since it tells us the lifetime of a substance if we know its steady-state concentration and rate of input into the environment.

In order to assess the impact of any substance upon the enhanced greenhouse effect, it is necessary to know how long the substance is expected to remain in the atmosphere, since the longer its atmospheric lifetime, the greater will be its total effect. Thus, for example, if the steady-state atmospheric concentration of a gas is 6.0 ppm, and if its global rate of input, as determined by dividing the yearly amount of input by the volume of the atmosphere, is 2.0 ppm per year, then according to the last equation above, its average residence time is 6.0 ppm/2.0 ppm y^{-1} or 3.0 y.

The residence times of greenhouse gases such as nitrous oxide and the CFCs are many decades, so the influence of recent emissions of them will extend over long periods of time. In contrast, methane has a residence time of less than a decade.

The above analysis is applicable only to substances having a single first-order sink process. Thus it does not apply to carbon dioxide, for example, since this gas has many different sinks (dissolution in the oceans; absorption by plant matter, etc.) and sources.

PROBLEM 5-10

If the average, steady-state residence time of a trace atmospheric gas is 50 y and its input rate is 2.0×10^6 kg y^{-1}, what is the total amount of it in the atmosphere?

PROBLEM 5-11

The steady-state concentration of an atmospheric gas of molar mass 42 g mol^{-1} is 7.0 μg g of air, and its residence time is 14 y. What is the annual total release of the gas into the atmosphere as a whole? See Problem 5-6 for additional data.

Review Questions 22–26 are based upon the material in the preceding sections.

Review Questions

1. Sketch a plot showing the main trends in global air temperature over the last century and a half.

2. What is the wavelength range, in μm, for infrared light? In what portion of this range does the Earth receive IR from the Sun? What are the wavelength limits for the *thermal IR* range?

3. Explain in terms of the mechanism involved what is meant by the *greenhouse effect*. Explain what is meant by the *enhancement* of the greenhouse effect.

4. Explain what is meant by the terms *symmetric* and *antisymmetric bond-stretching* vibrations, and by *angle-bending* vibrations.

5. Explain the relationship between the frequency of vibrations in a molecule and the frequencies of light it will absorb.

6. Why don't N_2 and O_2 absorb thermal IR? Why don't we consider CO and NO to be trace gases which could contribute to enhancing the greenhouse effect?

7. What are the two main anthropogenic sources of carbon dioxide in the atmosphere? What is its main sink? What is *fixed carbon*?

8. Is water vapor a greenhouse gas? If so, why is it not usually present on lists of such substances?

9. Explain what is meant by *positive* and *negative feedback*. Give an example of each as it affects global warming.

10. What is meant by the term *atmospheric window* as applied to the emission of IR from the Earth's surface? What is the range of wavelengths of this window?

11. What reaction is the dominant tropospheric sink for methane?

12. What are four important trace gases that contribute to the greenhouse effect?

13. What are the six most important sources of methane?

14. What are the three most important sinks for methane in the atmosphere? Which one of them is dominant? What is meant by the term *clathrate compound*?

15. Is the enhancement of the greenhouse effect by release of methane from clathrates due to increased temperature an example of feedback? If so, is it positive or negative feedback? Would an increase in the rate and amount of photosynthesis with increasing temperatures and CO_2 levels be a case of positive or negative feedback?

16. Explain in chemical terms what is meant by *nitrification* and *denitrification*. What are the conditions under which nitrous oxide production is enhanced as a by-product of these two processes?

17. What are the main sources and sinks for N_2O in the atmosphere?

18. Are the proposed CFC replacements themselves greenhouse gases? Why is their emission considered to be less of a problem in enhancing the greenhouse effect than was that of the CFCs themselves?

19. By which two mechanisms does light interact with atmospheric particles?

20. Explain how sulfate aerosols in the troposphere affect the air temperature at the Earth's surface, by both the direct and indirect mechanisms.

21. List four important signs, other than increases in average air temperature, that global warming is occurring.

22. Define the terms *geoengineering* and *solar radiation management*.

23. Describe how the use of sunlight reflectors in space could reduce global warming.

24. Describe how the scheme of increasing stratospheric sulfate concentration could reduce global warming. Why is particle size an important factor? What schemes have been suggested by which the sulfate could be delivered to the stratosphere?

