This electronic CinChE manual is a condensed version of your purchased CinChE manual. It contains mostly those pages that have popup notes and/or web links. Use the bookmarks to the left to go to a specific page.

Since the "**E-Z Solve**" software referenced in this manual is no longer supported, click here to learn how to replace it with an Excel macro called "**EZ Setup**".

Companion in Chemical Engineering

An Instructional Supplement

Michael E. Hanyak, Jr.

Department of Chemical Engineering
Bucknell University
Lewisburg, PA 17837

This electronic CinChE manual is a condensed version of your purchased CinChE manual. It contains mostly those pages that have popup notes and/or web links. Use the bookmarks to the left to go to a specific page.

Dr. Michael E. Hanyak, Jr., Publisher
Chemical Engineering Department
Bucknell University
Lewisburg, PA 17837

Email: hanyak@bucknell.edu

About the Author

Michael E. Hanyak, Jr. is Professor Emeritus of Chemical Engineering at Bucknell University in Lewisburg, PA. He received his B.S. from The Pennsylvania State University in 1966, M.S. from Carnegie Mellon in 1968, and his Ph.D. in Chemical Engineering from the University of Pennsylvania in 1976. From 1967-1970, he worked as a senior chemical engineer at Air Products, Inc. in Allentown, PA, where he developed process simulation software for cryogenic systems. He served as Professor of Chemical Engineering at Bucknell University from 1974 to 2010.

His teaching and research interests included computer-aided engineering and design, instructional design, pedagogical software tools, and the electronic classroom. With undergraduate and M.S. graduate students, he has developed a thermodynamic software system (BUTS), a linear equation system solver (BLESS), a formative assessment system for teamwork (TEAM 360), and an electronic learning system for engineering problem solving (eLEAPS), of which the last three are an integral part of the freshman introductory course and senior design course in Bucknell's curriculum for chemical engineering majors. His two manuscripts—*Companion in Chemical Engineering* (*CinChE): An Instructional Supplement* and *Chemical Process Simulation and the AspenTech HYSYS Software*— support a team-oriented and problem-based-learning environment for the introductory course in chemical engineering. The *CinChE* manual presents a novel application of a problem solving strategy that enhances students' higher-order thinking skills of analysis, synthesis, and evaluation. The HYSYS manual is a self-paced instructional document that teaches students how to use effectively a process simulator.

With grants from the Air Products Foundation, the General Electric Fund, and the National Science Foundation, Professor Hanyak provided leadership with groups of engineering faculty in pioneering the electronic classroom and active learning in the chemical engineering department and the engineering college at Bucknell University. As an outreach since 2003, he and his colleagues have annually presented summer workshops at Bucknell Univeristy on active learning, cooperative learning, and problem-based learning to nearly 300 engineering faculty from the U.S. and abroad.

In 1983, Professor Hanyak served on the original committee that formulated the Writing Program at Bucknell University. He has integrated teamwork, writing, oral communication, and professionalism in the freshman course on stoichiometry, the junior unit operations laboratory, and the two senior design courses, using a fictitious consultant company, the Bison Engineering and Evaluation Firm (BEEF, Inc.). He has authored two BEEF company handbooks to support this integration.

As department chairman from 1998-2002, Professor Hanyak supervised the migration to the first outcome-based format for the successful ABET accreditation in 2002, automated the course scheduling process, and spearheaded the electronic assessment of courses in the Chemical Engineering Department. For his love of teaching and non-traditional research in support of that teaching, he received the Lindback Award for Distinguished Teaching from Bucknell University in 2002. He has been a member of the American Institute of Chemical Engineers and the American Society for Engineering Education (ASEE). He is the recipient of the 2011 CACHE Award given by the Chemical Engineering Division of ASEE for significant contributions in the development of computer aids for chemical engineering education.

Preface

A **C**ompanion **in Ch**emical **E**ngineering (*CinChE*) is designed to aid you in the development of your critical thinking skills as an engineering problem solver. Note that your weekly time management will be an important factor in developing those skills. Your feedback is welcomed in order to improve the next version of this instructional companion. Please direct your feedback to the email address hanyak@bucknell.edu.

The creative problem-solving methodology emphasized in *CinChE* provides a general framework in which to solve any type of well-defined engineering problem involving material balances, phase equilibria, and energy balances. It is a systems strategy that heavily uses the mental processes of decomposition, chunking, and pattern matching, and it is specifically designed to enhance students' higher-order thinking skills of analysis, synthesis, and evaluation. The *CinChE* methodology is more systematic than the problem-solving strategies found in most textbooks for the introductory course on chemical engineering, like *Elementary Principles of Chemical Processes* [Felder and Rousseau, 2005], *Basic Principles and Calculations in Chemical Engineering* [Himmelblau and Riggs, 2004], or *Introduction to Chemical Processes: Principles, Analysis, Synthesis* [Murphy, 2007]. Therefore, we will use the *CinChE* methodology presented in this document, and **not the one** emphasized by your textbook. Your textbook will be used primarily for reading assignments, homework problems, physical property information, and thermodynamic data.

Many of the example problems presented in the *CinChE* manual are similar to ones found in the Felder and Rousseau textbook [2005], but their solutions are based on the problem-solving methodology emphasized in this *CinChE* manual. Because *CinChE* was compiled using the Adobe Acrobat® system for document processing, it contains many popup notes and web links. In the Acrobat Reader® version of this manual (the .pdf file), you can view the popup notes and access the web links that appear in many of the graphic organizers and example problems of the paper copy. You are encouraged to view electronically the ".pdf" version while you read the paper copy of this manual. Type the following web link to access it:

http://www.departments.bucknell.edu/chem_eng/cheg200/CinChE_Manual/a_whiteCinChE.pdf

The popup notes provide valuable information to help clarify the content within a graphic organizer or an example problem. The web links access text files, E-Z Solve files, Excel® files, Aspen HYSYS® files, and ".pdf" files. You can view but not copy or print the ".pdf" version of this *CinChE* manual. Errata for this version of the *CinChE* manual are available at the following web link:

http://www.departments.bucknell.edu/chem_eng/cheg200/CinChE_Manual/a_errataCinChE.pdf

If you are having difficulty downloading E-Z Solve files (.msp) from web links in the electronic *CinChE* manual while using the Internet Explorer® web browser, please consult the "errata" link for a possible solution. Downloading the E-Z Solve files using Firefox® or Safari® should work smoothly.

The *CinChE* manual contains seven chapters. Chapter 1 presents a lengthy but important discussion of the problem-solving methodology, using a simple example based on the concept of weight. Chapter 2 provides a general overview for chemical processes, force and pressure, material balances, phase equilibria, and energy balances. These important concepts serve as the first principles upon which to solve chemical engineering problems. Chapter 3 presents a graphical organizer called Table "gotche" that lists about forty fundamental quantities in chemical engineering, their symbols, their units, their basic relationships, and their conversion equivalences. Also, overviews for pressure-temperature diagrams, pressure-volume-temperature diagrams, pressure-enthalpy diagrams, and equations of state are presented. Chapter 4 describes the important strategies for the six steps in the problem-solving methodology that produce a conceptual model, a mathematical model, a mathematical algorithm, a numerical solution, the heuristic observations, and the formal documentation for the solution to a problem. Chapter 5 presents the general equations for the mass and mole balances around a system boundary. Furthermore, it provides graphical organizers and example problems for continuous, batch, semi-batch, and semi-continuous process units that illustrate the application of the problem-solving methodology from Chapter 4. Chapter 6 presents the general equations for rigorous vapor-liquid equilibrium, Raoult's Law, Henry's Law, and environmental equilibria. Also, graphical organizers and example problems are provided to use the concepts of phase equilibria and to illustrate the application of the problem-solving methodology from Chapter 4. Chapter 7 presents the two general forms of the energy balance—the heat-of-formation method and the heat-of-reaction method. Also, graphical organizers and example problems are provided to use the energy balances and to illustrate the application of the problem-solving methodology from Chapter 4.

