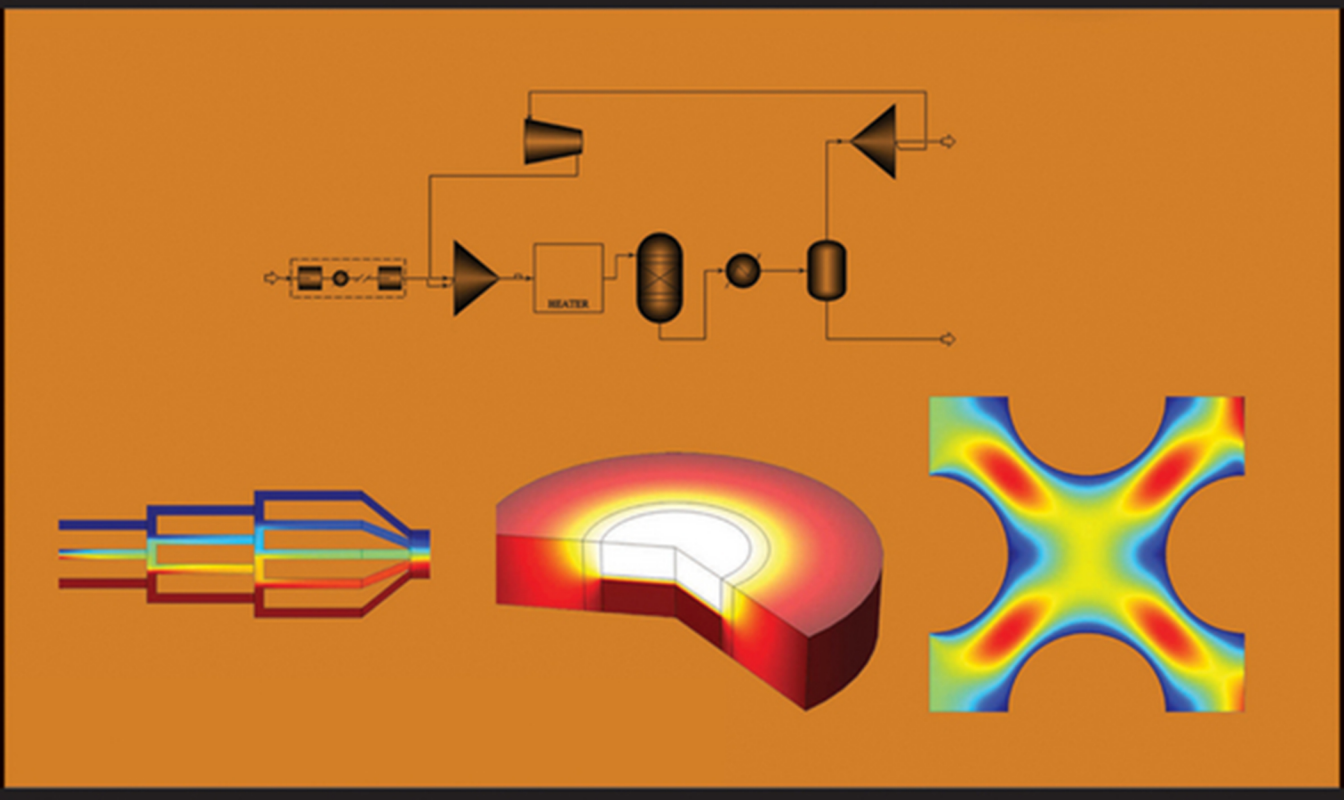
Second Edition

Introduction to Chemical Engineering Computing

UPDATED USING THE LATEST USER INTERFACE WITH ASPEN PLUS 8

Bruce A. Finlayson



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INTRODUCTION TO CHEMICAL ENGINEERING COMPUTING

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Second Edition

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Using the latest user interface with Aspen Plus 8.0

