

$$\begin{aligned} & \text{tonnes of sulfur from coal combustion in 1980} \\ &= \frac{90 \times 10^{18} \text{ J}}{29.3 \times 10^9 \text{ J/tonne(coal)}} \times 0.025 \text{ tonnes(S)/tonne(coal)} \quad (3) \\ &= 7.7 \times 10^7 \text{ tonnes(S)}. \end{aligned}$$

A mole of any material has a mass of M grams, where M is the molecular mass of the substance (number of protons and neutrons in a molecule). The following units conversion is used to convert tonnes to moles for any material, A :

$$\text{moles of } A = \frac{\text{tonnes}(A) \times [10^6 \text{ g}(A)/\text{tonne}(A)]}{M[\text{g}(A)/\text{mole}(A)]} \quad (4)$$

Using the fact that the atomic (and molecular) mass¹¹ of S is 32, and substituting the actual numbers into Eq. 4, we get:

$$\begin{aligned} & \text{moles(S) from coal combustion in 1980} \\ &= \frac{[7.7 \times 10^7 \text{ tonnes(S)}] \times [10^6 \text{ g(S)/tonne(S)}]}{32 \text{ g(S)/mole(S)}} \quad (5) \\ &= 2.4 \times 10^{12} \text{ moles(S)}. \end{aligned}$$

EXERCISE 1: Using additional data from the Appendix (VII.3), calculate the number of tonnes of cadmium, lead, zinc, selenium, mercury, and arsenic contained in the coal combusted worldwide 1980. Compare the rates at which these substances are emitted into the atmosphere worldwide from coal combustion with the natural background rates of mobilization to the atmosphere given in the Appendix (IX), under the assumption that all the trace substances found in fossil fuel are emitted into the atmosphere when the fuel is burned. In practice, some portion of the trace substances in fuels is left behind as solid waste in the form of ash when the fuel is burned. The pathways that the substances in fuel follow (through air, water, soil, and living organisms) and the chemical transformations they undergo in the environment (including reactions that can render them more or less toxic than they were in their initial emitted form) depend on many factors. Specific examples will be described later in this book.

EXERCISE 2: For further practice at converting units, use the data in the Appendix on the energy content of specified quantities of fossil fuels to calculate the present world's resources of petroleum, coal, and natural gas in units of barrels, metric tons, and cubic meters, respectively.

11. For a substance like molecular oxygen (O_2) consisting of two identical atoms, the molecular mass is twice the atomic mass; but for S or any other molecule consisting of a single atom, the molecular mass equals the atomic mass.

Chapter II Tools of the Trade

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... having a good question, a fundamental question, and having some tools of inquiry that allow you to take the first step toward an answer—those are the conditions that make for exciting science.

—Herbert A. Simon

Here you will be handed some of the tools that form the core of environmental science. They include residence-time methods and box models, practical methods in thermodynamics and chemical equilibrium kinetics, and a few relatively simple differential equations. (If you are typical, you were probably paralyzed with fear when you read the previous sentence. Relax—we will take it slowly.)

From: "Consider a Spherical Cow" by

John Harte

University Science Books . 1998 .

you know from watching the reflected glare of light off a roadway, the albedo of a surface depends on the angle between the incident rays and the surface. Perpendicular rays are more likely to be absorbed than are rays at a grazing angle. The optical coefficients given in Problem II.18 apply to an average incident solar flux angle. Notice, too, that we assumed light scattered off the cloud layer would be transmitted unaffected through the layer. In fact, however, the scattering of incident light by a cloud layer alters the average angle of the light striking Earth's surface and thus alters the effective albedo.

What qualitative effect do you think our oversimplification had on the answer? Include in your deliberations on this question the fact that the absorption probability in the cloud layer is proportional to the path-length of light through the layer. This is relevant because light reflected more obliquely off Earth's surface will have a greater path-length within the cloud on its subsequent pass upwards. On the other hand, because the cloud surface is relatively rough, the reflection coefficient of the cloud layer is not as dependent on incident angle as that of Earth's surface is.

C. *Chemical Reactions and Equilibria*

When chemicals are added to pure water, reactions can occur that cause changes in the types and concentrations of chemical species in solution. Usually within seconds or minutes, except in special cases such as when slow dissolution of a solid occurs, a steady state is reached in which the concentration of each chemical species is constant. This is called chemical equilibrium.

Suppose chemical species A and B are added to water and undergo the reaction



where the double arrow indicates that the reaction can go either way. At chemical equilibrium, the forward reaction, $A + B \rightarrow C + D$, occurs at the same rate as the reverse reaction, and a simple relation must hold among the concentrations of the species. Using the standard notation $[X]$ to indicate the concentration of chemical species X, in units of moles per liter, this relation reads

$$\frac{[C][D]}{[A][B]} = 10^{-pK}, \quad (2)$$

where pK is a constant characterizing the specific reaction. The term 10^{-pK} is often called a "dissociation constant" for the reaction. Values of 10^{-pK} for a number of reactions of environmental interest are given in the Appendix (X.2). A major problem in aqueous chemistry is the determination of equilibrium concentrations. In the above example, a single equation contains four unknowns. How is the problem to be solved?

Most such problems fall into one of two categories. Either (a) the system is completely closed to the atmosphere and to surrounding solids, in which case certain conservation laws can be used; or (b) the system is open to the surroundings and a combination of conservation laws and across-the-phase-boundary equilibrium relations can be used. These two methods are illustrated by the following examples.

CASE A: In a container of pure water, a certain amount of raw nitric acid is dissolved. The water + acid system is capped and thus isolated from the surroundings. (The container walls are assumed to be inert.) What will be the steady-state concentration of H^+ , OH^- , HNO_3 , and NO_3^- ?

CASE B: Into a container of water open to the atmosphere at sea level, a hunk of $CaCO_3$ (limestone) is dropped. What will be the steady-state concentration of H^+ , OH^- , H_2CO_3 , HCO_3^- , and Ca^{+2} ?

One important relation that will be applicable in both these cases and, in fact, is used in all aqueous equilibrium problems, stems from consideration of the reaction: $H_2O \rightleftharpoons H^+ + OH^-$. The forward reaction is called a dissociation reaction because water dissociates into its ionic products. The reverse reaction is called an association reaction. Eq. 2 can be applied here, of course, and because the pK for the dissociation of water²⁹ is 14,

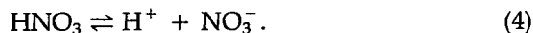
$$[H^+][OH^-] = 10^{-14}. \quad (3)$$

The convention adopted in writing Eq. 3 is that $[H_2O] = 1$, and the pK value of 14 is assigned with that convention in mind.

