

**BASIC
PHYSICAL
CHEMISTRY**
for the
**ATMOSPHERIC
SCIENCES**

Peter V. Hobbs

2nd Edition

BASIC PHYSICAL CHEMISTRY FOR THE ATMOSPHERIC SCIENCES

Second Edition

Modern studies of atmospheres, oceans, and Earth and planetary systems require a good knowledge of basic chemical principles. This book provides a clear, concise grounding in these principles. Undergraduate and graduate students with little formal training in chemistry can work through the chapters, and the numerous exercises, within this book before accessing more advanced texts in atmospheric chemistry, geochemistry, and the environmental sciences.

Basic Physical Chemistry for the Atmospheric Sciences covers the fundamental concepts of chemical equilibria, chemical thermodynamics, chemical kinetics, solution chemistry, acid and base chemistry, oxidation-reduction reactions, and photochemistry. This new edition has been updated and revised from the first edition.

In a companion volume entitled *Introduction to Atmospheric Chemistry* (2000, Cambridge University Press) Peter Hobbs provides an introduction to atmospheric chemistry itself, including its applications to air pollution, acid rain, the ozone hole, and climate change. Together these two books provide an ideal introduction to atmospheric chemistry for a variety of disciplines.

Peter V. Hobbs (University of Washington) is known internationally for his research on many aspects of the atmosphere: clouds, precipitation, aerosols, storms, atmospheric chemistry, and climate. He is the author of the definitive text *Ice Physics*, the author of *Introduction to Atmospheric Chemistry* (Cambridge University Press, 2000), co-author (with J. M. Wallace) of one of the most widely used textbooks in meteorology *Atmospheric Sciences: An Introductory Survey*, and editor of several other books. He has authored more than 300 scientific papers. Professor Hobbs has served on many national and international committees, including the Scientific Steering Committee of the International Global Atmospheric Chemistry Program, and international scientific bodies. He has been a visiting senior research scientist in England, France, Germany and Italy.

BASIC PHYSICAL
CHEMISTRY FOR THE
ATMOSPHERIC SCIENCES
SECOND EDITION

A Companion Text to
“Introduction to Atmospheric Chemistry”

PETER V. HOBBS
University of Washington



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Preface to first edition

A short account of the origins of this book will explain its purpose. In the 1970s I coauthored (with John M. Wallace) a textbook for senior undergraduates and first-year graduate students entitled *Atmospheric Science: An Introductory Survey* (Academic Press, 1977). At the time that text was written it was not considered necessary to include a chapter on atmospheric chemistry. By the early 1990s, when we began to think about a second edition of *Atmospheric Science*, the importance of atmospheric chemistry was such that it was inconceivable that such a book would not include a substantial chapter on this subject.

In the intervening years I had introduced a section on atmospheric chemistry into the survey course taken by all first-year graduate students in the Atmospheric Sciences Department at the University of Washington. I quickly discovered, however, that many of the students either had no previous instruction in chemistry or had long since forgotten what little they had known. I therefore wrote an (unpublished) primer on physical chemistry for these students; the present book grew out of that primer.

Reviewed herein are some of the fundamental concepts associated with chemical equilibrium, chemical thermodynamics, chemical kinetics, aqueous solutions, acid–base chemistry, oxidation–reduction reactions and photochemistry, all of which are essential to an understanding of atmospheric chemistry. The approach is primarily from the macroscopic viewpoint, which provides the tools needed by the pragmatist. A deeper understanding requires extensive treatment of the electronic structure of matter and chemical bonding, topics that are beyond the scope of this introductory text. This book can be used for either self-instruction, or as the basis for a short introductory class on chemistry, prior to courses in which chemistry is applied to one of the geosciences. In addition to

students (and I use this term in its broadest sense) of atmospheric sciences, I hope this book will be useful to others. It should be suitable, for example, as a precursor to undergraduate and graduate courses in which chemistry is applied to any of the geosciences and environmental sciences.

In keeping with the didactic approach of this book, and the view that any science is best learned by solving problems, I have provided solutions to 50 exercises in the text and posed 112 exercises for the student. Answers to all the quantitative problems, and hints and solutions to selected problems, are given in Appendix VII.