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PREFACE

Chemical engineering students and chemical engineers are being asked to solve problems that are increasingly complex, whether the applications are in refineries, fuel cells, microreactors, or pharmaceutical plants. Many years ago, students wrote their own programs, first in the FORTRAN programming language, then in languages such as MATLAB®. However, with the growth in personal computers, software has been written that solves many problems for students, provided they use the programs correctly. Thus, the emphasis shifted from a small group of people who were interested in writing their own programs to a large group of students who will use the programs, but do not write them. In my 42 years of teaching at the University of Washington, I taught those small groups of students how to use numerical analysis to solve complicated problems. Now, I teach *all* the students how to use the computer wisely. Only a few of the students I teach are interested in the numerical analysis (to my sorrow!), but all the students know they must be able to solve difficult problems, and they need to use the computer to do that.

The goals of this book are to illustrate (a) the problems chemical engineers have to solve, (b) the type of computer programs used to solve them, and (c) how engineers check to be sure they have solved the problems correctly. This is done in the context of how contemporary students learn—minimal reading, just-in-time learning, with lots of computer usage. The programs demonstrated here are Excel®, MATLAB®, Aspen Plus®, and Comsol Multiphysics®.

When writing this book, I assumed that readers are not absolute beginners. Junior and senior chemical engineering students have had experience with spreadsheet programs such as Excel, and they can easily learn on the computer when provided a direction and key ideas or phrases. In fact, many students are more computer-savvy than their instructors. However, a beginner chemical engineering student may not know the application very well and may not have gained a solid understanding of the physical phenomenon behind an engineering problem. Furthermore, they may not have solved very difficult problems. Thus, it is important to give some explanation of why students need to solve certain problems

and how to overcome the obstacles when the problems tax the numerical methods. I have drawn on my experience to give insights into the problems in this book.

My teaching philosophy is that the problems engineers are solving today are usually intractable with analytical methods, but they can be solved with the sophisticated software available today. Thus, every engineer will be solving a problem that no one knows the answer to, and it is the engineer's job to ensure that the problem is posed correctly on paper and in the computer, and it is correctly solved. Engineering students must know how to determine if the computer solved the problem correctly by validating the work done by the computer. If they can do this, they can convince their instructor—or their future boss—that they have a solution that is every bit as reliable as an analytical solution, although without the analytical form and for a problem that cannot be solved analytically. In fact, 98% of the problems in this book are nonlinear and only a few of them have analytical solutions.

HOW TO USE THIS BOOK IN TEACHING

This book grew out of a course I developed at the University of Washington, beginning in 2003. The course is part lecture and part hands-on computer work in a computer laboratory. I usually provide simple problems for the students to solve in the laboratory, when help is available, to help them get over the barrier of using an unfamiliar program. But then, students have to solve a problem that expands their knowledge of chemical engineering and demonstrates they have used the program correctly (and described the checks they made). Since the applications cover much of the chemical engineering field, I joke with the students, saying, "I'm teaching you the entire field in 20 hours." Although I retired from teaching the course in 2009, the same objectives still apply.

This book can also be used in other courses since each chapter is keyed to a course in the curriculum. Once chemical reaction equilibrium has been discussed in the Thermodynamics class, for example, instructors can hold a laboratory session that teaches computer applications, using the chapter on chemical reaction equilibrium. The material on choice of thermodynamic model (and comparisons) also adds a bit of realism to the Thermodynamics course. Other chapters could be used in other courses. In this way, the students would use the book during their entire education, in course after course: Mass and Energy Balances, Transport of Heat, Mass, and Momentum, Reactor Design, and courses concentrating on projects such as biomedical engineering. The hope is, of course, that students would then be able to concentrate more on the chemical engineering principles and use the computer as a tool.