The *CinChE* manual also contains seven appendices in support of the seven chapters. Appendix A presents detailed descriptions for the fundamental quantities in Table "gotche" of Chapter 3. Appendix B provides an overview of the methods and techniques used in units conversion. Appendix C reviews the fundamentals of algebraic equations, transcendental equations, and summation notation that are pertinent to this introductory course on chemical engineering. Appendix D shows the equation derivations for molecular weight, composition, specific volume, and specific gravity of non-reacting mixtures. Appendix E presents the documented solutions for six problems that use the problem-solving methodology from Chapter 4. The first five problems in Appendix E could be used as the first problem set in the introductory course on chemical engineering. Appendix F is an essay on the enthalpy reference states and why they are arbitrary. Appendix G contains the bibliography for the preface, seven chapters, and seven appendices. Some of the important web links that appeared in the chapters are also provided in the bibliography.

During the 1980's, a paradigm shift started to take place from the traditional lecture-based deductive approach in the classroom (i.e., sage on the stage) to the student-centered inductive approach (i.e., coach on the side) that incorporates one or more of the following learning techniques—active learning, collaborative learning, cooperative learning, and problem-based learning [Prince, 2004 and Prince and Felder, 2006]. Although the *CinChE* manual has been designed for a problem-based learning environment, it can easily be used in other active learning scenarios. Hanyak and Raymond [2009] present the design and application of a team-based cooperative learning environment for the introductory course in chemical engineering, where student learning is driven by solving problems and is supported by the *CinChE* manual.

In the introductory course on chemical engineering, students must develop their lower-order thinking skills—knowledge, comprehension, and application—and their higher-order thinking skills—analysis, synthesis, and evaluation—in Bloom's cognitive taxonomy [1956], in order to become effective problem solvers. The traditional lecture-based format tends to focus on the lower-order thinking skills and usually does not provide a formal emphasis on the higher-order thinking skills. In a problem-based learning environment, student teams that are required to follow the tenets of cooperative learning [Johnson, et al., 1998] can develop both their lower-order and higher-order thinking skills, as demonstrated by Hanyak and Raymond [2009] using team-based projects.

A two-week project of assigned analysis problems on material balances, phase equilibria, and energy balances can drive the learning in the introductory course on chemical engineering, where the number of problems in a project is equal to the number of members in a team (e.g., four problems for a four-member team). The six-step, problem-solving methodology—that produces a conceptual model, mathematical model, mathematical algorithm, numerical solution, heuristic observations, and formal documentation—serves as the critical framework in which to foster communication and teamwork skills using the five tenets of cooperative learning [Johnson, et al., 1998]. Using this methodology, team members complete their assigned roles while solving the analysis problems (A1, A2, A3, A4, and for a five-member team, A5) in each project. The assigned responsibilities for each role are given in the table below.

Major Responsibilities for the Project Roles

coordinator	helps the team to identify and understand its goals and keeps everyone on task during the work sessions.
observer	double-checks the problem solutions before they are submitted and conducts the group processing activity.
monitor	checks that everyone understands the problem solutions and the strategies used to get them.
assembler	prepares the project report packet and makes sure it is turned in on time.
troubleshooter	asks the "What if …?" questions and encourages the discussion of opposing ideas.

For a four-member team, the coordinator also takes on the role of the troubleshooter. Team members would rotate these roles from project to project to insure over the semester that each team member experiences the responsibilities of each role at least once.

During the two weeks for a project, a cooperative learning session (a.k.a. class time) would be devoted to each step in the problem-solving methodology, as illustrated in the table below for a four-member team. The format of this table incorporates the five tenets of cooperative learning—positive interdependence, individual accountability, face-to-face promotive interaction, appropriate use of teamwork skills, and regular self-assessment of team functioning—as defined by Johnson, et al. [1998]. At each co-op session, all students in a team are to focus on the same step in the problem-solving methodology, but each is doing it on a different analysis problem. Before a co-op session, a team member must develop a draft outside of class for that step in the problem-solving methodology and bring it to that session (e.g., a draft of the conceptual model, a.k.a. diagram, for the first Monday; a draft of the mathematical model for the first Wednesday, a draft of the mathematical algorithm for the first Friday, etc.). These drafted segments of the problem solution are used to focus the in-class reviews conducted by the groups of students working on the same problem. The instructor monitors these group reviews and also provides guidance and feedback. When team members move to the next co-op session, they will all have the same focus but on a different problem as shown in the above table. At the end of the two weeks, all team members will have worked on all four analysis problems and interacted with their team members, as well as with students from other teams. In the sixth session, each team is required to present for review their formal report (cover memo with attached problem solutions) and to spend time doing group processing; that is, doing self-assessment to examine and enhance their teamwork skills. The problem solutions for the documentation step in the problem-solving methodology have been done continuously over the two-week period, starting with the conceptual model and ending with the heuristic observations. Hanyak and Raymond [2009] present an alternative project format for the problem-solving methodology that incorporates a HSYYS® simulation problem, a laboratory experiment, and four analysis problems in each team project.

Four-Member Team Solving Analysis Problems A1, A2, A3, and A4

Project Role	First Week			Second Week		
	Monday	Wednesday	Friday	Monday	Wednesday	Friday
Coordinator	Diagram, A1	Model, A2	Algorithm, A3	Solution, A4	Heuristics, A1	Report, A2
Observer	Diagram, A2	Model, A3	Algorithm, A4	Solution, A1	Heuristics, A2	Report, A3
Monitor	Diagram, A3	Model, A4	Algorithm, A1	Solution, A2	Heuristics, A3	Report, A4
Assembler	Diagram, A4	Model, A1	Algorithm, A2	Solution, A3	Heuristics, A4	Report, A1

What might be the format for each co-op session in a project, if each session is 50-minutes in length? A co-op session must devote a significant amount of time to review the students' drafts produced by using the critical thinking skills outlined in the problem-solving methodology of the *CinChE* manual. A suggested time format for each co-op session is as follows:

10-15 minutes on the first co-op activity,
20-30 minutes on the problem feedback activity,
10-15 minutes on the second co-op activity.

The first co-op activity could be one of the following: 1) a brief mini-lecture, 2) an online survey to probe students' current understanding of topics, or 3) a student worksheet exercise completed individually and/or in teams while the instructor circulates to ask and answer questions. In the problem feedback activity, students working on the same problem would gather together and review their drafted solution segment of an analysis problem (A1, A2, A3, or A4), and the instructor would circulate and provide feedback to the student groups. The second co-op activity could be one of the following: 1) the introduction of a new topic and explanation by the instructor, 2) students working on laptop computers utilizing software such as E-Z Solve or HYSYS®, or 3) team preparation for the next co-op session.

This format force students to be prepared for each co-op session. Outside the classroom, students must accomplish just-in-time learning by developing their lower-ordered thinking skills through reading assignments in the *CinChE* manual and their textbook, drill-and-practice exercises, and *eLEAPS* exercises. The *eLEAPS* system [Oguzie, 2007] is a surrogate coaching technique that electronically guides students through an instructor-developed proof, derivation, or problem solution, before they come to the classroom. The problem solutions for five *eLEAPS* sessions are provided in this *CinChE* Manual, as shown in the table of contents.

The *CinChE* manual has been under continuous development since 1978. I thank the Bucknell chemical engineer majors (nearly 1000 of them) for their patience, understanding, and feedback while developing the manuscript. Two Bucknell colleagues—Drs. William J. Snyder and Timothy M. Raymond—have co-taught the introductory course in chemical engineering with me using the *CinChE* manual. Their feedback has been invaluable and has helped to enhance the final document. Finally, I thank Brian S. Hoyt for the written drafts he produced of Appendix C and a primer on units conversion. This primer is accessed through a web link in Appendix B. The development of these materials served as his practicum, under my supervision, in partial fulfillment of his Master's degree in instructional technology.

Michael E. Hanyak, Jr.

