

INTRODUCTORY CHEMICAL ENGINEERING THERMODYNAMICS



J. Richard Elliott
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What's New? Why another thermodynamics textbook? Read our Preface.

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View selected examples using computer programs.

View the subject index.

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Introductory Chemical Engineering Thermodynamics

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Brief Description and Outstanding Features

Introductory Chemical Engineering Thermodynamics is a textbook designed for *undergraduate* chemical engineering students. The text provides coverage of molecular concepts, energy and entropy balances, equations of state for thermodynamics property calculations, activity models. Programs are provided for HP and TI calculators, spreadsheets, and FORTRAN compilers (All PC platform). Computer programs are utilized in example problems. Practice problems are provided at the end of almost every chapter with the answers.

Overview

The format of the book matches conventional texts; introductory material is followed by examples, and each chapter ends with homework problems. Chapters are subdivided to permit instructors to select/omit special topics or more advanced material. There are several appendices of supporting material. Conversion factors and important balance equations are included in the front cover, and critical properties are included inside the back cover. We have attempted to keep the vocabulary to a minimum throughout the text, however a glossary is provided to help students review important terms, and interpret terms they may find used elsewhere. The text provides 131 examples for students to study -- on average, one example every 4.4 pages. We have marked the most important equations with text boxes, or clearly labeled their names to set them apart from the rest of the text. Margin notes are used throughout to highlight important concepts and named relations. Programs to complement the text are available on our website, and many examples are worked in the text using the programs.

Unit I (Topics are energy and entropy balances).

The text concentrates on the development of the energy balance and entropy balance as principle relations and develops their application using thermodynamic charts/tables or the ideal gas law. Equations based on assumptions of the ideal gas law or a temperature-independent heat capacity are clearly identified in the margins of the text. We develop the closed system and steady-state balances as a subset of the general energy balance. We provide sections on problem solving strategies for both energy and entropy balances. Our examples show reduction of the general energy balance, term by term, to arrive at the simplification required for the example problem. Unit I is discernible as generic engineering thermodynamics with tables and charts. One advantage of this approach is that some schools teach the generic engineering thermodynamics as a separate course. Our text can pick up where the other courses end. The spirit of Unit I is similar to that developed in Balzhiser's text ("Chemical Engineering Thermodynamics", R.E. Balzhiser, M.R. Samuels, J.D. Eliassen, Prentice-Hall, 1972) with respect to treatment of general energy and entropy balances and the molecular basis of entropy.

Unit II (Generalized analysis of fluid properties, behavior of real fluids, derivative properties, departure functions)

Methods for calculation of real fluid thermodynamic properties are introduced after students have gained confidence in application of the balances in Unit I. In the development of equations of state, Unit II begins by laying down the molecular perspective, then building the macroscopic equations with an emphasis on the important engineering tools of dimensional analysis, asymptotic approximation, parameter estimation, and model building. This methodical approach to model building is a common theme in all

modern engineering disciplines. The computer tools that students can use on exams as well as in homework reinforce the application of the derived models in a way that has not been possible previously.

To support this unit, we furnish calculator and spreadsheet programs for calculating entropy and enthalpy changes of ideal and real gases. We end Unit II by coverage of fugacity and phase equilibria in pure fluids calculated by equations of state.

Unit III (Phase equilibria in mixtures)

We introduce phase equilibria using ideal solutions and ideal gases. We then return to equations of state to apply them to phase equilibrium in mixtures, and closely parallel the development for pure fluids covered at the end of Unit II. We stress the relationship between the fugacity coefficient and departure functions developed in Unit II. In this way, Unit III builds on the conceptual foundation and methodology of Unit II. By keeping the conceptual framework tightly in step with that of Unit II, students can focus on the relatively large number of practical issues that arise from the fundamental extension of thermodynamic principles to binary and multicomponent systems. Our approach focuses on the equation of state approach more than previous undergraduate texts, but other model equations are shown to be simplified, approximate deductions from the equation of state, rather than a smorgasbord of models with little basis for distinguishing between them. In this way, our presentation maintains conciseness without sacrificing depth of understanding. We provide calculator, spreadsheet and compiled FORTRAN programs for calculations of phase equilibria.