There are four programs that are featured in this book. It is possible that your school does not use all four. Although the screen images may be different, the ideas and procedures are the same. Certainly the problems can be solved using other programs. In a working environment, engineers use what their company provides. Thus, engineers may use a less powerful program because it is available. The more powerful program may cost more, too. Thus, in several chapters, the same problem is solved using different programs, which lets students see first-hand that the more general purpose programs require significantly more programming to solve complicated problems. In my experience, when given a suite of programs, students will use the one that allows them to solve their problem fastest. The program Comsol Multiphysics comes in many modules. Nearly all the problems in this book can be solved by the basic module, although there are cases where the Chemical Reaction Engineering Module is useful. Connections with MATLAB are made with LiveLink™

for MATLAB, another module. There are only a couple of problems involving turbulent flow, and those require the CFD module. A complete list of what you get with various combinations is available from Comsol and my list is on the book website (see Appendix D).

Each chapter begins with a list of instructional objectives. In addition, the book website has a list of principles learned from each problem, both from a chemical engineering viewpoint and a computer/computer technique viewpoint. Professors that use the book are encouraged to discuss possible use in other chemical engineering courses so that more advanced problems can be solved in them, too. The indices are available on the book website, too, since students prefer using the Internet rather than turning to the back of the book; more importantly, they can be downloaded and searched for a phrase.

WHAT IS NEW?

One big change from the first edition is the fact that all four programs now have different interfaces than they did in 2005. More importantly, they have greatly enhanced capabilities. I have cut back on some explanations and refer the user to the help menus that come with the programs, since those have improved, too, and they give more information than the book can. But, I provide hints where to look.

The number of problems has approximately doubled. More importantly, the added problems are concentrated in the field of energy: integrated gas-combined cycle, including low temperature air separation, making ethanol from switchgrass, and pressure swing adsorption to make hydrogen to fuel cars. In each case a discussion of the field precedes the definition of the problem so that students can see the applicability. Microfluidics has expanded since 2005, and there are added problems in the field of biomedical applications. This has lead to many more examples and problems involving fluid flow and diffusion in two and three dimensions. An important addition was made in Aspen Plus 7.3: now you have direct access within the program to experimental data on pressure–volume–temperature of pure components and binary vapor–liquid equilibria as summarized by the National Institute of Standards and Technology. This is very important for chemical engineers, since the choice of thermodynamic model must usually be accompanied by a comparison with experimental data, and that is now made very easy—so easy that it would be unprofessional not to do the comparison. Thus, the thermodynamic sections of the book include industrial guidelines, some molecular considerations, and experimental data for comparison. Aspen Plus also has the capability to easily summarize the greenhouse impact of a process. There are talks made by professors about how they used AspenTech products in their courses; contact: University.Program@aspentech.com. One thing that is pointed out by Professor Luyben is that material and energy balances are primarily flow-based, whereas safety problems must be pressure based (and dynamic). The dynamic options are not treated here in detail, but are often covered in a control course. Aspen Plus runs under Microsoft Windows, but the author ran it under Windows by using Parallels Desktop for Mac on an Apple computer. The second edition also has examples running Aspen Plus with a simple user-defined FORTRAN program. The book uses Aspen Plus 8.0.

Some professors like to have more numerical programming in their courses, so a number of problems like that have been added to the end of many chapters. They make a good contrast—solve them using the numerical programming and then solve them using one of the four programs emphasized here to compare the ease of use of each method. Appendix E provides more detail about the numerical methods. While the programs make the numerical

analysis easy to use, it is also important to recognize that most problems involve an approximation from continuous to discrete variables. A few problems in the book ask the students to do the actual numerical analysis (and compare with other programs). Instructors may say, "If you don't program the method, you haven't really understood the problem." I reply by pointing out that when a doctor prescribes an MRI, you do not say you would not do it until he/she explains how the magnetic field works in the machine, discusses hydrogen molecules flipping orientation, and describes how the imaging takes place. The doctor and technician know how to interpret the results and how to detect if the machine is not operating correctly; engineering students can do that, too.

The number of problems has been doubled, and they are organized into easy problems (subscript 1), harder problems (subscript 2), and problems that are suitable as projects, either for one student or for teams. Finally, more techniques that are in Comsol Multiphysics are explained.