Table of Contents

Non-Reaction Examples Using the Heat-of-Reaction Method

Reaction Examples Using the Heat-of-Formation Method

Introduction

All engineering problems have an initial state and a goal state. For example, two towns (Lewisburg and Montandon) are separated by the Susquehanna River. The problem is to provide commerce between the two towns, which currently exchange no goods. The starting or initial state of this problem is that the two towns are separated by a river. The final or goal state is a physical connection between the two towns. Many alternative solutions exist for this problem, such as a highway bridge, a railroad trestle, and a helicopter service. All of the possible solution paths from the initial state to the goal state are the design and construction of all possible physical connections. As in this example, most engineering problems are ill-defined; that is, their goal is vague or incomplete. What physical connection is best to link Lewisburg and Montandon? Engineers solve ill-defined problems by using the following decision-making methodology, often called **engineering design**:

1. understand the problem,
2. generate alternative solutions, or designs,
3. analyze each alternative solution, or design,
4. select the "best" solution based on realistic constraints,
5. construct the "best" solution and review its worthiness.

This methodology provides a step-by-step structure that helps engineers to reach the final goal for any ill-defined problem. Although these steps or stages are sequential, feedback exists between stages. For example, while analyzing a specific alternative solution, an engineer might think of an idea for another alternative solution or obtain a better understanding of the problem.

Understanding the problem results in a conceptual representation of the problem on paper. The development of this representation aids in extracting from the problem statement the know information, the desired results, and their interrelationships, and this activity is critical in progressing toward the final goal—the problem solution [Halpern,1989, p. 356-367]. In engineering problems, this representation is usually a graph or a diagram that contains the given information. In the following diagram,

Lewisburg and Montandon are represented by the circles, and the straight line connecting the two towns is the link to increase the exchange of goods. The initial state is the two circles without the connecting line; the goal state is the two circles with the physical connection.

Generating alternative solutions is a creative thinking activity; that is, producing ideas or ways to solve the problem on paper. For engineers to be creative, they need the knowledge and skills of their domain, such as civil or chemical engineering. The alternative solutions are the designs of those physical objects that potentially can solve the problem. A design is a representation, expressed on paper, of the structure or form of the physical object. Several designs for the commerce example are represented simplistically as follows:

Well-Defined Problems

In this introductory course on chemical engineering, we will focus our attention on well-defined problems, ones that have a single correct answer (e.g., how much does 10 gallons of water weight at Denver, Colorado?). Ill-defined problems have many possible correct answers, as was the case for the four physical connections in our commerce example. When an engineer is ready to begin the third stage in the engineering design methodology, the analysis of an alternative solution is a well-defined problem, because it produces a single correct answer—a measure of performance for that alternative solution (e.g., the cost of construction and operation). In chemical engineering process design, the first thing to be done in this analysis stage is to solve the material and energy balances (MEB) of chemical process units (i.e., equipment like reactors, distillation columns, filter presses, and compressors). The subject matter of this introductory course is material balances, phase equilibria, and energy balances, while the topic of process design will be covered later in other chemical engineering courses.

Like the anatomy of an ill-defined problem, a well-defined problem has an initial state, a goal state, and solution paths; however, its solution paths will all give the same correct answer, provided they are all based on the same assumptions. Since a decision-making plan is important in order to reach the goal state from the initial state of any ill-defined engineering problem, a plan is also important to solve **any** well-defined engineering problem. Most engineers solve well-defined problems by using the following **problem-solving methodology**, which is an adaptation of Polya's method [1957]:

Activity	**Outcome**
1. understand the problem	conceptual model, a.k.a. diagram
2. model the phenomena	mathematical model
3. devise a plan	mathematical algorithm
4. carry out the plan	numerical solution
5. review the problem solution	heuristic observations
6. report the problem solution	formal documentation

This methodology provides a step-by-step structure that helps engineers to reach the final goal, a single correct answer. Although these steps or stages are sequential, feedback exists between stages. For example, while reviewing the numerical solution, an engineer might observe the need to calculate another quantity which was forgotten in the original mathematical model.

The formally-documented, problem solution of a simple example is presented in the four-page attachment entitled "A Well-Defined Problem," at the end of this chapter. The initial state of a well-defined problem is the "Problem Statement", as illustrated on Page 1 of the attachment, while its goal state is the correct answer, as illustrated by the boxed values for W_{sea} and W_{Den} under the "Numerical Solution" on Page 3. The problem solution, or solution path, from the initial state to the goal state, is **all of the outcomes** produced by applying the above problem-solving methodology. In the attachment, the problem solution is all four pages, not just the desired answers in the "Numerical Solution" part.

When applying the problem-solving methodology to the same well-defined problem, each engineer will produce a different solution path. These differing solutions will have some variations in their diagrams, assumptions, math models, math algorithms, and numerical solutions. Although each solution produces its own correct answer, these answers will be equivalent, only if all solutions are based on the same assumptions. In the attachment example, a different assumption for the temperature and/or pressure will results in a slightly different solution; however, the mathematical model and algorithm will still be the same in both solution paths.

Assuming you have mastered the above subject matters as individual topics, how would you apply the problem-solving methodology in concert with your knowledge of these topics to solve the example problem of determining the weight of a known volume of water? Although this example is not a chemically-related process problem, the generation of its solution will give us some initial insights into the application of each of the six-stages in the problem-solving methodology.

Understand the Problem

This first problem-solving stage converts the initial sub-state of a problem statement into the sub-goal of a conceptual model. An example conceptual model is illustrated on Page 1 of the attached four-page example problem at the end of this chapter.

A conceptual model is a representation on paper of one or more of the engineering phenomena acting on a physical object, such as heat, work, and force. What form of representation is the "best" for the conceptual model? Of the five forms of representation described by Halpern [1989, pp. 358-372]—diagram, graph, hierarchical tree, matrix, and mock-up (a miniature model), a diagram is the best form for an engineering problem that involves a physical object. When the problem involves the relationship between variables, a graph is the best form. The conceptual models for most engineering problems are diagrams and graphs; however, hierarchical trees, matrices, and mock-ups may be used.

A conceptual diagram depicts four things—the physical object, the engineering phenomena, the "givens", and the "finds". The object, "givens", and "finds" are directly identified from the problem statement. However, the engineering phenomena are indirectly implied, and their recognition is related to the "finds" and comes with experience. In the attached example problem, the object is a certain volume of water held in a simplistically-drawn container; and the phenomenon is the force of gravity acting on the object and represented by the arrow. The container is irrelevant in this problem but is drawn since a fluid, like water, takes the shape of its container. The "givens" and the "finds" are the initial state and the goal state of the problem, respectively. They are represented on the diagram with a symbol, called a **subscripted variable**, followed by an equal sign and then either a value with units for a "given" or a question mark for a "find". For example, "$V_w = 2\ ft^3$" is a given, while "$W_{sea} = ?$" is to be determined. Other pertinent information from the problem statement is also included in the example diagram. The conceptual model may also contain a listing of the "givens" and "finds", as illustrated in the attached example. These listings clearly delineate the initial and goal states and indicate the system of units for the known and unknown variables.

The use of subscripted variables in the conceptual model alleviates overloading of our short-term memory and aids the pattern recognition capabilities of our brain. Our short-term memory, where we retain information for up to approximately one minute, is limited to 7±2 items of information at one time [Miller, 1956]. Memory attention, organization, meaningfulness, and chunking are enhanced by mnemonic patterns [Halpern, 1989, p. 81]. For example, the volume of the water is represented by the pattern "V_w". The mnemonic "V" is easily associated with the concept of volume. The subscript mnemonic "w" represents water, and its placement in the pattern "V_w" makes it subservient to the major concept of volume. Pattern "V_w" means "volume of water". Our short-term memory can easily handle the pattern "V_w", because it contains two characters of information. However, the pattern "volume of water" contains 13 characters of information, and its appearance in the conceptual diagram would overload our short-term memory.

You are comfortable working with numbers; however, you must become equally comfortable working with symbols. In the conceptual model, you leave the world of numbers and entry the world of variables. This abstraction process is necessary because we will use the world of variables and equations to develop the solution to the problem. As reported by Halpern [1989, p. 4], only 25% of first-year college students have developed their mental abilities in logical abstract thought. You can become an effective critical thinker, but to do so you must be able to abstract. We will develop your critical-thinking skills in this introductory course on chemical engineering, in order for you to become an effective problem solver. The six-stage, problem-solving methodology aids the critical-thinking process, and the development of a conceptual model is the first step in that process.