Armed with this background, you are now ready to follow the procedures for analyzing cases A and B.

Case A

When nitric acid is added to water, the following reaction occurs:



The pK for this reaction is -1 and thus, in equilibrium

$$[H^+][NO_3^-] = 10 [HNO_3]. \quad (5)$$

In addition, an important conservation law can be applied. The amount of NO_3 in the system is constant because the system is

closed. The NO_3 may be in ionic form (NO_3^-) or in undissociated form (HNO_3), but the sum total of the two forms must equal the amount of NO_3 added initially. Therefore,

$$[NO_3^-] + [HNO_3] = A, \quad (6)$$

where A can be calculated from the amount of acid initially added. For example, if 126 g of pure HNO_3 were added to 1 liter of water, the number of moles of NO_3 added would be 126 g divided by the molecular weight of HNO_3 , which is 63. A would then be 2 moles per liter. If the same amount of acid were added to 4 liters of water, the value of A would be 0.5 moles per liter. If 2 cc (2×10^{-3} liters) of a 3 mole/liter solution of HNO_3 were added to 5 liters of water, then A would be $0.002 \times 3/5 = 0.0012$ moles/liter. In these examples, a small correction was ignored: after the acid is added, the volume of the liquid will be slightly greater than before. In the last example, the correct answer would actually be obtained by dividing 0.006 moles by $(5 + 2 \times 10^{-3})$ liters, a small correction, indeed.

So now we have four unknowns (H^+ , OH^- , NO_3^- , and HNO_3) and three equations (3, 5, and 6). The final equation (necessary if we are to maintain our faith in chemical determinism) is obtained from the principle of charge conservation, which tells us that the total concentration of positive charge must equal the total concentration of negative charge. The reason the conservation law takes this form is that we started with pure, neutral water and neutral nitric acid and so we must end up with an electrically neutral system as well.

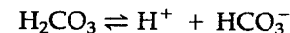
The charge conservation equation is:

$$[H^+] = [OH^-] + [NO_3^-]. \quad (7)$$

The left- and right-hand sides of this equation are the total number of moles per liter of positive and negative charge, respectively. The four equations (3, 5, 6, and 7) are sufficient to determine the four unknown concentrations. The best procedure to be used for solving the four equations will depend on the actual concentrations, because various kinds of approximations usually have to be made. We'll discuss this as we solve the problems later in this Section.

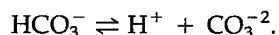
Case B

This example involves two sources of soluble chemicals. CO_2 from the atmosphere will come into solution in the water and $CaCO_3$ will dissolve from the limestone and produce dissociated Ca^{+2} and CO_3^{-2} . In the water, the CO_2 and the CO_3^{-2} will take part in the reactions



29. The pK of pure-water dissociation is 14 only at 25°C. Chemical equilibrium constants, such as the pK 's, Henry's constants, and solubility products, are all temperature dependent. A discussion of this and of most other aspects of aquatic chemistry as well is found in the excellent text by Stumm and Morgan (1981).

(remember, H_2CO_3 includes dissolved CO_2), and



At 25°C, the pK of the first reaction is 6.35 (often denoted pK_1) and that of the second is 10.33 (pK_2), so that

$$[\text{H}^+][\text{HCO}_3^-] = 10^{-6.35} [\text{H}_2\text{CO}_3] \quad (8)$$

and

$$[\text{H}^+][\text{CO}_3^{2-}] = 10^{-10.33} [\text{HCO}_3^-]. \quad (9)$$

The value of $[\text{H}_2\text{CO}_3]$ is obtained from the application of Henry's law. According to this law, when water is in contact with the atmosphere for a sufficient time to allow gas exchange between air and water to equilibrate (reach a point of no net flow), the ratio of the aqueous concentration of a gas to the atmospheric concentration of that gas is a constant (called Henry's constant) that depends only on temperature but not on the actual concentrations. Like many similar-looking laws, this one breaks down if the concentrations get too high; but for the problem at hand this presents no concern. Henry's law can be written for our case:

$$[\text{H}_2\text{CO}_3] = p(\text{CO}_2)K_H, \quad (10)$$

where $p(\text{CO}_2)$ is the atmospheric concentration of CO_2 at sea level (340 ppm) and K_H is Henry's constant for CO_2 . In units such that aqueous concentrations are expressed in moles per liter and atmospheric concentrations are expressed in atmospheres [10^6 ppm(v)], K_H for CO_2 has the value $10^{-1.47}$ (at 25°C), and so

$$[\text{H}_2\text{CO}_3] = 340 \times 10^{-6} \times 10^{-1.47} = 10^{-4.94}. \quad (11)$$

We now have four equations (3, 8, 9, and 11) for the six unknowns. Another equation is the charge conservation relation:

$$[\text{H}^+] + 2[\text{Ca}^{+2}] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]. \quad (12)$$

Note the factor of 2 in front of the calcium and carbonate terms in this equation. Do you see why it is there?

The final equation needed before we can solve for our unknowns involves the steady-state relation between the solid limestone and the dissolved Ca^{+2} and CO_3^{2-} . Every solid has a solubility product that tells you how much of the solid can dissolve before precipitation back

to the solid phase occurs. For limestone, the solubility product is $10^{-8.42}$, expressed in units of (moles/liter)² (see Appendix, X.3). Thus, at saturation,

$$[\text{Ca}^{+2}][\text{CO}_3^{2-}] = 10^{-8.42}. \quad (13)$$

To solve our problem, we must assume either (a) that the hunk of limestone was large enough to permit saturation to take place (before the hunk dissolved completely) or (b) that the hunk did dissolve completely and the amount of CaCO_3 in it was known precisely at the outset. Eq. 13 results if the first of these two assumptions is true. An equation analogous to Eq. 6 results if the second assumption is true, namely

$$[\text{Ca}^{+2}] = \text{specified constant}. \quad (14)$$

In either case, with six equations and six unknowns, the system can be solved. We'll use these tools in Problems II.20 and 21, and III.1, 2, and 4.