In discussion of non-ideal mixtures, we introduce activity coefficients, and discuss azeotropes. We provide a comprehensive treatment of solution models, and provide discussion as to their relationships to each other. Practical illustrations include water contamination with hydrocarbons, polymer blending/recycling, oxygenated fuels, and the traditional issues related to distillation. We provide spreadsheets for calculation of phase equilibria, and for fitting of activity coefficient parameters. Our discussion of high pressure phase behavior is more complete than any other undergraduate text.

Unit IV (Reacting Systems)

Our book differs from other texts by providing integration of spreadsheets for the calculation of chemical reaction equilibria. We also introduce equations of state for hydrogen bonding systems, a topic that would probably not be covered in most undergraduate courses today, but will become important in the future.

Level

The text is directed to sophomore or junior chemical engineering students. It also is comprehensive enough that it could be used for self study, but the majority of purchases are expected to be for class usage. The textbook level is at an introductory/intermediate level with a mixture of drill-oriented problems and advanced concepts. We have used it for part of our graduate courses as well as the introductory sophomore/junior course. Most students will have completed an introductory material and energy balance course before using the text but review of linear interpolation is included. Students should have also completed multivariable calculus to permit integration and partial differentiation.

PREFACE

“No happy phrase of ours is ever quite original with us; there is nothing of our own in it except some slight change born of our temperament, character, environment, teachings and associations.”

Mark Twain

Thank you for your interest in our book. We have developed this book to address ongoing evolutions in applied thermodynamics and computer technology. Molecular perspective is becoming more important in the refinement of thermodynamic models for fluid properties and phase behavior. Molecular simulation is increasingly used for exploring and improving fluid models. While many of these techniques are still outside the scope of this text, these new technologies will be important to practicing engineers in the near future, and an introduction to the molecular perspective is important for this reason. We expect our text to continue to evolve with the chemical engineering field.

Computer technology has made process simulators commonplace in most undergraduate curriculums and professional work environments. This increase in computational flexibility has moved many of the process calculations from mainframe computers and thermodynamic property experts to the desktop and practicing engineers and students. This increase in computational ability also increases the responsibility of the individuals developing process simulations to choose meaningful models for the components in the system because most simulators provide even more options for thermodynamic models than we can cover in this text. We have included background and comparison on many of the popular thermodynamic models to address this issue.

Computational advances are also affecting education. Thus we have significant usage of equations of state throughout the text. We find these computational tools remove much of the drudgery of repetitive calculations, which permits more class time to be spent on the development of theories, molecular perspective, and comparisons of alternative models. We have included FORTRAN, Excel spreadsheets, TI85, and HP48 calculator programs to complement the text. The programs are summarized in the appendices.

- (a) Solutions to cubic equations of state are no longer tedious with the handheld calculators available today for about \$100. We provide programs for calculation of thermodynamic properties via the Peng-Robinson equation, vapor pressure programs, Peng-Robinson K -ratios and bubble pressures of mixtures, and van Laar and UNIFAC activity coefficients as well as several other utility programs. Our choice of the HP48 calculator is due to its being one of the first to provide a computer interface for downloading programs from a PC and provide calculator-to-calculator communication, which facilitates distribution of the programs. If all students in the class have access to these engineering calculators, as practiced at the University of Akron, questions on exams can be designed to apply to these programs directly. This obviates the need for traditional methods of reading charts for departure functions and K -ratios and enables treatment of modern methods like equations of state and UNIFAC.
- (b) Spreadsheets have also improved to the point that they are powerful tools for solving engineering problems. We have chosen to develop spreadsheets for Microsoft[®] Excel because of the widespread availability. Certainly Mathcad[®], Mathematica[®], and other software could be used, but none has the widespread availability of spreadsheets. We have found the solver within Excel to provide a good tool for solving a wide variety of problems. We provide spreadsheets for thermodynamic properties, phase and reaction equilibria.
- (c) High-level programming is still necessary for more advanced topics. For these applications, we provide compiled programs for thermodynamic properties and phase behavior. For an associating system, such as an alcohol, we provide the ESD equation of state. These programs are menu-driven and do not require knowledge of a computer language.