In summary, a conceptual model helps to visualize the problem, to organize information, to connect variables and numbers, and to clarify your thinking. It is the first sub-goal in the solution path for the problem. In this introductory course, we will study three important concepts in chemical engineering. They are the flow of material through a process unit, the transfer of heat and work to and from a process unit, and the equilibrium of multiple phases (gas, liquid, and/or solids) within a process unit. Your conceptual models will be diagrams and graphs.

Model the Phenomena

This second problem-solving stage converts the initial sub-state of a conceptual model into the sub-goal of a mathematical model. The mathematical model is a mathematical abstraction that represents the engineering phenomena occurring in the problem statement. It contains four things—a set of equations, a list of assumptions, a degrees-of-freedom analysis, and a list of variable definitions—all of which are illustrated on Pages 1 and 2 in the attached four-page example problem at the end of this chapter. If standard nomenclature has been defined for all problems, then the variable descriptions are optional, which will be the case for this introductory course on chemical engineering.

Mathematical models are developed from first principles; that is, any axioms, laws, or abstractions assumed and regarded as representing the highest possible degree of generalization. The first principles in this introductory course are Newton's second law of motion, the conservation of mass, the conservation of energy, and fluid phase equilibria as applied to chemical process units. You begin the development of the mathematical model by identifying the first principles (there could be one or more) implied in the problem statement. For example, since the weight of water is a force caused by the acceleration of gravity, then Newton's second law of motion is the first principle implied in the attached example problem. As illustrated by this example, examining the "finds" variables can help identify the first principles.

How do you determine what equations should be in the math model? What are these things called assumptions? What are the degrees of freedom? Developing the math model is an ill-defined problem. The initial state is the conceptual model; the goal state is the mathematical model. The best critical-thinking strategy is a technique called working backwards [Halpern, 1989, p. 375]. You begin with the unknown variables (i.e., the "finds") and work backwards toward the known variables (i.e., the "givens").

In the attached example problem, the conceptual model or diagram on Page 1 identifies the unknown variables as $\mathbf{W_{sea}}$ and $\mathbf{W_{Den}}$. Assuming you have mastered the general significance of weight, density, and acceleration of gravity (as described above), you can begin the development of the math model. The required critical-thinking steps are as follows, where the notation of "Equation (…)" refers to an equation on Page 2 of the attached example problem:

- Since $\mathbf{W_{sea}}$ is a weight, you write Equation (1). Why? This equation is a specific application of Newton's second law ($W = m \cdot g$). Since the pattern **W** in variable $\mathbf{W_{sea}}$ matches part of the pattern in the first principle of "$\mathbf{W = m \cdot g}$", your brain recognizes this association, and you write Equation (1) using the appropriate subscripts on the variables.

  You examine each variable in the right-hand side of Equation (1), asking yourself the question of "Is that variable a given in the conceptual model?". If it is a "given", you proceed to examine the next variable in the equation. If it is not a "given", you must either write a new equation that used heavily in developing the math model. They alleviate the overloading of your short-term memory by allowing you to work with mnemonic variables and equations, instead of words, numbers, and units. Finally, a degrees-of-freedom (DOF) analysis is used continually during the model-developing process to monitor the potential solvability of the mathematical model.

Devise a Plan

This third problem-solving stage converts the initial sub-state of a mathematical model into the sub-goal of a mathematical algorithm. The math algorithm is a plan (or blueprint) that identifies the independent variables which satisfy the degrees of freedom (DOF) and states the order in which the equations from the math model are to be solved. A simple mathematical algorithm is illustrated on Page 2 of the attached example problem at the end of this chapter. Expressing how each equation or subsets of coupled equations in the math algorithm are to be solved is delayed until the fourth problem-solving stage of "carry out the plan".

The mathematical algorithm contains two essential parts—its functional equation and the ordered equations from the math model. Its functional equation is a concise statement which expresses the essence of the mathematical algorithm; that is, it represents chunked information. As illustrated on Page 2 of the attached example problem, this statement contains a list of the important dependent variables ($\mathbf{W}_{\mathbf{sea}}$ and $\mathbf{W}_{\mathbf{Den}}$), an assigned function name (WEIGHT), and a list of the independent variables ($\mathbf{T}$, $\mathbf{P}$, and $\mathbf{V}_{\mathbf{w}}$). By definition, the dependent variables are all of the calculated variables in the math algorithm, because their values are dependent upon the values assigned to the independent variables. The important dependent variables in the algorithm's functional equation are the "finds" in the conceptual model. From the six dependent variables on Page 2, the two important ones are $\mathbf{W}_{\mathbf{sea}}$ and $\mathbf{W}_{\mathbf{Den}}$. The independent variables are those variables in the math model that are selected to satisfy the degrees of freedom. These variables are the "givens" and any assumed variables, and they are commonly called **design variables**. For the example problem on Page 2, the three independent variables are $\mathbf{T}$, $\mathbf{P}$, and $\mathbf{V}_{\mathbf{w}}$, where $\mathbf{V}_{\mathbf{w}}$ is a "given" in the conceptual model, and $\mathbf{T}$ and $\mathbf{P}$ are two of the assumptions.

The ordered equations in the mathematical algorithm are systematically formulated by using a critical-thinking strategy called a **partitioning algorithm**. This partitioning algorithm identifies the next equation or set of equations in the mathematical model that is to be placed as the next step in the mathematical algorithm. Basically, it partitions the equations from the mathematical model into the following categories:

A. Those equations that contain only one unknown variable.
B. Those sets of coupled equations that contain either exclusively linear equations, exclusively nonlinear equations, or a combination of linear and nonlinear equations.
C. Those equations that contain the only occurrence of an unknown variable.

The partitioning algorithm is a systematic procedure that can be easily applied to a mathematical model containing two equations, or 2000 equations. In Chapter 4 of this *CinChE* manual, we will examine the details of how to apply the partitioning algorithm.

Partition Category B contains linear and/or nonlinear sets of equations. Each set of equations can only be solved as a collecting whole, because the equations are coupled. In the mathematical algorithm, a linear set is represented by a SOLVE construct, while a nonlinear set is represented by a NSOLVE construct. An example of a SOLVE construct is as follows:

In summary, a mathematical algorithm is a plan that describes the functional equation for that plan and outlines the order in which the equations from the mathematical model are to be solved. The functional equation identifies the important dependent variables (i.e., the "finds") and lists the independent variables that satisfy the degrees of freedom for the mathematical model. These independent variables are the "givens" and any assumed variables. How the ordered equations in the mathematical algorithm are to be solved is the objective of the fourth problem-solving stage of "carry out the plan".

Carry Out the Plan

This fourth problem-solving stage converts the initial sub-state of a mathematical algorithm into the sub-goal of a numerical solution. Using the mathematical algorithm as your plan, you substitute numbers with units and calculate the answers for all the dependent variables. The numerical solution contains three things—the basis, the "givens", and the solved equations, as illustrated on Page 3 of the attached example problem at the end of this chapter.

The basis identifies the base system of units and, when necessary, the mass or mass flow rate of a chemical substance on which the calculations are based. All units for the "givens" are converted to the base units, and all calculated variables are expressed in the base units. Once calculations are completed, the base units of the "finds" are converted to the requested units given in the problem statement. The "givens" part of the numerical solution lists the symbols, magnitudes, and units for all of the independent variables and shows any necessary conversions of units.

The "solved equations" part of the numerical solution parallels the mathematical algorithm, and it possibly contains the solutions to three types of equations:

- algebraic and/or transcendental equations that contain only one unknown variable,
- functional equations that could not be algebraically rearranged, and
- sets of coupled equations identified by the SOLVE and NSOLVE constructs in the mathematical algorithm.

Transcendental equations are those equations that contain either an exponential, logarithmic, or trigonometric term.