The code used to solve the examples in the book is not provided on the book website, because the author believes that learning takes place when you try to duplicate the steps in the book. However, some material needed to start problems is on the book website, such as geometries for three dimensional flow/diffusion problems. Depending upon the memory of your computer, and what can be allocated to Comsol Multiphysics, some of the three dimensional problems may not be soluble on your computer. The book website is http://www.ChemEComp.com.

ACKNOWLEDGMENTS

In writing this book, I owe a great thanks to the students in my classes. Sometimes students taught me how to use an advanced technique, and their questions brought out the best of the programs. I had over 100 undergraduate research students work with me over the past decade, and the results of their work are available on my websites: http://faculty.washington.edu/finlayso/ and http://courses.washington.edu/microflo. The Department provided a challenge grant to write textbooks, funded by a gift in the memory of alumnus Maurice Richford, BS 1926. Without that challenge grant, the first edition would not have been written so it could not have been revised. My daughter, Christine Finlayson, improved my writing greatly by serving as a copy editor of the first edition, and the clarity is due to her work; any confusion left is my responsibility. I thank especially Professor Stanley Sandler, University of Delaware, for reviewing the revised treatment of thermodynamics—I learned a lot, too! The folks at Comsol and Aspen Tech have been very helpful since both Comsol Multiphysics and Aspen Plus have been improved over the past few years. Most of all, I thank my wife, Pat, for putting up with the long hours of work that such a project requires. She has always supported me and made sacrifices that enabled me to finish. And I was smart enough to take a few weeks off from this rewrite to celebrate our 50th wedding anniversary!

BRUCE FINLAYSON

Seattle, October, 2011

1

INTRODUCTION

Computers have revolutionized the way chemical engineers design and analyze processes, whether designing large units to make polyethylene or small microreactors used to detect biological agents. In fact, the engineering problems that many of you will study as undergraduates are similar in complexity to problems PhD students solved 30 or 40 years ago. Computer programs can now solve difficult problems in a fraction of the time it used to take. Nowadays, you no longer have to write your own software programs to use computers effectively. Computer programs can do the numerical calculations for you, but you will still need to understand how to apply these programs to specific engineering challenges.

The goal of this book is to help you practice better chemical engineering. Computers are valuable tools that enable progressive, far-reaching chemical engineering. Unfortunately, computers are not as basic as DVD players, where you insert a DVD, push a button, and get the same result every time. Sometimes computer programs do not work properly for the parameters you have given them. Thus, you must be careful to use them wisely.

This book will also

1. Illustrate the problems that you as chemical engineers may need to solve.
2. Compare the types of computer programs you can use and illustrate which ones are best for certain applications.
3. Describe how to check your work to ensure you have solved the problems correctly.

This book demonstrates four computer programs: Excel®, MATLAB®, Aspen Plus®, and Comsol Multiphysics®. You may have access to other programs created by other companies. While the exact details will not be the same, the steps you take will be similar.

Computer skills are invaluable, but as an engineer, you also need to understand the physical phenomena. Each chemical engineering application chapter starts with a

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description of the physical problem in general terms. Then those general terms are put into a mathematical context so the computer can represent them. Next, the chapter gives several examples in which such problems are solved, providing step-by-step instructions so you can follow along on your own computer. Sometimes, the same problem is solved using different programs so you can see the advantages of each program. Finally, the chapters give more complicated problems your instructor may use as homework problems.