In preparing this book I benefited from the following texts, which are recommended to the reader: *Chemistry: An Experimental Science* edited by G. C. Pimentel (W. H. Freeman, 1963) gives a broad introduction to chemistry with emphasis on its experimental foundations; *Chemistry: The Central Science* by T. L. Brown and H. E. LeMay Jr. (Prentice-Hall Inc., 1981) and *General Chemistry: Principles and Modern Applications* by R. H. Petrucci (Macmillan Pub. Co., 1982) provide more extensive accounts of most of the topics discussed in the present book and deal with many other aspects of chemistry. Finally, for the student who wants to take the next step in chemistry beyond that presented here, *University Chemistry* by B. H. Mahan (Addison-Wesley, 1965) is highly recommended.

This book was started in 1984 when I was an Alexander von Humboldt Foundation Senior Scientist in Germany, and it was essentially finished in 1993 during a sabbatical at the Instituto FISBAT-CNR, Bologna, Italy. Thanks are due to both of these organizations for their generous support. It is also a pleasure to thank my colleagues Professors Dean Hegg and Conway Leovy, and many students, particularly John Herring and Cathy Cahill, who commented on various drafts of this book and made suggestions for its improvement. I am grateful to the National Science Foundation for supporting my own research in atmospheric chemistry over many years.

Any suggestions or corrections related to this book will be gratefully received.

Seattle
May 1994

Preface to second edition

The success of the first edition of this book encouraged me to write a companion text entitled *Introduction to Atmospheric Chemistry* (Cambridge University Press, 2000). On the occasion of the publication of the latter text, the opportunity has been taken to issue a second edition of *Basic Physical Chemistry for the Atmospheric Sciences*.

In this second edition a number of minor (and a few major) errors have been corrected, and the text has been clarified in several places. I hope that, taken together, these two companion volumes will provide students, researchers, and even the interested layperson, with a sound introduction to the fascinating subject of atmospheric chemistry, which has emerged as a discipline in its own right in just the past few decades.

Comments on this book, which will be gratefully received, can be sent by e-mail to: phobbs@atmos.washington.edu. Current information on the book, including any errata, can be found on <http://cargsun2.atmos.washington.edu/~debbie/HobbsWebPage/BasicChem/Info.html>.

Peter V. Hobbs

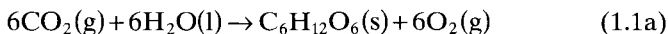
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Chemical equilibrium

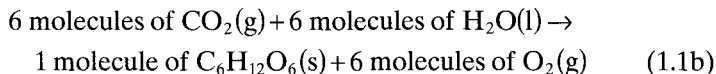
One of the major goals of chemistry is to predict what will happen when various substances come into contact. Will a chemical reaction occur, or will the substances just exist side by side? One way to approach this problem is through the concept of chemical equilibrium, which is the focus of this chapter.

1.1 Some introductory concepts

In a balanced equation for a chemical reaction, there are the same number of atoms of each element on the left side of the equation as there are on the right side. For example, the balanced equation for the chemical reaction representing photosynthesis is^{1,a}



In a balanced chemical equation (which we will often call a *reaction*), the relative numbers of the molecules involved in the reaction are given by the numerical coefficients preceding the chemical symbol for the molecule. Thus, Reaction (1.1a) indicates that six molecules of carbon dioxide, $\text{CO}_2(\text{g})$, react with six molecules of water, $\text{H}_2\text{O}(\text{l})$, to form one molecule of glucose, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$, and six molecules of oxygen, $\text{O}_2(\text{g})$



Reaction (1.1a) does not necessarily mean that if six molecules of $\text{CO}_2(\text{g})$ are mixed with six molecules of $\text{H}_2\text{O}(\text{l})$ they will react completely

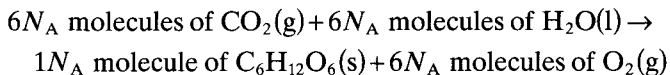
^a Numerical superscripts in the text (1, 2, . . . , etc.) refer to *Notes* at the end of each chapter.

and produce one molecule of $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$ and six molecules of $\text{O}_2(\text{g})$. Some chemical reactions proceed very quickly, others very slowly; and some never reach completion. However, what Reaction (1.1a) does tell us is that at any given instant in time the ratio of the numbers of molecules of $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$, and $\text{O}_2(\text{g})$ that have reacted is 6:6:1:6.