In the attached example problem, Steps 2, 4, and 6 on Page 3 are the solutions to the corresponding algebraic equations in the math algorithm on Page 2. Numbers and units are substituted for the variables and, when necessary, conversion factors (enclosed in angle brackets “<···>”) are applied to get the desired answer in the base units. Steps 1, 3, and 4 are the solutions to the corresponding functional equations in the math algorithm. For functional equations, the numerical solution shows only the functional results and any necessary conversion factors. How a function is resolved is indicated by the bracketed comment "{…}" found in the math algorithm. For example, the *density* function in Step 1 of the math algorithm on Page 2 is resolved by consulting a table in a literature source. The value of 0.997044 g/cm^3 for the density of water is placed in Step 1 of the numerical solution of Page 3. The *gravity* function in Step 3 of the math algorithm is resolved by the mathematical algorithm for *gravity* found on Page 4. The value of 980.665 cm/s^2 for the gravitational acceleration at sea level is placed in Step 3 of the numerical solution.

No SOLVE and NSOLVE constructs appear in the attached example problem. However, when one of these constructs does appear, the coupled equations must be solved collectively. In this course, you will learn algebraic and numerical analysis techniques to solve a linear or nonlinear set of equations, either simultaneously or sequentially. An example algebraic analysis technique for linear equations is Gaussian elimination. Example numerical analysis techniques for nonlinear equations are the Newton-Raphson method for a simultaneous solution and the Bisection and Secant methods for a sequential solution. These analysis techniques can be done either manually, on an engineering-type pocket calculator, or by a computer program such as E-Z Solve, MathCad® or Matlab®. When you have a SOLVE or NSOLVE appearing in a math algorithm, you would report the answers in the numerical solution and provide supporting documentation for the application of the appropriate analysis technique.

The final step in the numerical solution is to box-in the desired answers (i.e., the "finds") and account for precision in these answers; that is, the proper number of significant figures in each answer, as illustrated on Page 3 in the attached example problem.

Review the Solution

This fifth problem-solving stage reviews the numerical solution, the mathematical algorithm, the mathematical model, and conceptual model, in that order, to produce the heuristic observations. When used as an adjective, heuristic means serving to discover [Polya, 1945, pp. 112-113]. From your experience of solving the well-defined problem, what heuristic observations can you make that will give you a better understanding of both the technical subject matter and the application of the problem-solving methodology? These observations are to be general conclusions and/or recommendations that you could apply to the solution of any well-defined problem.

Your observations on the numerical solution involves three things—an order-of magnitude check, an equation-based check, and the significance of the results. In an order-of-magnitude check, you mentally approximate the calculations. On Page 3 of the attached example problem at the end of this chapter, the density is roughly 60, and the volume is 2 using the **fps** system of units. Then, the mass is roughly 120 and so are the weights, at both sea level and Denver. In an equation-based check, you select an equation or a set of equations not used in the mathematical model but related to that model and use it to check the consistency of the results. In material balance problems, this check equation is commonly the one that says the sum of the mass fractions must add to one. In other problems, this check might be based on a similar mathematical model that uses simplifying assumptions. Sometimes, an equation-based check is not needed, as is the case for the attached example problem. In the significance of the results, you deduce trends or heuristic rules from examining the results. On Page 3 of the attached example problem, mass and weight are equivalent numerically, only at sea level and 45° latitude. Also, weight does not vary that much on the Earth's surface (< 0.08%).

Your observations on the mathematical algorithm involve answering some or all of the following questions:

- What impact does changing the chemical substance or mixture have on the mathematical algorithm?
- How would the algorithm change if its independent variables were different?
- What significant patterns exist in the mathematical algorithm?
- What are the pros and cons for how you solved any SOLVE and NSOLVE constructs?

For the mathematical algorithm on Page 2 of the attached example problem, you might observe the effect when the independent variables are **T**, **P**, and $\mathbf{m_W}$, or **T**, **P**, and $\mathbf{W_{sea}}$.

Your observations on the mathematical model involve answering some or all of the following questions:

- What impact does changing the chemical substance or mixture have on the mathematical model?
- How good are the assumptions for the mathematical model?

- What significant patterns exist in the mathematical model?
- How could this mathematical model be simplified, without increasing the complexity?

When you develop a mathematical model, you commonly start with first principles. Several equations could be simplified by combining them to form a new equation that you would memorize for later use. For the mathematical model on Page 2 of the attached example problem, you might simplify the equation for weight by combining Equations (1) and (2) to form the general equation $\mathbf{W = \rho \cdot V \cdot g}$. When doing simplification, you should limit the number of variables and terms in the resulting equation to 7±2 items. This precaution is a guard against complexity and reduces the chances of overloading one's short-term memory.

In summary, reviewing the solution affords you the opportunity to obtain new insights on both the technical subject matter and the application of the problem-solving methodology. Your heuristic observations will increase your understanding and make you an effective problem solver.

Report the Solution

This sixth and final problem-solving stage formally documents the solution to the well-defined problem. This formal documentation contains the problem statement, conceptual model, assumptions, mathematical model, mathematical algorithm, numerical solution, your heuristic observations, and any supporting materials for the numerical solution, as illustrated in the four-page attachment entitled "A Well-Defined Problem" at the end of this chapter.

When you apply the six-stage problem-solving methodology, you are exercising your technical responsibilities as a **problem solver** and your rhetorical responsibilities as a **report writer**. You are a problem solver in the first five problem-solving stages and a report writer in the last problem-solving stage. Since writing is an evolutionary process, you are also a report writer during the first five problem-solving stages, because you are drafting components that will appear in the formally-documented problem solution.

After completing the first three problem-solving stages, you will have drafted the conceptual model, mathematical model, and mathematical algorithm. The drafts of these three components of the problem solution are commonly sketched out on paper and are probably loosely organized. You want your creative juices to flow during these drafting activities and not be hindered by formal documentation. Furthermore, your first drafts of these three components will probably need refinement, because the process of doing the next component will provide feedback on improving the previous component. Your refinement techniques will be loosely inserting new material and crossing-out unwanted material. You continue this refinement or drafting process until you feel confident that you have developed the correct conceptual model, mathematical model, and mathematical algorithm.

When you complete the fourth and fifth problem-solving stages, you will have drafted the numerical solution and heuristic observations. Again, these drafting activities are commonly sketched out on paper, but they are not loosely organized, because you are using the conceptual model, mathematical model, and mathematical algorithm as your guides. You will acquire information from literature sources and cite those sources. You will generate supporting materials, such as the manual application of a numerical technique or the application of a computer program. Finally, you will draft your heuristic observations about the numerical solution, mathematical algorithm, mathematical model, and conceptual model. These two drafting activities stop when you feel confident that you have the correct answers to the well-defined problem and have made the important heuristic observations.

Once you have done the drafting activities in the first five problem-solving stages, you complete the rhetorical (or writing) process of formally documenting the solution to the well-defined problem. As

larger

CHEG 200
Hanyak

A Well-Defined Problem

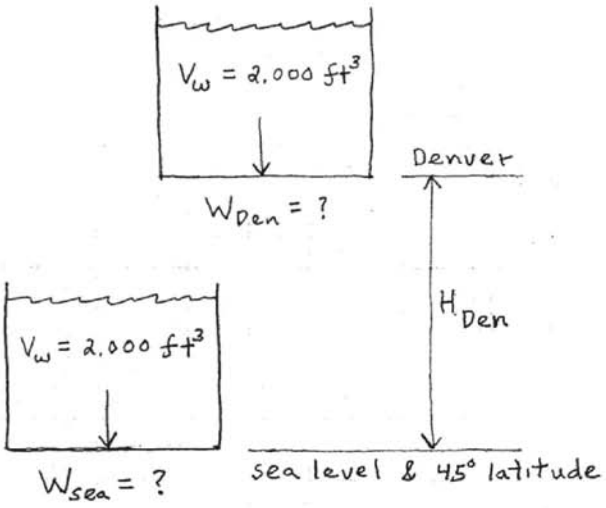
5/17/91
1 of 4

Problem Statement

{a simple example}

How much does 2.000 ft^3 of water weigh (a) at sea level and 45° latitude, and (b) at Denver, Colorado?