Examples throughout this book demonstrate how to check your work and how to learn from the answers the computer gives you. When using computers, it is always important to know if the computer obtained the correct answer. If you follow this strategy you will have no trouble convincing your instructor—or your boss—that you have a solution every bit as reliable as an analytical solution for a problem that cannot be solved analytically:

1. Solve the problem
2. Validate your work
3. Understand how you reached that answer

ORGANIZATION

The book is organized into eleven chapters followed by five appendices as listed in Table 1.1. Each chapter treats a type of chemical engineering phenomenon, such as process simulation

TABLE 1.1 Computer Programs Used in Different Chapters

	Chapters	Excel	MATLAB	Aspen Plus	Comsol Multiphysics	Numerical Methods
1	Introduction					
2	Equations of state	√	√	√		√
3	Vapor–liquid equilibria	√	√	√		√
4	Chemical reaction equilibria	√	√	√		√
5	Mass balances with recycle streams	√		√		
6	Simulation of mass transfer equipment			√		
7	Process simulation			√		
8	Chemical reactors and initial value problems	√	√	√	√	√
9	Transport processes in 1D and boundary value problems	√	√	√	√	√
10	Navier–Stokes equation in 2D and 3D				√	
11	Convective diffusion equation in 2D and 3D and elliptic partial differential equations				√	√
A	Hints when using Excel	√				
B	Hints when using MATLAB		√			
C	Hints when using Aspen Plus			√		
D	Hints when using Comsol Multiphysics				√	
E	Mathematical methods	√	√	√	√	√

or convective diffusion. Four of the appendices give additional details about each computer program. The fifth appendix provides the nitty-gritty details of many of the numerical methods. An appendix on parameter estimation that was in the 1st edition is available on the book website.

As a modern chemical engineering student, many of you are computer-savvy. This book assumes that you are not a complete beginner, but have some experience with spreadsheet programs such as Excel. The chapters provide examples and step-by-step instructions for using the computer programs to solve chemical engineering problems. If needed, you can find more detailed information about the individual programs in the appendices.

Algebraic Equations

Chapters 2–5 deal with chemical engineering problems that are expressed as algebraic equations—usually sets of nonlinear equations, perhaps thousands of them to be solved together. In Chapter 2, you can study equations of state that are more complicated than the perfect gas law. This is especially important because the equation of state provides the thermodynamic basis for not only volume but also fugacity (phase equilibrium) and enthalpy (departure from ideal gas enthalpy). Chapter 3 covers vapor–liquid equilibrium, and Chapter 4 covers chemical reaction equilibrium. All these topics are combined in simple process simulation in Chapter 5. This means that you must solve many equations together. These four chapters make extensive use of programming languages in Excel and MATLAB as well as Aspen Plus.

Process Simulation

Chapter 6 provides an extensive discussion of the possible (and reasonable) choices of thermodynamic models, and how you check your choice. It then introduces mass transfer problems such as distillation and absorption and single units. Chapter 7 gives a more detailed look at process simulation, where the power of process simulators like Aspen Plus really is evident. These chapters make use of commercial codes that are run by inserting data into their custom-designed interface.

Differential Equations

Chapters 8–11 treat problems that are governed by differential equations. Chapter 8 gives methods to model chemical reactors. These are usually initial value problems, which are illustrated in Eq. (1.1):

$$u\frac{\mathrm{d}c}{\mathrm{d}z} = -kc^2, \quad c(z=0) = c_0 \tag{1.1}$$

Note that the dependent variable, c, is a function of only one independent variable, z, and that the initial value is specified. For reactors, you start at the inlet and integrate down the reactor using either Excel, MATLAB, Aspen Plus, or Comsol Multiphysics.

Chapter 9 then solves transport problems in one space dimension (1D) using Comsol Multiphysics. If you consider heat transfer through a slab, one side of the slab is kept at

one temperature, T_0, and the other side of the slab is maintained at another temperature, T_L. The governing equation is

$$k\frac{\mathrm{d}^2T}{\mathrm{d}x^2} = 0 \tag{1.2}$$

with boundary conditions

$$T(0) = T_0, \quad T(L) = T_L \tag{1.3}$$

The differential equation, (1.2), is an ordinary differential equation because there is only one independent variable, x. In this case, equations in one space dimension are boundary value problems, because the conditions are provided at two different locations. While it is also possible to solve this problem using Excel, it is much simpler to use Comsol Multiphysics or MATLAB since the numerical analysis will have been done for you. Transient heat transfer in one space dimension is governed by

$$\rho C_p\frac{\partial T}{\partial t} = k\frac{\partial^2 T}{\partial x^2} \tag{1.4}$$

and this problem can be solved using Comsol Multiphysics or MATLAB, too.