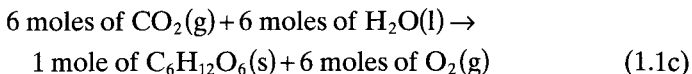
The relative masses of the various atoms are represented by their *atomic weights* (dimensionless) referenced to carbon-12 (i.e., a carbon atom containing six protons and six neutrons), where carbon-12 is arbitrarily assigned an exact atomic weight of 12. Atomic weights are listed in Appendix III. Similarly, the relative masses of molecules are represented by their *molecular weights* (dimensionless), where the molecular weight is obtained by adding together the atomic weights of all the atoms in the molecule. For example, since the atomic weights of hydrogen and oxygen are 1.008 and 15.999, respectively, the molecular weight of water (H_2O) is $(2 \times 1.008) + 15.999 = 18.015$.

One *gram-molecular weight* (abbreviation *mole* or *mol*) of any compound is a mass of that compound equal to its molecular weight in grams. Thus, 1 mole of water is 18.015 g of water. One mole of any compound contains the same number of molecules as one mole of any other compound.² The number of molecules in 1 mole of any compound is 6.022×10^{23} , which is called *Avogadro's number* (N_A). Since the volume occupied by a gas depends on its temperature, pressure, and the number of molecules in the gas, at the same temperature and pressure 1 mole of the gas of any compound occupies the same volume as 1 mole of the gas of any other compound. At *standard temperature and pressure* (STP), which are defined as 0°C and 1 bar ($= 10^5 \text{ Pa}$),³ the volume occupied by 1 mole of any gas is about 22.4 liters (L).

If we now multiply every term in the Relation (1.1b) by N_A we get



or,



Relations (1.1b) and (1.1c) demonstrate how we can move directly from a balanced chemical equation, such as Reaction (1.1a), to a statement about the relative numbers of molecules (1.1b) or the relative numbers of moles (1.1c) involved in the reaction.

Exercise 1.1. An important chemical reaction in atmospheric, earth, and ocean sciences is that of dissolved carbon dioxide with liquid water to form carbonic acid, $\text{H}_2\text{CO}_3(\text{l})$,

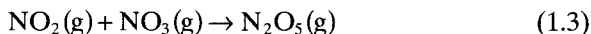


Calculate the mass of carbonic acid that forms for every kilogram of carbon dioxide that reacts with liquid water.

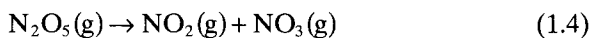
Solution. From the balanced chemical equation (1.2) we see that for every mole of carbon dioxide that reacts with water one mole of carbonic acid is formed. Since the molecular weight of CO_2 is 44.01, the number of moles of CO_2 in 1 kg is $1000/44.01 = 22.72$. Therefore, 22.72 moles of carbonic acid will form for every kilogram of CO_2 that reacts with water. The molecular weight of carbonic acid is 62.02; therefore, the number of grams of carbonic acid in 22.72 moles is $(22.72 \times 62.02) = 1409$. Therefore, for every kilogram of CO_2 that reacts with water 1.409 kg of carbonic acid are formed.

1.2 Equilibrium constants

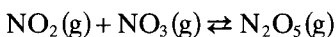
A vapor is in equilibrium with its liquid when the rate of condensation is equal to the rate of evaporation. An analogous state of equilibrium exists in a chemical system when the rate at which the reactants combine to form products is equal to the rate at which the products decompose to form the reactants. For example, a reaction that plays a role in tropospheric and stratospheric chemistry is



However, some of the N_2O_5 molecules so formed break up again

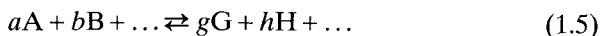


Reaction (1.3) is called the *forward* reaction and Reaction (1.4) the *reverse* reaction. Reactions (1.3) and (1.4) can be combined as follows



At every temperature there exists partial pressures of the gases for which the forward and reverse reactions occur at the same rate; under these conditions, the system is said to be in *chemical equilibrium*.