Conceptual Model (a.k.a. Diagram)



Givens

$V_w = 2.000\ ft^3$

Finds

W_{sea} in lb_f

W_{Den} in lb_f

Assumptions

1. Temperature is constant at $T = 77\ °F$.
2. Pressure is constant at $P = 1$ atm.
3. Liquid in the container is <u>pure</u> water

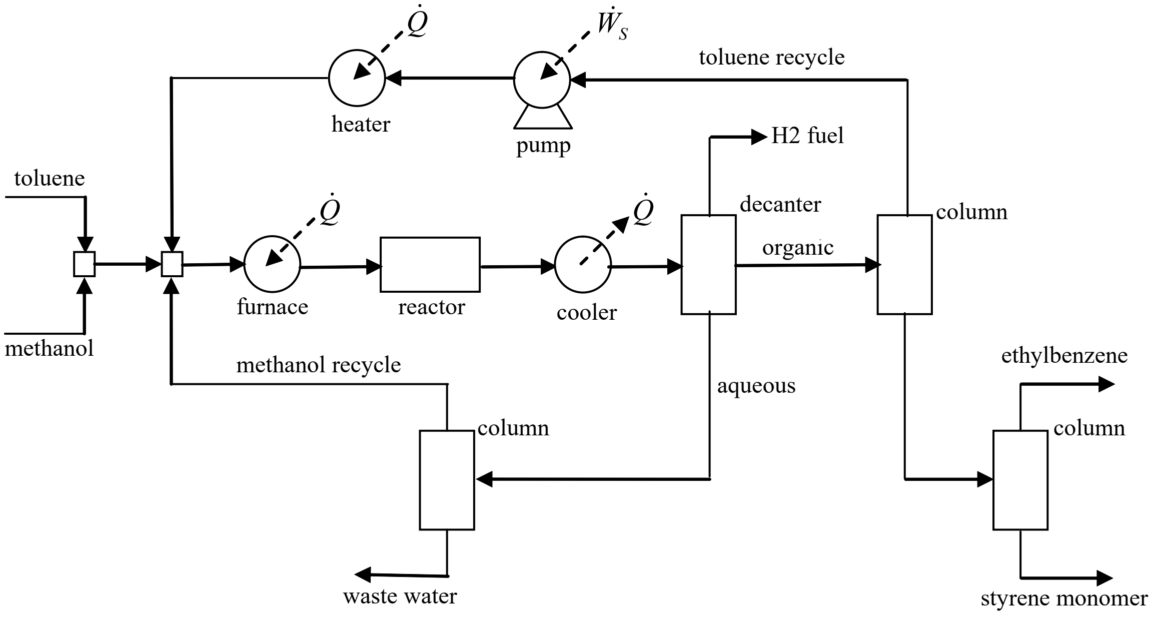
Introduction

This introductory course on chemical engineering has three major learning objectives—intellectual development, content learning, and professionalism. The intellectual development objective is to enhance your skills to apply the problem solving methodology introduced in Chapter 1. The content learning objective is to apply the first principles for material balances, phase equilibria, and energy balances, as you determine the process requirements for individual chemical process units (i.e., equipment) and combinations of process units, called a chemical process. The professionalism objective is to develop your professional skills as a problem solver in a team environment and as a report writer for team-oriented, bi-weekly projects.

The focus of this chapter is to provide you with a broad overview about chemical processes, force principles, material balances, phase equilibria, and energy balances. The remaining chapters in this *CinChE* manual demonstrate how to apply the problem solving methodology to solve chemical process problems that use these first principles.

Example Chemical Process

We will begin with the description of an example chemical process to make styrene monomer and then follow that with some fundamental observations about a chemical process. Styrene monomer is an intermediate material used to make such consumer plastic products as polystyrene packaging and film, cushioning materials, radio and television sets, and toys. The example chemical process for converting toluene and methanol to styrene monomer is depicted in the following block flowsheet:



This flowsheet is a collection of blocks, circles, and arrowed lines. The blocks and circles represent process units, such as reactors, heaters, coolers, pumps, and distillation columns. The solid arrowed lines are process streams (i.e., chemical material flowing in pipes) that are assumed to have uniform temperature, pressure, flow rate, and composition (as a first approximation, these four variables do not vary along the length of a pipe). The dashed arrowed lines represent energy streams of heat ($\dot{Q}$) and work ($\dot{W}_S$). Usually, they are draw as solid lines but were drawn as dashed ones above, in order to distinguish them from material streams. Basically, the block flowsheet conceptually shows the flow of material and energy from the raw materials (toluene and methanol) to the product (styrene), by-product (ethylbenzene), and wastes (H_2 and water).

E. Styrene Monomer Interactive Demonstration

As described above, the chemical process fundamentals are process streams, process units, and a process flow diagram (PFD) or flowsheet. Click here to complete an interactive demonstration on the construction of a simple flowsheet to produce styrene monomer from toluene and methanol.

This interactive demo takes about two to three hours to complete. You can stop the demo at any time. When you restart it, you can begin where you had left off. The interactive demo illustrates the basic concepts that you will be learning about in this introductory course on chemical engineering principles.

F. Required Engineering Courses in Bucknell University's Chemical Engineering Curriculum

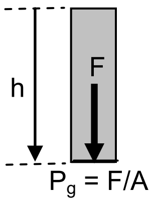
Year	**Semester**	**Course**	**Course Title**
First Year	Fall	ENGR 100	**Exploring Engineering**
	Spring	CHEG 200 ENGR 215	**Chemical Engineering Principles** **Experimental Design and Data Analysis**
Sophomore	Fall	ENGR 211 ENGR 240	**Intro to Chemical Engineering Computing** **Science of Materials**
	Spring	CHEG 210 ENGR 233	**Applied Math for Chemical Engineering** **Fluid Mechanics**
Junior	Fall	CHEG 300 CHEG 302	**Heat and Mass Transfer** **Equilibrium Stage Processes**
	Spring	CHEG 310 CHEG 315	**Chemical Engineering Thermodynamics** **Unit Operations Laboratory**
Senior	Fall	CHEG 320 CHEG 400	**Chemical Reaction Engineering** **Process Engineering**
	Spring	CHEG 330 CHEG 410	**Process Control** **Project Engineering**

This *CinChE* manual is for the CHEG 200 course, and it introduces you to the first principles of force, material balance, phase equilibrium, and energy balance that you will be using often in the upper-level required courses in the chemical engineering curriculum.

height of the column of air above the mercury exert a combined force per unit area (i.e., a pressure) at the lower dotted-line position that is equal to the pressure (P) in the process vessel. The pressure exerted by the column of air is read from a barometer device, and it is called the atmospheric or barometric pressure (P_b). Since this column of air extends to the outer limits of the Earth's atmosphere where the pressure is zero, the barometric pressure is an absolute pressure because it is measured relative to zero. The pressure exerted by the column of mercury for the given height h is expressed as $\Delta P = P - P_b = \rho \cdot g \cdot h$. This pressure difference (ΔP) is the gauge pressure (P_g), because it is always measured relative to atmospheric pressure (P_b). Thus, the absolute pressure (P) inside the process vessels is equal to $P_b + P_g$.

If the pressure (P) inside of the process until where less than atmospheric pressure, the mercury would be drawn up the right side of the U-tube. The absolute pressure would be calculated using the equation of $P = P_b - \rho \cdot g \cdot h = P_b - P_g$.

In the diagram above, the pressure drop (ΔP) is the force per unit of area exerted by gravity on the column of mercury between the two dotted horizontal lines. Pictorially, this gauge pressure is:



Mercury Fluid, h is its height.

$$\Delta P = P_g = F / A = W_{Hg} / A = m_{Hg}\, g / A$$

but $m_{Hg} = \rho_{Hg} \cdot V_{Hg}$

and $V_{Hg} = h_{Hg} \cdot A$

Thus, $P_g = \rho_{Hg} \cdot g \cdot h_{Hg} = \rho \cdot g \cdot h$

Note that the mass density (ρ) of any liquid like mercury varies with temperature but is not affect by pressure because most liquids are considered incompressible. The acceleration of gravity (g) is a function of the distance from the center of the Earth. For a column of mercury 760 centimeters (or about 25 *ft*) height at sea level and 45° latitude, the Earth's gravity at its base would be 980.665 cm/s^2, while the Earth's gravity at its top would be 980.663 cm/s^2. Since the difference in these gravities is about 0.0002%, the assumption of a constant g for the height of the column of mercury is practical because most measured quantities like mass density and height have only two to four digits of precision.