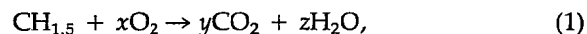
19. Altering the Atmosphere by Burning Fossil Fuels

In 1980, how much O_2 was removed from the atmosphere due to the combustion of fossil fuel on Earth, and how much CO_2 and H_2O were produced in the combustion process?

.....

The primary elemental constituents of the three major types of fossil fuel (natural gas, petroleum, and coal) are carbon and hydrogen. When fossil fuel is burned, oxygen from the atmosphere combines with the carbon to make CO_2 and with the hydrogen to make H_2O . In addition, coal contains some water (typically 10–15% by weight), which is released to the atmosphere upon combustion of the coal. All three types of fossil fuel contain various other substances such as ash, sulfur, and trace metals in even lower concentrations.

The Appendix (VII.2–4) provides detailed information about the average chemical composition of the three fossil fuels, the heat value of a unit amount of each fuel, and the total amount of heat energy derived worldwide from each in 1980. To use this information to compute the rates of CO_2 and H_2O emission and of oxygen consumption, we need to balance the chemical combustion reactions for each fuel. Consider petroleum, first, with the approximate chemical composition $CH_{1.5}$. The combustion reaction for this fuel is



where x , y , and z are called stoichiometric constants. Their values, to be determined below, provide the answer to our problem: For each mole of petroleum consumed, x moles of oxygen are consumed, and y and z moles, respectively, of CO_2 and H_2O are produced. The number of moles of petroleum burned in 1980, in turn, can be determined from the data in the Appendix (VII.2–4).

Let's first determine the stoichiometric constants. Equating moles of C, H, and O on each side of the reaction reveals constraints on x , y , and z . One mole of carbon in $CH_{1.5}$, for example, produces y moles of C in the form of CO_2 , and so

$$y = 1. \quad (2)$$

Similarly, one and a half moles of H in $CH_{1.5}$ produces z moles of H_2 or $2z$ moles of H, and so

$$2z = 1.5 \quad (3)$$

or

$$z = 0.75. \quad (4)$$

Finally, $2x$ moles of O produces $2y$ moles of O in CO_2 and z moles of O in H_2O , or

$$2x = 2y + z. \quad (5)$$

Combining Eqs. 2, 4, and 5, we get

$$x = 1.375. \quad (6)$$

The number of moles of $CH_{1.5}$ burned worldwide in 1980 now has to be determined. From the Appendix (VII.2–4), we learn that the energy content of the combusted petroleum was 1.35×10^{20} J; petroleum has a heat content of 4.3×10^{10} J/tonne. By weight, petroleum is 98% $CH_{1.5}$; thus, the amount of $CH_{1.5}$ consumed in 1980 was

$$\begin{aligned} 0.98 \times \frac{1.35 \times 10^{20} \text{ J}}{4.3 \times 10^{10} \text{ J/tonne}} &= 3.08 \times 10^9 \text{ tonnes}(CH_{1.5}) \\ &= 3.08 \times 10^{15} \text{ g}(CH_{1.5}). \end{aligned} \quad (7)$$

Since one mole of $CH_{1.5}$ has a mass of $12 + 1.5$ or 13.5 g, the number of moles of $CH_{1.5}$ consumed in 1980 was

$$\frac{3.08 \times 10^{15}}{13.5} = 2.28 \times 10^{14} \text{ moles}(CH_{1.5}). \quad (8)$$

Hence $n(O_2)$, the number of moles of consumed O_2 , was x times this value, or

$$\begin{aligned} n(O_2) &= 1.375 \times 2.28 \times 10^{14} \\ &= 3.14 \times 10^{14} \text{ moles}(O_2). \end{aligned} \quad (9)$$

The values of $n(CO_2)$ and $n(H_2O)$ can be obtained by multiplying 2.28×10^{14} moles($CH_{1.5}$) by y and z , respectively. Hence,

$$n(CO_2) = 2.28 \times 10^{14} \text{ moles}(CO_2) \quad (10)$$

and

$$n(H_2O) = 1.71 \times 10^{14} \text{ moles}(H_2O). \quad (11)$$

A similar procedure is used for calculating $n(\text{O}_2)$, $n(\text{CO}_2)$, and $n(\text{H}_2\text{O})$ from coal and natural gas combustion. However, now the more diverse chemical nature of the fuel must be taken into account. Referring to the Appendix (VII), we find that the composition of natural gas, expressed as mole fractions, is CH_4 (75%), C_2H_6 (6%), C_3H_8 (4%), C_4H_{10} (2%), and C_5H_{12} (1%). The remaining 12% is noncombustible. Using these mole fractions of each hydrocarbon in natural gas, you can show that a mole of that fuel contains $[0.75(1) + 0.06(2) + 0.04(3) + 0.02(4) + 0.01(5)]$ moles of C and $[0.75(4) + 0.06(6) + 0.04(8) + 0.02(10) + 0.01(12)]$ moles of H. Thus, the effective formula of the combustible portion of the fuel is $\text{C}_{1.12}\text{H}_4$.

The stoichiometric constants can now be determined as before, resulting in



The number of moles of natural gas burned in 1980 will equal the total heat value derived (6.0×10^{19} J; see Appendix, VII.2) divided by the number of joules per cubic meter of gas (3.9×10^7 J/m³; see Appendix, VII.4), and then multiplied by the number of moles per cubic meter (44.6 moles/m³ for any gas, since one mole of any gas occupies 22.4 liters at standard temperature and pressure). This works out to be 6.9×10^{13} moles of natural gas. Multiplying by 0.88 (the combustible fraction) and by the approximate stoichiometric constants gives the number of moles of O_2 consumed and of CO_2 and H_2O produced.

For coal, the only subtlety is that 13% of coal is water, which is liberated to the atmosphere upon combustion. This must be included in the calculation.

The final result for all three fuels is conveniently summarized in the following table (see Exercise 1).

	$n(\text{CO}_2)^*$	$n(\text{H}_2\text{O})^*$	$n(\text{O}_2)^*$
Petroleum	2.28	1.71	3.14
Natural gas	0.68	1.21	1.28
Coal	1.80	0.94	2.16
Total	4.76	3.86	6.58

*($\times 10^{14}$ moles)

EXERCISE 1: Derive the results for natural gas and coal shown in the table above.

EXERCISE 2: If all the CO_2 released to the atmosphere in 1980 from fossil-fuel burning remained there, by what percentage would that year's CO_2 emission increase the atmospheric concentration?