A general chemical reaction can be represented by



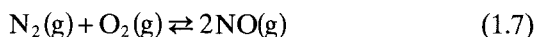
where A, B, ... and G, H, ... represent the chemical *reactants* and *products*, respectively, and $a, b, \dots$ and $g, h, \dots$ their coefficients in the balanced chemical equation. If Reaction (1.5) is in chemical equilibrium, and if the reactants and products are ideal gases or are present as solutes in an ideal solution,⁴ then

$$\frac{[G]^g [H]^h \dots}{[A]^a [B]^b \dots} = K_c \quad (1.6)$$

where [A], [B], ... and [G], [H], ... represent the equilibrium concentrations of the reactants and products, and K_c is called the *equilibrium constant* for the forward reaction (or, simply, the equilibrium constant for the reaction).⁵ Equilibrium constants for some chemical reactions are given in Appendix IV. The value of K_c for a chemical reaction depends only on temperature (see Section 2.2), not on the concentrations of the chemical species or the volume or pressure of the system.

The concentrations in Eq. (1.6) may be expressed in *molarity* (M). For a gas the molarity is the number of *moles* of gas per liter of air; for a solution, it is the number of moles of solute per liter of solution. If any of the reactants or products are pure liquids or pure solids, their concentrations (i.e., densities) are essentially constant, compared to the large changes that are possible in the concentrations of the gases. Therefore, the concentrations of liquids and solids are incorporated into the value of K_c . The practical consequence of this is that the concentration of any pure liquid or pure solid may be equated to unity in Eq. (1.6).

Exercise 1.2. At 2000°C the value of K_c for the reaction



is 1.0×10^{-4} . If the equilibrium concentrations of $O_2(g)$ and $NO(g)$ are 50M and 0.030M, respectively, what is the equilibrium concentration of $N_2(g)$?

Solution. Application of Eq. (1.6) to Reaction (1.7) yields

$$K_c = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]}$$

Therefore,

$$1.0 \times 10^{-4} = \frac{(0.030)^2}{[N_2(g)](50)}$$

and,

$$[\text{N}_2(\text{g})] = 0.18 \text{ M}$$

At 25°C the value of K_c for Reaction (1.7) is only 1×10^{-30} ! This implies that the equilibrium concentration of $\text{NO}(\text{g})$ is very low at normal temperatures and that the equilibrium “lies to the left” of Reaction (1.7), favoring the reactants. Hence, in the troposphere, negligible quantities of $\text{NO}(\text{g})$ are produced by Reaction (1.7).

In the case of chemical reactions involving only gases, it is often more convenient to express the equilibrium constant for the reaction in terms of the partial pressures of the reactants and products instead of their molarities. However, before doing this we must review the ideal gas equation.

Laboratory experiments show that for a wide range of conditions the pressure (p), volume (V), and temperature (T) of all gases follow closely the same relationship, which is called the *ideal gas equation*. In SI units (see Appendix I), the ideal gas equation can be written in the following forms. For mass m (in kilograms) of a gas

$$pV = mRT \quad (1.8a)$$

where p is in pascals, V in cubic meters, T in K ($\text{K} = ^\circ\text{C} + 273.15 \approx ^\circ\text{C} + 273$), and R is the gas constant for 1 kg of a gas. The value of R depends on the number of molecules in 1 kg of the gas, and therefore varies from one gas to another. Since $m/V = \rho$, where ρ is the density of the gas,

$$p = R\rho T \quad (1.8b)$$

For 1 kg of gas ($m = 1$), Eq. (1.8a) becomes

$$p\alpha = RT \quad (1.8c)$$

where α is the specific volume of the gas (i.e., the volume occupied by 1 kg of the gas). One mole of any gas contains the same number of molecules (N_A). Therefore, the gas constant for 1 mole is the same for all gases and is called the *universal gas constant* R^* ($8.3143 \text{ J deg}^{-1} \text{ mol}^{-1}$). Therefore,

$$pV = nR^*T \quad (1.8d)$$

where n is the number of moles of the gas, which is given by

$$n = \frac{1000m}{M}$$

where $1000m$ is the number of grams of the gas and M the molecular weight of the gas. Also,

$$R^* = M \frac{R}{1000} \quad (1.8e)$$

where R is divided by 1000 to obtain the gas constant for 1 g of gas. It can be seen from Eq. (1.8d) that at constant temperature and pressure the volume occupied by any gas is proportional to the number of moles (and therefore the number of molecules) in the gas. The gas constant for 1 molecule of any gas is also a universal constant, called the *Boltzmann constant* k . Since the gas constant for N_A molecules is R^*

$$k = \frac{R^*}{N_A} = \frac{8.3143}{6.022 \times 10^{23}} = 1.381 \times 10^{-23} \text{ J deg}^{-1} \text{ molecule}^{-1} \quad (1.8f)^6$$