In a limited number of instances, we provide FORTRAN source code. We provide FORTRAN code because of our own abilities to program faster in FORTRAN, although other languages are finding increasing popularity in the engineering community. We have tried to avoid customization of the code for a specific FORTRAN compiler, which improves portability to other operating platforms but also limits the “bells and whistles” that a specific interface could provide. These programs provide a framework for students and practicing engineers to customize for their own applications.

Energy and entropy balances are at the heart of process engineering calculations. We develop these approaches first using the ideal gas law or thermodynamic tables, then revisit the topics after developing equation-of-state techniques for thermodynamic properties. We are well aware of the concern that students often apply the ideal gas law inappropriately. Therefore we clearly mark equations using the ideal gas law or assuming a temperature-independent heat capacity. From a pedagogical standpoint, we are faced with the issues of developing first and second law balances, equations of state (and their departure functions) for fluid properties, and then combining the principles. We have found it best that students quickly develop ability and confidence in application of the balances with simple calculational procedures before introducing the equation of state. The balance concepts are typically more easily grasped and are essential for extension to later courses in the curriculum. Another benefit of this approach is that the later development of the equation of state can be directly followed by departure functions, and the reasons for needing properties such as enthalpy and entropy are well understood from the earlier emphasis on the balances. This enables students to focus on the development of the departure functions without being distracted by not completely understanding how these properties will be used.





Fugacity is another property which is difficult to understand. We have tried to focus on the need for a property which is a natural function of T and P , and also stress how it is related to departure

functions. There are many ways to calculate fugacities (which provides many trees to block the view of the forest), and we have tried to provide tables and diagrams to show the inter-relations between fugacity coefficients, activity coefficients, ideal gases, ideal solutions, and real solutions.

A distinct feature of this text is its emphasis on molecular physics at the introductory level. Our perspective is that this background must be made available to students in an integrated manner, but it is up to instructors to decide the level of emphasis for the entire spectrum of their students. We have organized this material such that it may be covered as a supplementary reading assignment or as a homework and test assignment. With the latter emphasis, it is possible to formulate a graduate course based on this text.

Throughout the text, we have used text boxes to highlight important statements and equations. Boxed equations are not always final results of derivations. In some cases, the boxes highlight mathematical definitions of important intermediate results that might be useful for homework problems.

We consider the examples to be an integral part of the text, and we use them to illustrate important points. In some cases, derivations and important equations are within an example because the equations are model-specific (e.g., ideal gas). Examples are often cross-referenced and are therefore listed in the table of contents.

There are many marginal notes throughout the text. Where you find a , it means that an important point is made, or a useful equation has been introduced. Where you find a  or , it means that a calculator program is available to assist in calculations. The calculator programs are sometimes not necessary, but extremely helpful. Where you find a , it means that an Excel spreadsheet or a compiled program is available. In some cases, the program is simply convenient, but typically you will find that these calculations are tedious without the program. For calculator or PC icons, the program names are given by the icons. See the computer appendix or the readme files for specific program instructions.

We periodically update computer software and the computer appendix. The latest software is available from our website <http://www.egr.msu.edu/~lira/thermtxt.htm>. We hope you find our approaches helpful in your learning and educational endeavors. We welcome your suggestions for further improvements and enhancements. You may contact us easily at the email addresses below. Unfortunately, we will be unable to personally respond to all comments, although we will try.

NOTES TO STUDENTS

Computer programs facilitate the solution to homework problems, but should not be used to replace an understanding of the material. Always understand exactly which formulas are required before turning to the computer. Before using the computer, we recommend that you know how to solve the problem by hand calculations. If you do not understand the formulas in the spreadsheets it is a good indication that you need to do more studying before using the program so that the structure of the spreadsheet will make sense. When you understand the procedures, it should be obvious which spreadsheet cells will help you to the answer, and which cells are intermediate calculations. It is also helpful to rework example problems from the text using the software.