In the English (or *fps*) system of units, the typical unit for pressure is pounds-force per square inch (lb_f/in^2 or *psi*). For example, a manometer's height is 22.6 *in of Hg* and the barometric pressure is 14.6 *psi*, both at Denver, CO. If the temperature of the mercury is 25°C, what is the pressure within the process unit in *psi*? Using the above equation for absolute pressure, we can do the following calculation:

$$P = P_b + \rho \cdot g \cdot h$$

$$P = 14.6 \frac{lb_f}{in^2} + \left(844.88 \frac{lb_m}{ft^3}\right)\left(32.1423 \frac{ft}{s^2}\right)(22.6\, in)\left\langle \frac{1\, ft}{12\, in} \cdot \frac{lb_f}{32.174\, lb_m\, ft/s^2} \cdot \frac{1\, ft^2}{144\, in^2} \right\rangle$$

$$P = 14.6 \frac{lb_f}{in^2} + 11.039 \frac{lb_f}{in^2} = 25.639\, psi = 25.6\, psi$$

The mass density of *Hg* and the acceleration of gravity were obtained from literature sources. The second conversion factor in the angle brackets < ⋯ >converts the combined units of mass times acceleration $lb_m\ ft/s^2$ to the force unit of lb_f for the English system of units. If you lack confidence in converting units, you should consult Appendix B of this *CinChE* manual to sharpen your skills on doing units conversions.

ethylbenzene and stryene). The fugacity coefficient describes the relative balance between attractive and repulsive forces between molecules within a phase. A fugacity coefficient of one means the two forces are in balance. A value less than one means attractive forces between molecules dominate. A value greater than one means repulsive forces between molecules dominate.

In general, a distribution coefficient for a chemical component is a function of the temperature, pressure, and compositions of the equilibrium system. For example, as temperature increases, its value will increase. Conversely, as temperature decreases, its value will decrease. Later, we will be developing in Chapter 6 different mathematical models to represent the equilibrium between multiple phases. These models not only will incorporate the K_j relationships but also the dependency of K_j on the intensive quantities of temperature, pressure, and compositions.

The **Gibbs phase rule** indicates the number of intensive quantities like temperature, pressure, and composition that can be specified independently for only equilibrium systems and their mathematical models. This rule states:

$$DOF = 2 + nc - \prod$$

where DOF is the degrees of freedom, the number of intensive quantities that can to be specified to fix the equilibrium system,
nc is the number of chemical components in the system,
$\prod$ is the number of phases that are in equilibrium,

This form of the Gibbs phase rule is only applicable to phases in equilibrium with no chemical reactions occurring. In this introductory course, we will not examine the situation where chemical reactions occur in phases at equilibrium. This situation will be investigated in a later course on chemical engineering thermodynamics.

Based on the **Gibbs phase rule**, the degrees of freedom for pure liquid water in equilibrium with its vapor is one ($DOF = 2 + 1 - 2 = 1$). Thus, one intensive quantity like pressure (P) can be specified to fix the state of the equilibrium system. After you specify the pressure for the system, you can determine other intensive quantities like temperature, density, viscosity, and specific enthalpy for the two phases at equilibrium. For example, at 1 atmosphere you know that pure water boils at 100°*C*. As long as the saturated liquid and saturated vapor phases coexist during the boiling process, then this process at 1 *atm* must occur at a constant temperature of 100°*C*. The saturated vapor phase is often called steam for water.

For an equilibrium system that contains just a pure chemical compound and has three phases—liquid, solid, and vapor—coexisting, the degrees of freedom is zero ($DOF = 2 + 1 - 3 = 0$). Thus, all intensive variables are fixed, and the temperature and pressure at which this condition occurs is called the **triple point**. Triple points are determined experimentally and are tabulated in technical literature sources. An appendix in your textbook for this introductory course should provide such tabulation for a limited number of pure chemical compounds.

The **Gibbs phase rule** can also be applied to phases in equilibrium with two or more chemical components existing in those phases. In Chapter 6 of this *CinChE* manual, we will be developing the mathematical models for multicomponent phase equilibrium using such relationships as Raoult's law, Henry's law, humidity, and solubility. As we will see, these relationships will incorporate the first principle of the distribution coefficient. When developing these equilibrium mathematical models, we will determine their degrees of freedom (DOF) by subtracting the equation count from the variable count. We will check this DOF by comparing it to the one gotten from the **Gibbs phase rule**.

Energy Balance Principles

As described in an earlier section, material balances account for the amount of material that flows into and out of a system as well as the amount of material within the system boundary for a single process unit or set of process units. For that same system boundary, we can write an energy balance to account for the energy of material that flows into and out of a system, the heat and work that crosses the system boundary, and the energy of material within the system boundary. The first principle for the energy balance is:

$$\textbf{Energy Balance:}\quad \begin{matrix}\text{energy rates}\\ \text{flowing in}\end{matrix} \;-\; \begin{matrix}\text{energy rates}\\ \text{flowing out}\end{matrix} \;\pm\; \dot{Q} \;\pm\; \dot{W}_S \;=\; \frac{d(energy)_{sys}}{dt}$$

Starting from the left, the first two parts of this first principle account for energy flowing into and out of the system boundary by way of process streams. If three streams were flowing in and two streams were flowing out of a system boundary, then the "flowing in" part would have three energy rate (*energy/time*) terms with positive signs in front of them. The "flowing out" part would have two energy rate (*energy/time*) terms with negative signs in front of them. The third part of this first principle accounts for heat transfer ($\dot{Q}$) across the system boundary (*energy/time*). The fourth part of this first principle accounts for shaft work ($\dot{W}_S$) that crosses the system boundary (*energy/time*); that is, a physical shaft goes through the system boundary like the shaft from an electric motor to drive a pump or compressor. The fifth part of this first principle that appears on the right of the equal sign accounts for the accumulation or depletion of energy (*energy/time*) within the system boundary.

The sign in front of the **heat and shaft work** variables will be positive or negative, based on the following convention:

		PFD† Stream
Sign in front of $\dot{Q}$:	+ when $T_{surroundings} > T_{system}$	energy stream's arrow points into the system
	− when $T_{system} > T_{surroundings}$	energy stream's arrow points out of the system
Sign in front of $\dot{W}_S$:	+ when the surroundings does work on the system	energy stream's arrow points into the system
	− when the system does work on the surroundings	energy stream's arrow points out of the system
		†**P**rocess **F**low **D**iagram

With this convention, the heat and work variables ($\dot{Q}$ and $\dot{W}_S$) will always have absolute or positive values of energy per time. As shown in the above table, if the temperature within the system boundary is less than the temperature of the surroundings outside the system boundary, then the heat term will have a positive sign in front of it, because energy will be transferred from the surroundings to the system. If the temperature within the system boundary is greater than the temperature of the surroundings outside the system boundary, then the heat term will have a negative sign in front of it, because energy will be transferred from the system to the surroundings. When the surroundings does work on the system, like an electric motor driving a shaft that goes into the system to operate a pump to move liquid, the work term will have a positive sign in front of it. When the system does work on the surroundings, like a gas expanding in a turbine system rotating a shaft that goes out of the system to driver an electric generator, the work term will have a negative sign in front of it. The energy streams for heat and work in a process flow diagram (PFD) will be pointing into or out of the system boundary as indicated in the above convention table. Be careful when you consult other textbooks about the energy balance, because these textbooks may use a different sign convention for heat and work.