EXERCISE 3: By what percentage did the O_2 consumed in 1980 by fossil-fuel burning deplete the atmosphere's stock of O_2 ?

EXERCISE 4: There is great concern that the CO_2 we add to the atmosphere from fossil-fuel burning will result in a so-called "greenhouse" effect because that gas traps outgoing infrared radiation and thereby warms Earth's surface (see Problem III.8). We will see later (also in Problem III.8) that H_2O is a more effective absorber of infrared radiation than is CO_2 . Given that emissions of H_2O were comparable to those of CO_2 , why don't we worry about the effect of our H_2O emissions on the radiation balance in the atmosphere? (Hint: answering this requires only stock-flow-residence time considerations.)

20. The pH of Pristine Precipitation

What would the pH of rain be in the absence of anthropogenic sources of sulfuric and nitric acids?

.....

In the absence of sulfur and nitrogen oxide emission from fuel burning, Earth's atmosphere would still contain N_2 , O_2 , water vapor, dust, and trace gases of natural origin such as CO_2 , SO_2 , and NH_3 . A raindrop falling through Earth's pristine atmosphere will absorb these gases to some extent. If, dissolved in water, these gases form acids or bases, the pH of the rain will be affected. Geological history suggests that pristine precipitation very likely was acidic. The weathering processes that slowly convert many common hard minerals to clays result from chemical reactions between precipitation runoff and mineral substrate. These are usually acid-induced reactions.

Since CO_2 , dissolved in water, forms carbonic acid (H_2CO_3), let's look quantitatively at that one first. The method outlined in the introduction to this section is applicable. Using the 1983 value of 340 ppm(v) for the concentration of CO_2 in Earth's atmosphere, and the values of Henry's constant and the dissociation constants from the Appendix (X.2, 3),

$$[H_2CO_3] = 10^{-4.94}, \quad (1)$$

$$[H^+][HCO_3^-] = 10^{-6.35} [H_2CO_3], \quad (2)$$

and

$$[H^+][CO_3^{2-}] = 10^{-10.33} [HCO_3^-]. \quad (3)$$

In addition to these equilibrium equations, we have the equilibrium relation for water:

$$[H^+][OH^-] = 10^{-14}. \quad (4)$$

Eq. 1 is valid provided the raindrop is at sea level, where CO_2 has a partial pressure of 340×10^{-6} atm. At higher altitude, where the partial pressure of CO_2 is lower, $[H_2CO_3]$ will be proportionately lower as well.

The charge conservation equation reads

$$[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-], \quad (5)$$

and now there are five equations for five unknowns. Usually the best way to solve the equations in chemical equilibrium problems is to start with the charge conservation equation, rewritten with the term

you want to solve for on the left-hand side and all the others on the right. We want to know $[H^+]$, so we've written Eq. 5 in this form. The next step is to replace the terms on the right-hand side with functions of $[H^+]$, alone. This is accomplished by substitution, using the equilibrium relations. In particular for our problem, if Eq. 1 is substituted into Eq. 2 we obtain

$$[H^+][HCO_3^-] = 10^{-11.29} \quad (6)$$

or

$$[HCO_3^-] = \frac{10^{-11.29}}{[H^+]}, \quad (7)$$

giving us $[HCO_3^-]$ written as a function of $[H^+]$. Using Eq. 7, Eq. 3 becomes

$$[H^+][CO_3^{2-}] = \frac{10^{-21.62}}{[H^+]} \quad (8)$$

or

$$[CO_3^{2-}] = \frac{10^{-21.62}}{[H^+]^2}. \quad (9)$$

Now $[CO_3^{2-}]$ is a function of $[H^+]$, alone. Using Eq. 4 we determine that

$$[OH^-] = \frac{10^{-14}}{[H^+]}. \quad (10)$$

Substituting Eqs. 7, 9, and 10 into Eq. 5, we arrive at an equation involving only $[H^+]$:

$$[H^+] = \frac{10^{-11.29}}{[H^+]} + \frac{10^{-21.32}}{[H^+]^2} + \frac{10^{-14}}{[H^+]}. \quad (11)$$

This cubic equation can be solved, now, for $[H^+]$ [for the procedure, see Birkhoff and MacLane (1953)]. Instead of solving for the exact solution, however, we will employ a simple method for finding an approximate solution. Since this method is often applicable in chemical equilibrium problems, it is worth learning.

To start, let's suppose that the first term on the righthand side of Eq. 11 is much larger than the other two terms—so much greater that, essentially,

$$[H^+]^2 = 10^{-11.29} \quad (12)$$

7

or

$$[\text{H}^+] = 10^{-5.65}. \quad (13)$$

If this provisional value for $[\text{H}^+]$ is substituted back into the right-hand side of Eq. 11, the three terms, reading from left to right, equal $10^{-5.65}$, $10^{-10.33}$, and $10^{-8.35}$. The first of these is, in fact, considerably larger than the other two, which tells us that our hypothesis was consistent with the correct solution. Summarizing the method (see also Figure II-18): By hypothesizing that two terms were much smaller than the third we were led to an equation (Eq. 12) whose solution indicates that the two terms were, indeed, smaller. Remembering that $\text{pH} = -\log_{10} [\text{H}^+]$, we determine the pH of rain in equilibrium with atmospheric CO_2 to be $-\log_{10} 10^{-5.65} = 5.65$.

Another acid-forming gas is SO_2 . The reactions $\text{H}_2\text{SO}_3 \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$ and $\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$ govern the dissociation of dissolved SO_2 . Using the two values of the dissociation constants, Henry's constant from the Appendix (X.3), and an approximate background concentration of SO_2 in Earth's atmosphere of 0.2 ppb(v), the equilibrium relations are:

$$\begin{aligned} [\text{H}_2\text{SO}_3] &= (0.20 \times 10^{-9} \text{ atm}) \times (10^{0.096} \text{ moles/liter-atm}) \\ &= 10^{-9.60} \text{ moles/liter}, \end{aligned} \quad (14)$$

$$[\text{H}^+][\text{HSO}_3^-] = 10^{-1.77} [\text{H}_2\text{SO}_3], \quad (15)$$

and

$$[\text{H}^+][\text{SO}_3^{2-}] = 10^{-7.21} [\text{HSO}_3^-]. \quad (16)$$

$$\text{Given: } X = \frac{a}{X} + f(X) \quad 1.$$

$$\text{Assume: } X \approx \frac{a}{X} \text{ or } X \approx \sqrt{a} \quad 2.$$

Substitute 2 into 1:

$$\sqrt{a} \approx \frac{a}{\sqrt{a}} + f(\sqrt{a}) \quad 3.$$

3 and, therefore, 2 are valid if
 $f(\sqrt{a}) \ll \sqrt{a}$

Figure II-18 A procedure for finding an approximate solution to the chemical equilibrium problem.