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1.1 EXAMPLE PROBLEMS

The following examples have been taken from the book to demonstrate the use of spreadsheets and fortran programs. Note that *no effort has been taken to include cross references to original pages* that are not included in these extracted examples. .

Example 1.1 Solution of the Peng-Robinson equation for molar volume

Find the molar volume predicted by the Peng-Robinson equation of state for argon at 105.6 K and 4.98 bar.

Solution: Use PREOS.xls. The critical data are entered from the table on the endflap of the text. The spreadsheet is shown in Fig. 6.6. The answers are given for the three-root region, whereas the cells for the one-root region are labeled #NUM! by EXCEL. This means that we are in the three-root region at these conditions of temperature and pressure. Many of the intermediate calculations are also illustrated in case you want to write your own program some day. The answers are 27.8, 134, and 1581 cm³/mole. The lower value corresponds to the liquid volume and the upper value corresponds to the vapor.

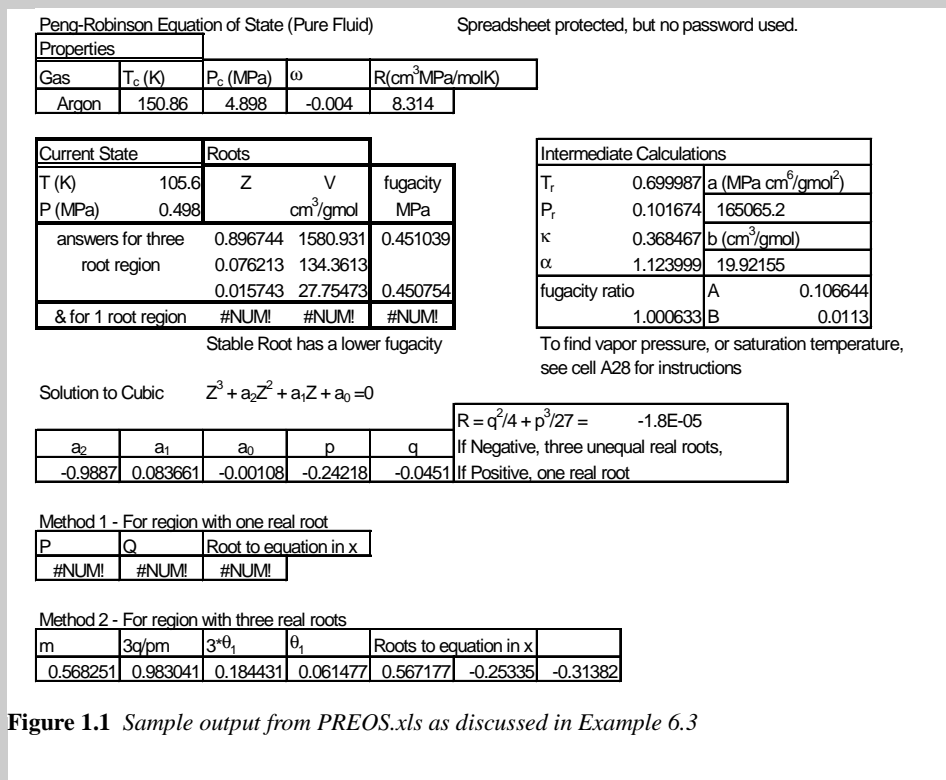


Figure 1.1 Sample output from PREOS.xls as discussed in Example 6.3

HP UHSG (See PrI)
 PREOS.xls,
 PRPURE.

Example 1.2 Liquefaction revisited

Reevaluate the liquefaction of methane considered in Example 4.6 on page 155 utilizing the Peng-Robinson equation. Previously the methane chart was used. Natural gas, assumed here to be pure methane, is liquefied in a simple Linde process. Compression is to 60 bar, and precooling is to 300 K. The separator is maintained at a pressure of 1.013 bar and unliquefied gas at this pressure leaves the heat exchanger at 295 K. What fraction of the methane entering the heat exchanger is liquefied in the process?

