycle

b) Write the four reactions name in part (a).

$O_2 + h\nu \Rightarrow O + O$

$O + O_2 + M \Rightarrow O_3 + M$

$O_3 + h\nu \Rightarrow O_2 + O$

$O + O_3 \Rightarrow 2O_2$

c) Name the three factors needed to calculate the rate constant (j) for the photolysis reactions in part (b). 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 because light absorbed higher in the atmosphere does not penetrate to lower levels in the atmosphere (light is filtered out as it moves down through the atmosphere).

d) Does the set of reactions in (a) over-predict or under-predict the background ozone level? What is missing?

Over-predicts because additional natural sinks of ozone such as Cl, Br, or NOx are not included.

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3. Ozone Hole (60 pts: 5, 20, 10, 20, 5)

a) What anthropogenic emissions cause the formation of the ozone hole? How and where are these compounds removed?

CFCs cause the ozone hole and they are removed by photolysis in the stratosphere.

b) Describe the five steps required for the formation of the ozone hole.

1. Polar vortex transports HCl, ClO and $ClONO_2$ produced by photolysis at 25 km down to Polar Stratospheric cloud levels.
2. Polar stratospheric clouds form (-80C)
3. HCl and $ClONO_2$ make Cl_2 gas by aqueous phase reactions on PSCs
4. Cl_2 is photolyzed by spring time sunlight.
5. Cl and ClO catalyzes O_3 destruction

c) Write the reaction mechanism responsible for approximately 25% of ozone loss in the ozone hole. Include the net reaction and name the catalyst.

ClO + O ⇒ Cl + O2
Cl + O3 ⇒ ClO + O2
Net: O + O3 ⇒ 2O2 catalyst is Cl

d) State the net reaction for the cycle below. Why is this cycle able to play a larger role in the ozone hole?

$$ClO + ClO + M \xrightarrow{k_1} (ClO)_2 + M$$

$$(ClO)_2 + h\nu \xrightarrow{j_2} Cl + ClOO$$

$$ClOO + M \xrightarrow{k_3} Cl + O_2 + M$$

$$2Cl + 2O_3 \xrightarrow{k_4} 2ClO + 2O_2$$

Assuming that the concentrations of Cl, ClOO, and $(ClO)_2$ are in steady state, write an expression for the concentration of Cl in terms of the concentrations of ClO, O_3, and M and the constants k_1 and k_4.

2O3 3O2. This cycle does not require atomic O, which is scarce.

$$[Cl] = \frac{2k_1[M][ClO]^2}{k_4[O_3]}$$

e) What compound made from NO_2 is quickly formed throughout the year in the stratosphere and stores Cl in an unreactive state?

$ClONO_2$

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4. Atmospheric Composition (40 pts: 10, 10, 16, 4)
a) Name the five most abundant components of the atmosphere. Give the volumetric percentage of the top two most abundant components.

N_2 (78%), O_2 (21%), Ar, H_2O, CO_2.

b) Which of the five major constituents has the most variable concentration? Describe the difference in its concentration in the troposphere and stratosphere.

H_2O is the most variable. It ranges from 1% to 4% in the troposphere and is less than 1% in the stratosphere.

c) i) If the mass of the atmosphere is $5*10^{18}$ kg and if CO_2 makes up 400 ppm, what is the mass of CO_2 in the atmosphere? (MW_{CO2} = 44, MW_{air} = 29 g/mole). For simplicity you may assume 44/29≈1.

400 CO_2 molecules/10^6 air molecules = 400 kg CO_2/10^6 kg air * $5*10^{18}$ kg air = $2000*10^{12}$ kg CO_2 = $2*10^{15}$ kg CO_2

ii) Given the mass of CO_2 you calculated in i) and the residence time of CO_2 in the atmosphere as 100 years, what is the approximate removal rate for CO_2?

Tau = M/F
F = M/tau
F = $2*10^{15}$ kg CO_2 / 100 years = $2*10^{15}$ kg CO_2 / year

iii) Is the spatial scale of variability of CO2 closer to 1 km or 10,000 km? What about OH?

CO2 = 10,000 km
OH = 1 km

d) Give a major source type (biological, solid earth, oceanic, or in situ) of atmospheric constituents for the following compounds. There may be more than one correct answer for each, but one answer is sufficient.

i) Ozone: in situ
ii) CO2: biological or solid earth
iii) SO2: in situ, biological, or volcanic
iv) CFCs: biological