These relations are correct regardless of how much CO_2 is dissolved in the rain; similarly Eqs. 1–3 are correct regardless of how much SO_2 is dissolved in the rain. The relation that links CO_2 and SO_2 is the charge balance equation, which for the combined $\text{CO}_2 + \text{SO}_2$ systems reads

$$[\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] + [\text{OH}^-]. \quad (17)$$

Using Eqs. 7, 9, 10, and 14–16, this becomes

$$[\text{H}^+] = \frac{10^{-11.29}}{[\text{H}^+]} + \frac{10^{-21.32}}{[\text{H}^+]^2} + \frac{10^{-11.37}}{[\text{H}^+]} + \frac{10^{-18.26}}{[\text{H}^+]^2} + \frac{10^{-14}}{[\text{H}^+]}. \quad (18)$$

Supposing that the first and third terms on the righthand side are bigger than the others, we calculate that

$$[\text{H}^+]^2 = 10^{-11.29} + 10^{-11.37} \quad (19)$$

or

$$[\text{H}^+] = 10^{-5.51}. \quad (20)$$

The pH of the rain is thus 5.51. Substitution of Eq. 20 into Eq. 18 verifies that the second, fourth, and fifth terms were indeed small compared to the first and third.

The pH we have calculated should be corrected for two effects ignored up to this point. First, ammonia gas in the atmosphere forms a base when dissolved in water. Exercise 3 deals with this correction. Second, alkaline dust is present in the atmosphere over certain continental regions of Earth, such as the Great Basin of the United States (the land between the Sierra Nevada and the Rocky Mountains). Precipitation falling in the Rocky Mountains is sometimes found to be acidic ($\text{pH} \approx 4.5$) owing to human activities, but occasionally it has a pH greater than 6.0. The rain or snow storms with high pH usually contain CaCO_3 (limestone) or $\text{CaMg}(\text{CO}_3)_2$ (dolomite). Exercise 4 will give you practice in applying equilibrium chemistry to limestone dissolution in raindrops.

Because the "background" pH of precipitation should be in the mid fives, only precipitation with pH around five or below is now referred to as "acid precipitation." For a further discussion of this issue, with a treatment of background SO_4^{2-} , see Charlson and Rodhe (1982).

EXERCISE 1: Before the industrial revolution, the concentration of CO_2 in Earth's atmosphere was about 275 ppm(v). Considering the effect of dissolved CO_2 only, calculate the effect that the increase in CO_2 has had on the pH of precipitation.

EXERCISE 2: Here's a chance to practice solving some cubic equations by trial and error. (a) Consider the equation: $x^3 - 5x = 125$. Which of the following yields the best approximate solution to this equation: the x^3 term is small and $-5x \approx 125$; the $5x$ term is small and $x^3 \approx 125$; 125 is small and $x^3 \approx 5x$? (b) What is an approximate positive solution to $x^3 + 30x^2 - 10x - 40 = 0$?

* **EXERCISE 3:** In raindrops, the reaction $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ occurs, which tends to elevate pH. Henry's constant and the NH_3 dissociation constant are given in Sections X.2, 3 of the Appendix. The actual influence of background ammonia in the atmosphere on precipitation pH is difficult to estimate because the atmospheric NH_3 concentration, $p(\text{NH}_3)$, is poorly known. The Appendix (Section V.2) only provides an upper limit on $p(\text{NH}_3)$. One clue about the value of $p(\text{NH}_3)$ is provided by the observation that in remote areas, the measured NH_4^+ concentration in rainwater is generally less than about 5 micromoles per liter. Show that in the presence of atmospheric CO_2 at 340 ppm and SO_2 at 0.2 ppb a rainwater value of $[\text{NH}_4^+] < 5 \times 10^{-6}$ implies an upper limit on $p(\text{NH}_3)$. What is that upper limit? What will the pH of pristine precipitation be with $p(\text{CO}_2)$ equaling 340 ppm(v), $p(\text{SO}_2)$ equaling 0.2 ppb(v), and $p(\text{NH}_3)$ equaling 0.01 ppb(v)?

* **EXERCISE 4:** A sample of rain water is observed to have a pH of 7.4 (a) If only atmospheric CO_2 at 340 ppm(v) and limestone dust are present in the atmosphere to alter the pH from a neutral value of 7, and if each raindrop has a volume of 0.02 cm^3 , what mass of Ca is present in each raindrop? (b) Suppose there was so much CaCO_3 in the raindrops that the rainwater was saturated. What would the pH of the raindrops be?

* **EXERCISE 5:** Show that the residence time for atmospheric SO_2 with respect to its dissolution and subsequent removal through precipitation (as dissolved H_2SO_3 , HSO_3^- , and SO_3^{2-}) is independent of the atmospheric concentration of SO_2 and depends only on the pH of the precipitation and the precipitation rate. At a pH of 5.51 (Eq. 18) and a precipitation rate of 1 m/yr, what is the residence time? In a pristine atmosphere, what fraction of the SO_2 emitted to the atmosphere from natural sources would be removed via this rain-out process?

21. Natural Acidity from Biological Processes

The nitrification process is a source of acidity. In typical freshwater lakes, the nitrification rate averages about 10^{-4} moles (N)/liter/yr. Compare the influx of H^+ to a lake receiving inflow water with a pH of 4 (presumed due to acid rain) with the influx of H^+ from the internal nitrification process in the lake. Assume the residence time of water in the lake is half a year.