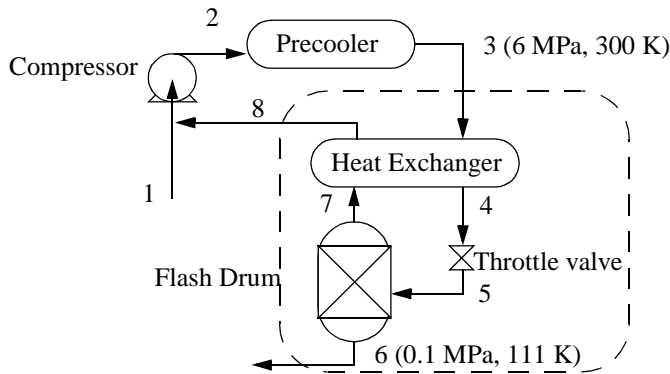


Figure 1.2 Linde liquefaction schematic.

Solution: The solution is easily obtained by using PREOS.xls. When running PREOS, we must specify the temperature of the flash drum which is operating at the saturation temperature at 1.013 bar. This is specified as the boiling temperature for now (111 K).¹

Before we calculate the enthalpies of the streams, a reference state must be chosen. A convenient choice is the enthalpy of the inlet stream (Stream 3, 6 MPa and 300 K). The results of the calculations from PREOS are summarized in Fig. 1.3.

State 8							
Current State		Roots		Stable Root has a lower fugacity			
T (K)	295	Z	V	fugacity	H	U	S
P (MPa)	0.1013		cm ³ /gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.9976741	24156.108	0.101064	883.5669	-1563.45	35.86805
State 6							
Current State		Roots		Stable Root has a lower fugacity			
T (K)	111	Z	V	fugacity	H	U	S
P (MPa)	0.1013		cm ³ /gmol	MPa	J/mol	J/mol	J/molK
answers for three root region		0.9666276	8806.4005	0.09802	-4736.62	-5628.7	6.758321
		0.0267407	243.61908		-6972.95	-6997.63	-26.6614
		0.0036925	33.640222	0.093712	-12954.3	-12957.7	-66.9014

Figure 1.3 Summary of enthalpy calculations for methane as taken from the file PREOS.xls.

Example 1.2 Liquefaction revisited (Continued)

The fraction liquefied is calculated by the energy balance:

$$m_3 H_3 = m_8 H_8 + m_6 H_6; \text{ then incorporating the mass balance: } H_3 = (1 - m_6/m_3)H_8 + (m_6/m_3)H_6$$

Fraction liquefied = $m_6/m_3 = (H_3 - H_8)/(H_6 - H_8) = (0 - 883)/(-12,954 - 883) = 0.064$, or 6.4% liquefied. This is in good agreement with the value obtained in Example 4.6 on page 155.

Example 1.3 Phase diagram for azeotropic methanol + benzene


Methanol and benzene form an azeotrope. For methanol + benzene the azeotrope occurs at 61.4 mole% methanol and 58°C at atmospheric pressure (1.01325 bars). Additional data for this system are available in the *Chemical Engineers' Handbook*.¹ Use the Peng-Robinson equation with $k_{ij} = 0$ (see Eqn. 10.10) to estimate the phase diagram for this system and compare it to the experimental data on a T - x - y diagram. Determine a better estimate for k_{ij} by iterating on the value until the bubble point pressure matches the experimental value (1.013 bar) at the azeotropic composition and temperature. Plot these results on the T - x - y diagram as well. Note that it is impossible to match both the azeotropic composition and pressure with the Peng-Robinson equation because of the limitations of the single parameter, k_{ij} .


The experimental data for this system are as follows:

x_m	0.000	0.026	0.050	0.088	0.164	0.333	0.549	0.699	0.782	0.898	0.973	1.000
y_m	0.000	0.267	0.371	0.457	0.526	0.559	0.595	0.633	0.665	0.760	0.907	1.000
$T(K)$	353.25	343.82	339.59	336.02	333.35	331.79	331.17	331.25	331.62	333.05	335.85	337.85