Chapters 10 and 11 use Comsol Multiphysics to solve fluid flow, heat transfer, and mass transfer problems in 2D and 3D. Here, again the power of the software program shows through. You get to solve real problems that go beyond the simple 1D cases in your textbook. Those 1D problems are good for learning the subject, but in real-life situations, complications often arise that can only be handled numerically. These problems are partial differential equations, because there are two or more independent variables (say x and y). For example, the Navier–Stokes equations in Cartesian geometry and two dimensions are

$$\begin{aligned}
\rho\left(\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y}\right) &= -\frac{\partial p}{\partial x} + \mu\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right)\\
\rho\left(\frac{\partial v}{\partial t} + u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y}\right) &= -\frac{\partial p}{\partial y} + \mu\left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2}\right)\\
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} &= 0
\end{aligned} \tag{1.5}$$

Appendices

If you need more background information while solving the problems in the book, consult the appendices. Appendices A–D discuss hints, examples, and step-by-step instructions for the four computer programs demonstrated in this book. You are encouraged to consult the appendices while looking at examples or solving problems using those programs—many of the details are summarized in the appendices. Appendix E illustrates the mathematical methods built into each computer program. While you will not usually need to program the methods, you may be curious about the mathematical analysis behind the programs. An appendix on parameter estimation using Excel or MATLAB is available on the book website.

Whether you tackle one chemical engineering problem or work chapter by chapter through the book, try to enjoy yourself. You and a classmate can sit down and work together—possibly on adjacent computers—to share insights and answer each others' questions. Remember, too: go back and forth from the application chapters to the computer program appendices; build up your knowledge bit by bit. Your reward is to be a better-trained engineer, be able to use your inherent creativity, and be able to compete in a fast-paced global environment. As you take other chemical engineering courses you can use the programs to solve more advanced problems that are not soluble using analytical methods. Ninety-eight percent of the problems in this book are nonlinear and few of them have analytical solutions.

Version 8.0 of Aspen Plus is different from 7.3, but mainly in the top menu items. Most of the windows are the same, once you get to them, and the nomenclature is somewhat different. Thus the book has been revised to use the new nomenclature and be consistent with Aspen Plus 8.0. The windows look different, but the information is the same, so that those haven't been changed except where necessary. Note that Aspen Plus 8.0 is used in the Aspen Suite 8.2.

2

EQUATIONS OF STATE

Solving equations of state (EOS) allows us to find the specific volume of a gaseous mixture of chemicals at a specified temperature and pressure. Without using equations of state, it would be virtually impossible to design a chemical plant. By knowing this specific volume, you can determine the size—and thus cost—of the plant, including the diameter of pipes, the horsepower of compressors and pumps, and the diameter of distillation towers and chemical reactors. Imagine how challenging it would be to design a plant without knowing this important information!

Determining the specific volume is the first step in calculating the enthalpy and vapor–liquid properties of mixtures. Calculating this enthalpy is especially important when making energy balances to reduce energy use and help the environment. In this chapter, we work only with the vapor phase, and the liquid phase is introduced in the next chapter.

To solve equations of state, you must solve algebraic equations as described in this chapter. The later chapters cover other topics governed by algebraic equations, such as phase equilibrium, chemical reaction equilibrium, and processes with recycle streams. This chapter introduces the ideal gas EOS, then describes how computer programs such as Excel®, MATLAB®, and Aspen Plus® use modified EOS to easily and accurately solve problems involving gaseous mixtures.