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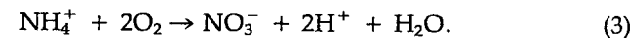
The rate of inflow of H^+ to the lake in stream water, $F_{H,S}$, equals the rate of inflow of stream water, F_W , times the concentration of H^+ in that water, $[\text{H}^+]$. The rate of inflow of water equals the lake volume, V , divided by the residence time, T . Hence, we can state

$$\begin{aligned} F_{H,S} &= F_W [\text{H}^+] \\ &= \frac{V[\text{H}^+]}{T} \end{aligned} \quad (1)$$

With V in liters, $[\text{H}^+]$ in moles per liter, and T in years, the rate of inflow of H^+ will be in units of moles of H^+ per year. Substituting numerical values for $[\text{H}^+]$ and T , we obtain

$$F_{H,S} = \frac{10^{-4} V}{0.5} = 2 \times 10^{-4} V. \quad (2)$$

To calculate the influx of H^+ from internal nitrification, $F_{H,N}$, we turn to Section X.1 of the Appendix to find the nitrification reaction:



The structure of this reaction tells us that for every mole of NH_4^+ that is nitrified to NO_3^- , two moles of H^+ are produced. Hence, if 10^{-4} moles(N)/liter are nitrified each year, then 2×10^{-4} moles(H^+)/liter will also be produced each year. Multiplying this by the number of liters of water in the lake, V , we get an inflow of H^+ from nitrification of

$$F_{H,N} = 2 \times 10^{-4} V, \quad (4)$$

in units of moles/yr. Thus, the two inflow rates are equal.

EXERCISE 1: (a) Using the data in Sections XII.1 and XIII.2 of the Appendix, estimate the total annual amount of H^+ produced on the continents in the nitrification process. (b) What pH of precipitation on the continents would yield an equal flux of H^+ ?

EXERCISE 2: Given the result above, and given that hydraulic residence times for lakes are often larger than half a year, why should we be worried about acid damage to lakes only from precipitation? After all, it appears that a natural biological process contributes as much acidity as does acid rain.

D. Non-Steady-State Box Models

The problems in Section A were solved by equating compartment inflows to compartment outflows. This was appropriate because the problems involved steady-state situations. A more difficult class of problems involves stocks that change over time, a situation arising when inflows are not in balance with outflows. When the inflow, F_{in} , is not equal to the outflow, F_{out} , then the rate of change of the stock is given by

$$\text{rate of change of } M = F_{in} - F_{out}. \quad (1)$$

If $F_{in} > F_{out}$, M increases with time; while if $F_{in} < F_{out}$, M decreases. In either case, there is no longer a well-defined residence time.

Eq. 1 is the starting point for many non-steady-state box models. If the flows are known functions of the stock, then the equation can be solved for $M(t)$. The problems in this section illustrate how this is done for the case in which the stocks vary smoothly, so that a differential equation

$$\frac{dM}{dt} = F_{in} - F_{out} \quad (2)$$

can be written.

In a multi-box model, a set of equations like Eq. 1 results. If the flow in or out of one box depends upon the stocks in that box and also the stocks in other boxes, then a set of interconnected, or coupled, equations results. The treatment of the interconnected boxes in a non-steady-state model is more complicated and is deferred to Chapter III (Problems III.5 and 14).

22. Exhausting Fossil Fuel Resources (II)

If the present worldwide rate of consumption of petroleum increases by 2% every year, how long will it take to use up Earth's petroleum resource?

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In this problem the non-steady-state quantity in the box is Earth's petroleum resource. The statement that consumption increases by a fixed percentage every year implies that the resource is being removed at an exponentially increasing rate. Of course, it is not being added to at all. Thus, the instantaneous consumption rate, or out-flow, $F(t)$, is an exponential of the form

$$F(t) = F(0) e^{rt}, \quad (1)$$

where $t = 0$ refers to the present. Using the 1980 value for the present rate of petroleum consumption (see Appendix, VII.2), $F(0) = 1.35 \times 10^{20}$ J/yr. The rate constant, r , in units of $(\text{yr})^{-1}$ can be determined by the condition that $F(1) = 1.02 F(0)$, or

$$e^{r(1)} = 1.02. \quad (2)$$

Because $\log_e(1.02) \approx 0.0198$,

$$r \approx 0.0198. \quad (3)$$

If $M(t)$ is the amount of petroleum remaining at time t [with $M(0) = 1.0 \times 10^{22}$ joules as given in the Appendix, VII.2] then the rate of change of $M(t)$ is given by

$$\frac{dM}{dt} = -F(0) e^{rt}. \quad (4)$$

This equation can be integrated to yield an equivalent equation. If the integration variable is called t' and if the integral extends from $t' = 0$ to $t' = t$, this equivalent equation takes the form

$$\int_{M(0)}^{M(t)} dM = - \int_0^t dt' F(0) e^{rt'}. \quad (5)$$

The integrals are easily carried out to yield

$$M(t) - M(0) = \frac{-F(0)}{r} e^{rt} + \frac{F(0)}{r}, \quad (6)$$

or,

$$M(t) = M(0) + \frac{F(0)}{r} (1 - e^{rt}). \quad (7)$$

The petroleum resource will be entirely consumed when M vanishes. $M(t)$ will vanish at time T , where T is given by

$$M(0) + \frac{F(0)}{r} (1 - e^{rT}) = 0, \quad (8)$$

or

$$e^{rT} = 1 + \frac{rM(0)}{F(0)}. \quad (9)$$

Taking the natural log of both sides, we obtain

$$rT = \log_e \left[1 + \frac{rM(0)}{F(0)} \right]. \quad (10)$$

Substituting the numerical values for r , $F(0)$, and $M(0)$ gives the final answer:

$$T = 45.6 \text{ yr.}$$

EXERCISE 1: If coal and natural gas consumption are increasing at an annual rate of 4% per year and 1% per year, respectively, how long will Earth's resources of these fuels last?

EXERCISE 2: Eq. 2 implies that the instantaneous rate of consumption at the end of a year is 2% larger than at the beginning of that year. Suppose we interpret the statement that the "rate of consumption of petroleum increases by 2% every year" to mean that the total consumption in year n is 2% greater than the total consumption in year $n - 1$. Using the fact that consumption in year n equals $\int_{n-1}^n F(t) dt$, show that Eq. 2 is still correct.

EXERCISE 3: Problem II.22 can also be tackled using discrete time rather than continuous time. Let years be labeled with a symbol, n , that takes on values $n = 0$ (1980), $n = 1$ (1981), etc. If the amount of petroleum consumed in year n is $F(n)$, then $F(1) = 1.02 F(0)$, $F(2) = (1.02)^2 F(0)$, etc. By summing a finite geometric series, determine how big n must be so that $F(0) + F(1) + \dots + F(n)$ roughly equals $M(0)$.