For a gas containing n_0 molecules per cubic meter, the gas equation can be written

$$p = n_0 k T \quad (1.8g)$$

In chemistry, it is common because it is convenient, to depart from SI units in the gas equation and, instead, to express pressure in atmospheres and volume in liters (T is still in K). In this case, for n_A moles of gas A with pressure p_A and volume V_A we can write the ideal gas equation as

$$p_A V_A = n_A R_c^* T \quad (1.8h)$$

where R_c^* is the universal gas constant in “chemical units” (indicated by the subscript c); the value of R_c^* is $0.0821 \text{ L atm deg}^{-1} \text{ mol}^{-1}$. Since n_A/V_A is the number of moles of the gas per liter, that is, the molarity $[A]$ of the gas

$$[A] = \frac{n_A}{V_A} = \frac{p_A}{R_c^* T} \quad (1.8i)$$

Exercise 1.3. Carbon dioxide occupies about 354 parts per million by volume (ppmv) of air. How many CO_2 molecules are there in 1 m^3 of air at 1 atm and 0°C ?

Solution. Let us calculate first the number of molecules in 1 m^3 of any gas at 1 atm and 0°C (which is called the *Loschmidt number*). This is given by n_0 in Eq. (1.8g) with $p = 1 \text{ atm} = 1013 \times 10^2 \text{ Pa}$, $T = 273 \text{ K}$ and $k = 1.381 \times 10^{-23} \text{ J deg}^{-1} \text{ molecule}^{-1}$. Therefore,

$$\text{Loschmidt number} = \frac{1013 \times 10^2}{(1.381 \times 10^{-23}) 273} = 2.69 \times 10^{25} \text{ molecule m}^{-3}$$

Since, at the same temperature and pressure, the volumes occupied by gases are proportional to the numbers of molecules in the gases, we can write

$$\begin{aligned} & \frac{\text{Volume occupied by CO}_2 \text{ molecules in air}}{\text{Volume occupied by air}} \\ &= \frac{\text{Number of CO}_2 \text{ molecules in 1 m}^3 \text{ of air}}{\text{Total number of molecules in 1 m}^3 \text{ of air}} \end{aligned}$$

Therefore,

$$354 \times 10^{-6} = \frac{\text{Number of CO}_2 \text{ molecules in 1 m}^3 \text{ of air}}{2.69 \times 10^{25}}$$

Hence, the number of CO₂ molecules in 1 m³ of air is $(354 \times 10^{-6}) \times (2.69 \times 10^{25}) = 9.52 \times 10^{21}$.

We can now derive an expression for the equilibrium constant for a chemical reaction involving only gases in terms of the partial pressures of the gases. From Eqs. (1.6) and (1.8i)

$$K_c = \frac{[p_G/R_c^*T]^g [p_H/R_c^*T]^h \dots}{[p_A/R_c^*T]^a [p_B/R_c^*T]^b \dots} = \frac{p_G^g p_H^h \dots}{p_A^a p_B^b \dots} (R_c^*T)^{\Delta n}$$

or,

$$K_c = K_p (R_c^*T)^{\Delta n} \quad (1.9a)$$

where,

$$K_p = \frac{p_G^g p_H^h \dots}{p_A^a p_B^b \dots} \quad (1.9b)$$

and,

$$\Delta n = (a + b + \dots) - (g + h + \dots) \quad (1.9c)$$

K_p is generally used as the equilibrium constant in problems involving gaseous reactions. As in the case of K_c , terms for pure liquids and solids do not appear in the expression for K_p , and the coefficients for these

terms are taken to be zero in the expression for Δn . Note that the units, as well as the numerical values, of K_c and K_p may differ. For example, for Reaction (1.3) the units of K_c are those of

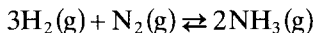
$$\frac{[\text{O}_3(\text{g})]}{[\text{O}(\text{g})][\text{O}_2(\text{g})]} \text{ or } \frac{\text{M}}{(\text{M})(\text{M})} = \text{M}^{-1}, \text{ the units of } K_p \text{ are}$$

$$\frac{p_{\text{O}_3}}{(p_{\text{O}})(p_{\text{O}_2})} \text{ or } \frac{\text{atm}}{(\text{atm})(\text{atm})} = \text{atm}^{-1}.$$

Nevertheless, it is common practice in chemistry not to indicate the units of equilibrium constants, with the understanding that when K_c is used the concentrations are in molarity, and when K_p is used the partial pressures are in atmospheres.