Step-by-step instructions will guide you in using each of these computer programs to determine the specific volume of gaseous mixtures. Practice problems are given at the end of the chapter. The lessons learned from this chapter are carried forward to other applications involving algebraic equations in Chapters 3–6 and 8. After completing this chapter, not only will you be able to solve algebraic equations but you will also be able to determine the size of the equipment in a chemical plant, certainly the size of those pieces of equipment containing gases.

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Instructional Objectives: After working through this chapter, you should have

1. Updated your skills using Excel.
2. Learned to use MATLAB for simple problems.
3. Learned to use Aspen Plus to perform thermodynamic calculations.
4. Learned to check your numerical work.
5. Reviewed and expanded your chemistry and chemical engineering knowledge of EOS.

EQUATIONS OF STATE—MATHEMATICAL FORMULATION

The ideal gas EOS, which relates the pressure, temperature, and specific volume, is a familiar equation:

$$pV = nRT \quad \text{or} \quad p\hat{v} = RT \text{ where } \hat{v} = \frac{V}{n} \tag{2.1}$$

The term p is the absolute pressure, V is the volume, n is the number of moles, R is the gas constant, and T is the absolute temperature. The units of R have to be appropriate for the units chosen for the other variables. This equation is quite adequate when the pressure is low (such as 1 atm). However, many chemical processes take place at very high pressure. For example, ammonia is made at pressures of 220 atm or more. Under these conditions, the ideal gas EOS may not be a valid representation of reality. In particular, the ideal gas, while it includes rotational and vibrational degrees of freedom, ignores intramolecular potential energy, which is important when the molecules are closer together at high pressure. The rule-of-thumb is that the ideal gas is a good approximation for pressures up to 10 atm, although this can change depending on the temperature.

Other equations of states have been developed, usually in conjunction with process simulators, to address chemical processes at high pressure. There are two key criteria: (1) the equation is able to represent the real p–V–T behavior and (2) the parameters must be easily found, including for mixtures. This last criterion is no small requirement. There are more than 25 million chemicals, leading to an infinite number of different mixtures. Obviously, you cannot look up the properties of all those mixtures on the Web.

The first generalization of the ideal gas law was the van der Waals EOS:

$$p = \frac{RT}{\hat{v} - b} - \frac{a}{\hat{v}^2} \tag{2.2}$$

In this equation, the "b" accounts for the excluded volume (a second molecule cannot use the same space already used by the first molecule), and the "a" accounts for the force of interaction between two molecules. This extension is just a first step, however, because it will not be a good approximation at extremely high pressures. The constants a and b are given in Table 2.1.

The Redlich–Kwong EOS (1949) is a modification of the van der Waals EOS:

$$p = \frac{RT}{\hat{v} - b} - \frac{a}{\hat{v}(\hat{v} + b)} \tag{2.3}$$

TABLE 2.1 Equations of State for Pure Components

Model	EOS	a	b	α	ω	Z_c
Ideal gas	$pV = nRT$					
van der Waal	$p = \dfrac{RT}{\hat{v} - b} - \dfrac{a}{\hat{v}^2}$	$a = 0.42188\left(\dfrac{R^2T_c^2}{p_c}\right)$	$b = 0.125\left(\dfrac{RT_c}{p_c}\right)$			0.375
Redlich–Kwong	$p = \dfrac{RT}{\hat{v} - b} - \dfrac{a}{\hat{v}\,(\hat{v} + b)}$	$a = 0.42748\left(\dfrac{R^2T_c^2}{p_c}\right)\alpha$	$b = 0.08664\left(\dfrac{RT_c}{p_c}\right)$	$\alpha = \dfrac{1}{T_r^{0.5}}$		0.333
RK–Soave	$p = \dfrac{RT}{\hat{v} - b} - \dfrac{a}{\hat{v}\,(\hat{v} + b)}$	$a = 0.42748\left(\dfrac{R^2T_c^2}{p_c}\right)\alpha$	$b = 0.08664\left(\dfrac{RT_c}{p_c}\right)$	$\alpha = \left[1 + m\left(1 - T_r^{0.5}\right)\right]^2$	$m = 0.480 + 1.574\omega - 0.176\omega^2$	0.333
Peng–Robinson	$p = \dfrac{RT}{\hat{v} - b} - \dfrac{a}{\hat{v}\,(\hat{v} + b) + b\,(\hat{v} - b)}$	$a = 0.45724\left(\dfrac{R^2T_c^2}{p_c}\right)\alpha$	$b = 0.07780\left(\dfrac{RT_c}{p_c}\right)$	$\alpha = \left[1 + m\left(1 - T_r^{0.5}\right)\right]^2$	$m = 0.37464 + 1.54226\omega - 0.26992\omega^2$	0.307