Solution: Solving this problem is computationally intensive enough to write a general program for solving for bubble-point pressure. Fortunately, computer and calculator programs are readily available. We will discuss the solution using the PC program PRMIX.EXE. Select the option KI for adjusting the interaction parameter. This routine will perform a bubble calculation for a guessed value of k_{ij} . When prompted, enter the temperature (331.15 K) and liquid composition $x_m = 0.614$. The program will give a calculated pressure and vapor phase composition. The vapor-phase composition will not match the liquid-phase composition because the azeotrope is not perfectly predicted; however, we continue to change k_{ij} until we match the pressure of 1.013 bar. The following values are obtained for the bubble pressure at the experimental azeotropic composition and temperature with various values of k_{ij} .

k_{ij}	0.0	0.1	0.076	0.084
$P(\text{bars})$	0.75	1.06	0.9869	1.011

 PRMIX offers bubble pressure.

 PRMIX offers option KI for iterating on a single point.

Example 1.3 Phase diagram for azeotropic methanol + benzene (Continued)

The resulting k_{ij} is used to perform bubble temperature calculations across the composition range resulting in Fig. 1.4. Note that we might find a way to fit the data more accurately than the method given here, but any improvements would be small relative to the improvement obtained by not estimating $k_{ij} = 0$. We see that the fit is not as good as we would like for process design calculations. This solution is so non-ideal that a more flexible model of the thermodynamics is necessary. Note that the binary interaction parameter alters the magnitude of the bubble pressure curve very effectively but hardly affects the skewness at all.

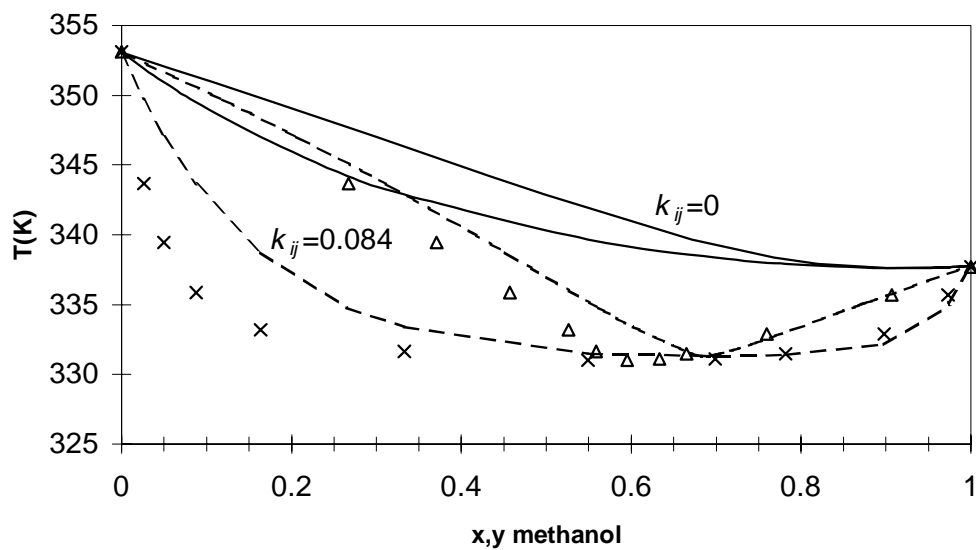




Figure 1.4 T - x,y diagram for the azeotropic system methanol + benzene. Curves show the predictions of the Peng-Robinson equation ($k_{ij} = 0$) and correlation ($k_{ij} = 0.084$) based on fitting a single data point at the azeotrope. x 's and triangles represent liquid and vapor phases, respectively.

Example 1.4 Phase diagram for nitrogen + methane

Use the Peng-Robinson equation ($k_{ij} = 0$) to determine the phase diagram of nitrogen + methane at 150 K. Plot P versus x , y and compare the results to the results from the shortcut K -ratio equations.

 PRMIX offers bubble pressure.

 PRMIX offers other routines as well.