23. Pollution Buildup in a Lake

A lake has a volume of 10^6 m^3 and a surface area of $6 \times 10^4 \text{ m}^2$. Water flows into the lake at an average rate of $0.005 \text{ m}^3/\text{sec}$. The amount of water that evaporates yearly from the lake is equivalent in volume to the lake's top meter of water. Initially, the lakewater is pristine, but at a certain time a soluble, noncodistilling pollutant is discharged into the lake at a steady rate of 40 tonnes/yr. Derive a formula for the concentration of pollutant in the lake as a function of time since the pollutant discharge began.

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A noncodistilling pollutant is a substance that does not evaporate away with evaporating water. Therefore, evaporation of lakewater is not an exit pathway for the pollutant. However, if the lakewater flows out of the lake in an outlet stream or via underground seepage, that water outflow will remove pollutant. So to begin, let's calculate the stream and seepage outflow rate for the lakewater. The lakewater is in a steady state, with stock, M_w , equal to 10^6 tonnes(H_2O) (since 1 m^3 of water has a mass of 1 tonne). The water inflow rate, F_w , is 0.005 tonnes(H_2O)/sec = 1.6×10^5 tonnes(H_2O)/yr and therefore the total water outflow rate must also equal 1.6×10^5 tonnes(H_2O)/yr. The evaporation outflow rate is 1 m/yr times the area of the lake, or 0.6×10^5 tonnes(H_2O)/yr, and hence the stream and seepage outflow rate is 10^5 tonnes(H_2O)/yr.

At any time, t , let $M_p(t)$ equal the mass of pollutant in the lake in units of tonnes. The concentration of pollutant at time t is $M_p(t)/M_w$ in units of tonnes(pollutant)/tonne(water). If the stream-plus-seepage outflow rate is multiplied by the concentration of pollutant, and if the pollutant is well mixed in the lakewater the rate of pollutant outflow, $F_{p,out}(t)$, is obtained:

$$\begin{aligned} F_{p,out} &= 10^5 \frac{M_p}{M_w} \\ &= 0.1 M_p \end{aligned} \quad (1)$$

in units of tonnes(pollutant)/yr.

The rate at which pollutant flows into the lake, $F_{p,in}$, equals 40 tonnes(pollutant)/yr. Equating the rate of change of M_p to the net difference between inflow and outflow,

$$\begin{aligned} \frac{dM_p}{dt} &= F_{p,in} - F_{p,out} \\ &= 40 - 0.1 M_p \end{aligned} \quad (2)$$

with M_p in units of tonnes(pollutant) and time in units of years. This equation is of the form,

$$\frac{dX}{dt} = a + bX \quad (3)$$

and has a general solution³⁰

$$X(t) = \frac{-a}{b} + ce^{bt}. \quad (4)$$

The constant, c , must be determined from a specified condition on $X(t)$. Thus if $X(0)$ is a known amount, the relation

$$X(0) = \frac{-a}{b} + c, \quad (5)$$

which follows from Eq. 4, determines the unknown constant, c . In our case, $a = 40$, $b = -0.1$, and, if $t = 0$ is the time the pollutant discharge began, then $X(0) = 0$. Therefore, $c = a/b$. In units of tonnes, the mass of pollutant in the lake is given by

$$M_p(t) = \frac{40}{0.1} - \frac{40}{0.1} e^{-0.1t}. \quad (6)$$

EXERCISE 1: What amount and what concentration of pollutant will exist in the lake as t approaches infinity?

EXERCISE 2: Since the water in the lake is in steady state, its residence time, T_w , can be computed. What is the value of that residence time? As t approaches infinity, the pollutant approaches a steady state; therefore a residence time, T_p , is derivable. What is the

30. You can derive the general solution by rewriting Eq. 3 in the form $dX/(a + bX) = dt$ and integrating both sides. You can also verify that Eq. 4 is correct by direct substitution into Eq. 3. An excellent introduction to differential equations, with considerable emphasis on practical applications, is the text by Boyce and DiPrima (1973).

value of that residence time? Explain why T_p is greater than T_w , and interpret the difference $T_w^{-1} - T_p^{-1}$, using your answer from Exercise 3, Problem II.6.

EXERCISE 3: Draw a plot of Eq. 6 to get a visual sense of how pollution builds up in a lake. Include values of $X(t)$ at 2-year intervals for a 20-year period starting at $t = 0$.

* **EXERCISE 4:** This exercise will give you some practice deriving and solving a differential equation. Consider a slab of material of thickness, x , and area, A . One face of the slab, the hotter face, is kept at a fixed temperature, T_1 . The opposite face is fixed at temperature, T_2 . Heat will flow across the slab, from the hotter face to the cooler one. The formula for the rate of heat conduction across the slab is

$$\frac{dQ}{dt} = \frac{kA(T_1 - T_2)}{x},$$

where Q is heat, t is time, and k is a constant called the coefficient of heat conductivity. Imagine that the slab of material is a layer of ice on a lake. A is the area and x is now the thickness of the ice. The air temperature right above the ice is a constant -30°C and the water temperature just below the ice is a constant 0°C . Thus $T_2 = -30^\circ\text{C}$ and $T_1 = 0^\circ\text{C}$. To form new ice from liquid water at 0°C , 80 calories must be removed from every gram of the liquid water. The value of k for ice is $2.2 \text{ J/m}^\circ\text{C sec}$. If the ice is 1 cm thick at $t=0$, how thick will it be two months later? (Hint: you first have to write a differential equation for dx/dt .) The answer you derive is roughly the amount of ice that would form on many lakes in the northern hemisphere in the aftermath of a major nuclear war. This is discussed in more detail in an article on "nuclear winter" by Ehrlich et al. (1983); see also Exercise 4 of Problem III.6.

Chapter III

Beyond the Back of the Envelope

Problems worthy of attack, prove their worth by hitting back.

—Piet Hei

The problems in this chapter are more open-ended than the Chapters I and II. Solving them requires the creation and application of mathematical models. If you haven't had much experience you may think systems modeling is a well-defined, somewhat procedure akin to building an erector-set likeness of a bridge. Actually, the process is a dynamic one, involving flexible and creative thinking that results in a flexible product amenable to further refining and refining as the modeling process continues. A good problem-solving model affords an array of elegant revelations about a complex system or situation. With a good model, you can view a situation from many perspectives. By tinkering with the model, you can vary it mentally to extreme conditions and thereby learn more about how the system works. (For example, you can ask what our world would be like if urbanization covered Earth's surface—see Problem III.9.)