where equations for a and b are given in Table 2.1 in terms of the critical temperature and pressure and the reduced temperature, $T_r = T/T_c$. In these equations, T_c is the critical temperature (in absolute terms), p_c is the critical pressure, T_r is called the reduced temperature (the absolute temperature divided by the critical temperature). α is particular to the Redlich–Kwong EOS.

The Redlich–Kwong EOS was modified further by Soave to give the Redlich–Kwong–Soave EOS (Soave, 1972) (called RKS in Aspen Plus, see Table 2.1)[1], which is a common one in process simulators. The purpose of the modification was to account for situations in which the molecular structure was asymmetric by introducing the Pitzer acentric factor, ω, which is a tabulated quantity for many substances. Thus, the value of α can be computed for each chemical and reduced temperature.

The Peng–Robinson EOS (1976) is another variation appropriate for molecules that are asymmetric, and it is an important one that is used in later chapters to improve the simulation of vapor–liquid equilibria:

$$p = \frac{RT}{\hat{v} - b} - \frac{a}{\hat{v}(\hat{v} + b) + b(\hat{v} - b)} \tag{2.4}$$

One criterion that can be applied to the EOS is the value of the compressibility factor at the critical point. Experimental values range from 0.23 to 0.31 (Sandler, 2006). As Table 2.2 shows, the Peng–Robinson EOS is closest to satisfying this condition.

All these equations can be rearranged into a cubic function of specific volume. The form of the Redlich–Kwong and Redlich–Kwong–Soave EOS is

$$\hat{v}^3(p) - \hat{v}^2(RT) + \hat{v}(a - pb^2 - RTb) - ab = 0 \tag{2.5}$$

When the temperature and pressure of a gaseous mixture, and the parameters a and b are given, then to find the specific volume you would have to solve the cubic EOS for specific volume, $\hat{v}$. This represents one algebraic equation in one unknown, the specific volume. The Peng–Robinson EOS results in

$$\hat{v}^3(p) + \hat{v}^2(bp - RT) + \hat{v}(a - 3pb^2 - 2RTb) + (pb^3 + RTb^2 - ab) = 0 \tag{2.6}$$

For a pure component, the parameters a and b are determined from the critical temperature and critical pressure, and possibly the acentric factor. These are all tabulated quantities, and there are even correlations for them in terms of vapor pressure and normal boiling point, for example. For mixtures, it is necessary to combine the values of a and b for each component according to the composition of the gaseous mixture. Since the parameters a and b come about because of intramolecular potential energy, it can be justified that when species 1 is in a mixture with species 2, the molecule 1 will interact differently with molecule 2 than it does with another molecule 1. Furthermore, the interaction of molecule 1 with another molecule 1 will be the same as in a pure species (usually), and will be proportional to the mole fraction squared (i.e., the relative amount of both of them). Thus, an expected form of the mixing rule for a binary is (Koretsky, 2004)

$$a = y_1^2 a_1 + y_1 y_2 a_{12} + y_1 y_2 a_{21} + y_2^2 a_2 = y_1^2 a_1 + 2 y_1 y_2 a_{12} + y_2^2 a_2 \tag{2.7}$$

[1] Aspen Plus also has a Soave–RK equation, which differs slightly. In this text, they are used interchangeably.