Example 1.4 Phase diagram for nitrogen + methane (Continued)

Solution: First, the shortcut K -ratio method gives the dotted phase diagram on Fig. 1.5. Applying the bubble pressure option of the program PRMIX on the PC or the HP, we calculate the solid line on Fig. 1.5. For the Peng-Robinson method we assume K -values from the previous solution as the initial guess to get the solutions near $x_{N_2} = 0.685$. The program PRMIX assumes this automatically, but we must also be careful to make small changes in the liquid composition as we approach the critical region. The figure below was generated by entering liquid nitrogen compositions of: 0.10, 0.20, 0.40, 0.60, 0.61, 0.62..., 0.68, 0.685. This procedure of starting in a region where a simple approximation is reliable and systematically moving to more difficult regions using previous results is often necessary and should become a familiar trick in your accumulated expertise on phase equilibria in mixtures. We apply a similar approach in estimating the phase diagrams in liquid-liquid mixtures.

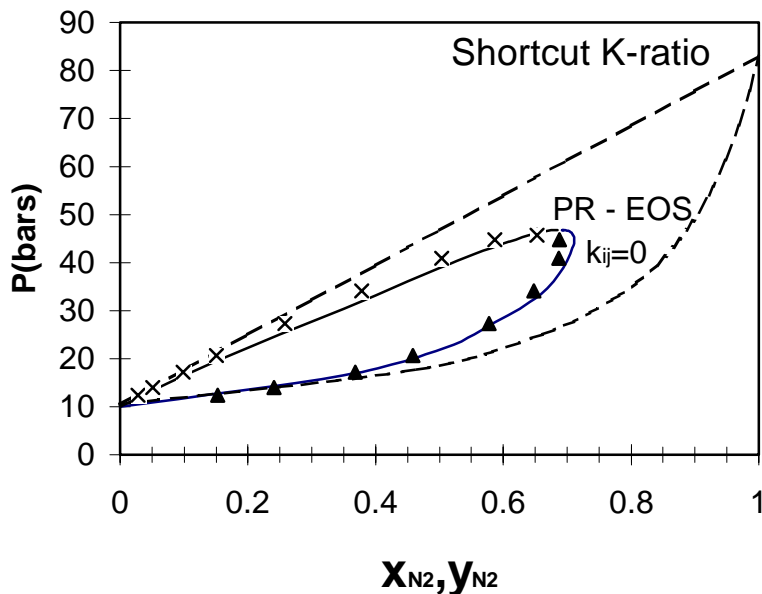


Figure 1.5 High pressure P - x - y diagram for the nitrogen + methane system comparing the shortcut K -ratio approximation and the Peng-Robinson equation at 150 K. The data points represent experimental results. Both theories are entirely predictive since the Peng-Robinson equation assumes that $k_{ij} = 0$.

⚠ The shortcut K -ratio method provides an initial estimate when a supercritical component is at low liquid-phase compositions, but incorrectly predicts VLE at high liquid-phase concentrations of the supercritical component.

Example 1.4 Phase diagram for nitrogen + methane (Continued)

Comparing the two approximations numerically and graphically, it is clear that the shortcut approximation is significantly less accurate than the Peng-Robinson equation at high concentrations of the supercritical component. This happens because the mixture possesses a critical point, above which separate liquid and vapor roots are impossible, analogous to the situation for pure fluids. Since the mixing rules are in terms of a and b instead of T_c and P_c , the equation of state is generating effective values for A_c and B_c of the mixture. Instead of depending simply on T and P as they did for pure fluids, however, A_c and B_c also depend on composition. The mixture critical point varies from the critical point of one component to the other as the composition changes. Since the shortcut approximation extrapolates the vapor pressure curve to obtain an effective vapor pressure of the supercritical component, that approximation does not reflect the presence of the mixture critical point and this leads to significant errors as the mixture becomes rich in the supercritical component.

The mixture critical point also leads to computational difficulties. If the composition is excessively rich in the supercritical component, the equation of state calculations will obtain the same solution for the vapor root as for the liquid root and, since the fugacities will be equal, the program will terminate. The program may indicate accurate convergence in this case due to some slight inaccuracies that are unavoidable in the critical region. Or the program may diverge. It is often up to the competent engineer to recognize the difference between accurate convergence and a spurious answer. Plotting the phase envelope is an excellent way to stay out of trouble. Note that the mole fraction in the vapor phase is equal to the mole fraction in the liquid phase at P_{max} . What are the similarities and differences between this and an azeotrope?

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