You will find that after you've created a model to answer a question, it will start to ask *you* questions—ones you wouldn't have thought of before. Models also have a way of letting you know when you've made them clumsy and useless—when you must return to the drawing board. This is a recognition I experienced many times while preparing this book's problems and solutions. Indeed, the problems presented here can certainly be improved or refined further by an ambitious reader.

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Answers To Exercises

- I. 1.2 10^3
 1.3 10^2
 1.4 10^{-4}
 2.1 5.06 cm^3
 2.2 3 Å
 3.1 500 m
 3.2 (a) 5×10^{-7} ; (b) 6×10^{-5}
 3.3 3.94
 3.4 (a) $3.6 \times 10^{18} \text{ m}^2$; (b) $1.8 \times 10^{17} \text{ m}^2$
 4.1 gas: 170 yr; coal: 2800 yr
 4.2 15,000 yr
 5.1 1.5×10^{12}
 5.2 $\log_e^2 = 1/\log_2 e = 0.693$; $\log_{10} 2 = 1/\log_2 10 = 0.301$; $\log_e 10 = 1/\log_{10} e = 2.303$
 5.3 8 times
 5.4 0.405
 6.1 $f = 0.0056$
 6.3 0.1
 6.4 2236
 7.1 Cd: 300 tonnes; Pb: 30,000 tonnes; Zn: 150,000 tonnes; Se: 3,000 tonnes; Hg: 300 tonnes; As: 30,000 tonnes
- II. 1.1 42 cows
 1.2 (a) 4 yr; (b) 4.75 yr
 2.1 2960 yr
 2.2 40 in
 3.1 1.3
 3.3 (a) 1/14; (b) 14/100
 4.2 $2.1 \times 10^{11} \text{ kg}(\text{N}_2\text{O})/\text{yr}$
 6.2 (a) $S_A - E_A$; $S_A - E_A + S_B$; (b) V_A/S_A ; $V_B/(S_A - E_A + S_B)$; (c) $C_A = P/(S_A - E_A)$ g/liter; $C_B = P/(S_A + S_B - E_A - E_B)$ g/liter

- 7.1 1.2×10^6 tonnes/yr
 7.2 $\alpha^{-1} = 1.125$ yr
 7.3 $\beta^{-1} = 1.125$ yr
 7.4 $\alpha^{-1} = 2.8$ yr
 7.5 1 or 2%
 7.6 (a) 0.6×10^{11} moles/yr; (b) 0.8×10^{11} moles/yr
 8.2 $\bar{X}_1 = 0.183$,
 $\bar{X}_2 = 0.1$, $\bar{X}_3 = 1.017$
 8.3 $\bar{X}_1 = 0.8 \bar{X}_1$; $\bar{X}_2 = \bar{X}_2$; $\bar{X}_3 = 1.08 \bar{X}_3$
 9.1 2.4% decrease
 10.2 (a) 53 kg(fuel)/km²day; (b) order of magnitude of 10 people/km²
 11.3 (a) 7×10^{-10} Ci/m³; (b) 9.4×10^{-8} Ci/m³
 11.4 6.4×10^7 atoms
 11.5 1.1×10^{-14} ppm(v)
 12.1 0.001
 12.2 4%
 13.2 10.9 W/m² (180 × Earth's)
 13.3 1.16×10^9 m
 14.1 (a) 100 W; (b) 75 W
 14.2 250 W
 15.1 0.0083
 16.1 15%
 16.2 160 km²
 16.3 5/3
 16.5 180 km
 17.1 $n = 1.1 \times 10^3$ moles/m³; $P = 2.65 \times 10^6$ J/m³
 17.2 (a) 2/3; (b) 1300 yr
 18.2 0.713
 18.3 $f_s = (1 - R')[T/(1 - R'R)]$, $f_C = (1 - R - T)[1 + R'T/(1 - R'R)]$
 18.5 high particles: $a = T^2R' + (TT')^2R''/(1 - R'R'')$, $f_s = TT'A''/(1 - R'R'')$
 low particles: $a = R' + (TT')^2R''/(1 - T^2R'R'')$, $f_s = TT'A''/(1 - T^2R'R'')$
 19.2 0.78%
 19.3 0.0017%
 20.1 a decrease of 0.046 pH units
 20.2 (a) $x^3 \approx 125$; (b) dropping the x^3 and $10x$ terms, $x = (4/3)^{1/2}$; dropping only the x^3 term, $x = 4/3$
 20.4 (a) 5.1×10^{-8} g; (b) pH = 8.26
 21.1 (a) 2.4×10^{14} moles(H⁺)/yr; (b) pH = 2.66
 22.1 coal: 120 yr; gas: 98 yr
 23.1 400 tonnes; 400 ppm by weight
 23.4 1.4 m
- III. 1.2 3.82
 1.3 5.6
 2.2 (liters/mole)²
 2.3 2.1 ppm by weight
 2.4 1.4×10^6 g/yr
 2.5 2.4×10^4 yr
 3.3 1563 yr
- 3.4 8220 yr
 3.5 9 yr
 3.6 8.3×10^9 tonnes/yr
 3.7 (a) 8.6 years; (b) about 7.4 yr
 4.2 $dY/dX = 2.3 \times 10^{-21} M_s$
 4.3 - 0.14 pH units
 4.5 957 micromoles/liter
 6.2 $g/C_p = 9.76$ K/km
 6.4 $T_0 = 255$ K, $T_1 = 253$ K, $T_s = 243$ K
 6.3 $T_0 = T_1 = T_s = T_{\text{dust}} = 221.8$ K
 6.5 (c) 81.0%; 19.6%; 5.47 km
 (d) 80.5%; 17.2%; 5.67 km
 6.6 roughly 1.7 km
 7.3 $T_0 = 249.6$ K, $T_1 = 278.5$ K, $T_s = 289.7$ K
 7.4 70% increase
 8.2 $(1 - A)^{-1} = 0.61$
 8.6 $(1 - A)^{-1} = 3.7$
 9.2 345 km × 345 km
 13.3 $\bar{n} = r/(1 - r)$
 13.4 first method: $T = 200$ days; second method: $T = 250$ days
 14.5 (a) 74%; (b) 54%; (c) 20%
 14.7 $X = 0.525884288$