25. What would the likely effects of solar radiation management be on (a) rainfall levels and (b) stratospheric ozone recovery?

26. How is the residence time of a substance related to its rate *R* of input/output and to its total concentration C?

Additional Problems

1. The tropospheric pollutant gases SO_2 and NO_2 have nonlinear molecular structures which, like that of CO_2, have the central atom connected to two oxygen atoms. The wavelengths for their vibrations are given in the table shown on the next page. (a) Which of the vibrations are capable of absorbing infrared energy? (b) Based upon the wavelengths for the IR-absorbing vibrations and the spectrum in Figure 5-7, decide which if any vibrations could contribute much to global warming. (c) What lifetime characteristic of these gases would limit their role in global warming?

Gas	Symmetric stretch	Antisymmetric stretch	Bending
SO_2	8.7 μm	7.3 μm	19.3 μm
NO_2	7.6 μm	6.2 μm	13.3 μm

2. (a) How can the fact that nitrous oxide has three vibrations that absorb infrared light be used to prove that its structure is NNO rather than NON? (b) Would methane molecules absorb IR during the vibration in which all four C—H bonds stretched or contracted in phase?

3. Anthropogenic carbon dioxide emissions into the atmosphere amounted to 178 Gt from January 1990 to December 1997. Calculate the fraction of this emitted carbon dioxide that remained in the air, given that in that same eight- year period, the carbon dioxide concentration in air rose by 11.1 ppm. Note that the molar masses of C, O, and air, respectively, are 12.0, 16.0, and 29.0 g, that the mass of the atmosphere is 5.1×10^{21} g, and that 1 Gt is 10^{15} g.

4. The total amount of methane in the atmosphere in 1992 was about 5,000 Tg, and was increasing by about 0.6% annually due to the fact that the annual input rate exceeded the annual output rate of 530 Tg y^{-1}. Calculate the percentage by which anthropogenic releases of methane, which account for two-thirds of the total, had to be reduced if the atmospheric concentration of this gas was to be stabilized in 1992.

5. As mentioned in the text, the fraction F of light that is absorbed by any gas in air is logarithmically related to the concentration c of the gas and the distance d through which the light travels; this relationship is called the Beer–Lambert law:

$$\log_e (1 - F) = -Kcd$$

Here K is a proportionality constant. Show by simple trial calculations that for concentrations near zero (e.g., where $Kcd = 0.001$), that F is related almost linearly to c, whereas for larger Kcd values (e.g., near 2), that doubling the concentration does not nearly double the light absorption.

6. The vapor pressure P of a liquid rises exponentially when it is heated according to the equation

$$\ln(P_2/P_1) = -\Delta H/R\ (1/T_2 - 1/T_1)$$

Here P_2 and P_1 are the vapor pressures of the liquid at the Kelvin temperatures T_2 and T_1 after and before the temperature increase, R is the gas constant 8.3 J K^{-1} mol^{-1}, and ΔH is the liquid's enthalpy of vaporization, which for water is 44 kJ mol^{-1}. Calculate the percentage increase in the vapor pressure of water that occurs if the temperature is raised from 15°C to 18°C. Give several reasons why the amount of outgoing thermal infrared in water's absorption bands may not be increased by exactly the percentage you calculate if the average air/surface temperature is increased to 18°C.

7. Suppose that some climatic crisis inspired the Earth's population to switch to energy systems that did not emit carbon dioxide, and that the transition occurred within a decade. What would be the predicted immediate effect to the Earth's average air temperature of this change, given that both carbon dioxide and sufur dioxide emissions from fossil fuels would have rapidly declined?

8. Given that the concentration of CH_4 in the atmosphere is 1.8 ppm, calculate the total mass of this gas that is present in the atmosphere. Note that the total mass of the atmosphere is 5.1×10^{18} kg and that its average molar mass is 29.0 g mol^{-1}.

9. Consider an area of space measuring $10D \times 10D$, in which there are ten aligned rows, each of ten spheres lined up one on top of the other. Calculate the total volume occupied by the spheres, and the total area they cover (of the $100D^2$ maximum if there were no "empty spaces"). [*Hint:* The volume V of a sphere equals $4\pi r^3/3$, where r is its radius.]