Exercise 1.4. Ammonia, $\text{NH}_3(\text{g})$, is produced commercially from the reaction of hydrogen, $\text{H}_2(\text{g})$, and atmospheric nitrogen, $\text{N}_2(\text{g})$, at high temperatures. If $\text{H}_2(\text{g})$, $\text{N}_2(\text{g})$, and $\text{NH}_3(\text{g})$ attain equilibrium at 472°C when their concentrations are 0.12 M, 0.04 M, and 0.003 M, respectively, calculate the values of K_c and K_p for the reaction at 472°C .

Solution. The balanced chemical equation for the reaction is



Hence, from Eq. (1.6)

$$K_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{H}_2(\text{g})]^3 [\text{N}_2(\text{g})]} = \frac{(0.003)^2}{(0.12)^3 (0.04)} = 0.1$$

From Eq. (1.9a)

$$K_c = K_p (R_c^* T)^{\Delta n}$$

where $K_c = 0.1$, $R_c^* = 0.0821 \text{ L atm deg}^{-1} \text{ mol}^{-1}$, $T = 745\text{K}$ and, from Eq. (1.9c), $\Delta n = (3 + 1) - (2) = 2$. Therefore,

$$K_p = \frac{0.1}{(0.0821 \times 745)^2} = 3 \times 10^{-5}$$

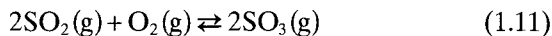
1.3 Reaction quotient

If the general chemical reaction represented by Eq. (1.5) is not in equilibrium, we can still formulate a ratio of concentrations that has the same form as Eq. (1.6). This is called the *reaction quotient*, Q

$$Q = \frac{[G]^g [H]^h \dots}{[A]^a [B]^b \dots} \quad (1.10)$$

Clearly, if $Q = K_c$, the reaction is in chemical equilibrium. If $Q < K_c$, the reaction is not in equilibrium, and it will proceed in the forward direction until $Q = K_c$. If $Q > K_c$, the reaction will proceed in the reverse direction until $Q = K_c$.

Exercise 1.5. If 0.80 mole of $\text{SO}_2(\text{g})$, 0.30 mole of $\text{O}_2(\text{g})$, and 1.4 mole of $\text{SO}_3(\text{g})$ simultaneously occupy a volume of 2L at 1000K, will the mixture be in equilibrium? If not, in what direction will it proceed to establish equilibrium? Consider only the species $\text{SO}_2(\text{g})$, $\text{O}_2(\text{g})$, and $\text{SO}_3(\text{g})$ in the reaction



with $K_c = 2.8 \times 10^2$.

Solution. The reaction quotient for Reaction (1.11) is

$$Q = \frac{[\text{SO}_3(\text{g})]^2}{[\text{SO}_2(\text{g})]^2 [\text{O}_2(\text{g})]}$$

To evaluate the initial value of Q we must determine their initial molarities. These are: for $\text{SO}_2 = 0.80/2 = 0.40\text{M}$, for $\text{O}_2 = 0.30/2 = 0.15\text{M}$, and for $\text{SO}_3 = 1.4/2 = 0.70\text{M}$.

Hence,

$$Q = \frac{(0.70)^2}{(0.40)^2 (0.15)} = 20$$

Since this value of Q is not equal to K_c (namely, 2.8×10^2), the initial mixture is not in equilibrium. Moreover, since $Q < K_c$, Reaction (1.11) will proceed in the forward direction.

Exercise 1.6. What are the equilibrium concentrations of $\text{SO}_2(\text{g})$, $\text{O}_2(\text{g})$, and $\text{SO}_3(\text{g})$ in Exercise 1.5?

Solution. If y moles (or $\frac{y}{2}\text{M}$) of $\text{SO}_3(\text{g})$ are formed, it follows from Reaction (1.11) that y moles (or $\frac{y}{2}\text{M}$) of $\text{SO}_2(\text{g})$ and $\frac{y}{2}$ moles (or $\frac{y}{4}\text{M}$) of $\text{O}_2(\text{g})$ disappear. If this change establishes chemical equilibrium we have