In the first principle above for the energy balance, the energy rate terms for process streams flowing in and out of the system boundary have net units of energy per time. Each of these terms is expressed as the product of two quantities as follows:

	stream energy rate flowing in or out	=	stream amount rate flowing in or out	*	stream's specific enthalpy
example units	kJ / h		kg-mol / h		kJ / kg-mol
	kJ / h		kg / h		kJ / kg

The variable symbol for the specific enthalpy of a process stream is $\hat{H}$, with units of energy per amount, where the amount is either moles or mass. If the flow rate of the process stream is in moles per time, then $\hat{H}$ will have units of energy per mole. However, if the flow rate of the process stream is in mass per time, then $\hat{H}$ will have units of energy per mass. Specific enthalpy is a thermodynamic quantity that represents the internal energy ($\hat{U}$) plus flow work ($P\hat{V}$) associated with the material in the flowing process stream; that is, $\hat{H} = \hat{U} + P\hat{V}$. We described these quantities later in Chapter 7 of this *CinChE* manual.

In general, the specific enthalpy is a function of temperature, pressure, and composition. The first principle for this functionality is expressed as follows:

$$\hat{H} \;=\; hmix\left[T, P, composition\right]$$

The composition quantity is mole fractions $(\bar{x})$ or mass fractions $(\bar{w})$ depending upon what the units are for the flow rate of the process stream—moles/time or mass/time—respectively. The symbol of $\bar{x}$ is short hand notation for all of the mole fractions ($x_1, x_2, x_3, \cdots, x_{nc}$), while the symbol of $\bar{w}$ is short hand notation for all of the mass fractions ($w_1, w_2, w_3, \cdots, w_{nc}$). In this notation, the process stream contains a mixture of non-reacting chemical compounds called components of which a total of "*nc*" of them exists.

While the first principle for material balances accounted for chemical reactions, the first principle for the energy balance above appears not to account for chemical reactions. You are familiar with the fact that chemical reactions can be exothermic or endothermic; that is, give off energy or require energy, respectively. Given this fact, how does the energy balance account for the exothermic or endothermic energies associated with chemical reactions? As we will see in Chapter 7 of this *CinChE* manual, these energies are accounted for in how we mathematically model the specific enthalpy quantity. To do this accounting, we will be using the concept of the standard heat of formation.

The general notation of ***iq* = *iqmix*[*T*, *P*, *composition*]** is a functional equation, which says that by knowing the material state properties within the brackets, one can find the intensive quantity (***iq***) for a non-reacting, chemical mixture on the left side of the equation. Some examples of intensive mixture quantities and their functional forms are as follows:

mass density: *dmix*[*T, P, composition*]
specific internal energy: *umix*[*T, P, composition*]
molar volume: *vmix*[*T, P, composition*]
specific enthalpy: *hmix*[*T, P, composition*]

Any functional form (*iqmix*[*T*, *P*, *composition*]) can be represented by a graph, table, equations, or computer software tool like the Aspen HYSYS® simulator. In Chapter 7 of this *CinChE* manual, we will develop the mathematical models and algorithms to find the specific internal energies and enthalpies for non-reacting, chemical mixtures. In the next chapter, we will examine how to find the mass densities and molar volumes for non-reacting, chemical mixtures.

Introduction

If you carefully inspect the overview given in Chapter 2 about the first principles for force, material, equilibrium, and energy, you would note that a number of quantities were identified, like temperature, pressure, amount, flow rate, composition, density, specific volume, and specific enthalpy. In this introductory course, you will need to work with about 40 quantities and their interrelationships, in order to solve the material, equilibrium, and energy requirements for individual process units and a combination of connected process units called a chemical process. Solving these types of problems is dependent on your ability to understand variable quantities, perform units conversions, and manipulate algebraic equations.

Learning about 40 quantities can tax anyone's short-memory (remember the premise of Miller's 7±2 rule). Table "gotche" is an important learning tool, and it is given below. The acronym for this table means a graphic organizer table in chemical engineering. Table "gotche" is designed to handle complexity by using a chunking strategy. This four-page, learning tool organizes the fundamental quantities into eight groups with about five quantities per group, as follows:

Group	Fundamental Quantities
Primary Quantities:	length, mass, time, temperature, and mass-mole
General Quantities:	area, volume, velocity, acceleration, and gravity
Force Quantities:	force, weight, absolute pressure, and gauge pressure
Chemical Quantities:	stoichiometric coefficient, mass-atom, atomic weight, pure-substance molecular weight, and mixture molecular weight
Composition Quantities:	mass fraction, mole fraction, volume fraction, mass concentration, and molar concentration
Physical Quantities:	mass density, specific gravity, molar density, specific volume, and molar volume
Rate Quantities:	mass flow, molar flow, volumetric flow, mass velocity, and molar flux
Energy Quantities:	specific internal energy, pressure-volume work, specific enthalpy, heat, and shaft work

Table "gotche" has five major columns—Name, Symbol, Dimension, Dimensional Units, and Units Equivalences/Basic Relationships—for each quantity. **You should consult this table often when you are trying to solve problems in this introductory course.** If you need more clarification about any quantity in the first seven groups, you should consult Appendix A for a detailed explanation. For clarification on the last group about energy quantities, you will need to sharpen your life-long learning skills by consulting your textbook for this course or doing a browser search on the internet.

Column "Dimensional Units" provides three sub-columns for the three system of units—**cgs**, **mks**, and **fps**—for each quantity. As a chemical engineer, you must be knowledgeable of all three systems of units. The **cgs** (or centimeter-gram-second) system is the formerly-used common scientific system of units. The **mks** (or meter-kilogram-second) system is the SI (Systèm International) system of units, adopted as the international standard. The United States is the last large country that is slowly converting to the SI standard. The **fps** (or foot-pound-second) system is the American engineering system of units, currently used by engineers in the United States. In this introductory course, we assume that you know how to do units conversion. If you are rusty or lack confidence in doing units conversion, you should consult Appendix B and try the exercises to sharpen your units conversion skills. Also, the website www.onlineconversion.com provides numerous conversion factors for all kinds of quantities.

We further assume that you understand the mathematical topics of algebraic equations, transcendental equations, and linear systems of algebraic equations. Linear independence, equation transformations, transcendental identities, and summation notations are also important topics in this introductory course. You should sharpen your skills about these topics by consulting Appendix C.

When you solve material balance problems, sometimes you will be given volume (or volumetric flow rate) and/or sometimes you will be asked to determine volume (or volumetric flow rate). Since material balances are only expressed in terms of mass or molar quantities, you will need to use mass density to relate mass and volume quantities, and you will need to use molar volume to relate molar and volume quantities. Usually, mass densities for pure chemical compounds are tabulated in literature sources. The molar volume is typically found using an equation of state. These two important quantities—mass density and molar volume—are defined below for non-reacting chemical mixture using graphic organizers.

The list below summarizes the graphic organizers (**go**) that appear in the remainder of this chapter. The example problems appearing in the Chapters 4 thru 7 of this *CinChE* manual require the application of information found in Table “gotche” and the graphic organizers.

If you have any questions about the graphic organizers, please consult with one of your teammates or contact the instructor. The instructor is very willing to help you, if you ask.

In the Acrobat Reader version (.pdf file) of this *CinChE* manual, you can view popup notes that appear in many of the remaining pages of the graphic organizers and example problems. You are encouraged to view the “pdf” version while you read the paper copy of this manual. Type the following web link to access it:

http://www.departments.bucknell.edu/chem_eng/cheg200/CinChE_Manual/a_whiteCinChE.pdf

The popup notes provide valuable information to help clarify the content within a graphic organizer or an example problem. You can view but not copy or print the “pdf” version of this *CinChE* manual.

Mass Density of a Chemical Mixture

Mass density (ρ) relates mass and volume. It is an intensive property that is most often associated with liquid or solid mixtures of chemical compounds. Mass density is defined in Table "gotche" above, and its amount and rate forms for a mixture of chemical components are as follows:

$$\rho = \frac{m}{V} \qquad or \qquad \rho = \frac{\dot{m}}{\dot{V}}$$

where the density of a liquid or solid mixture of chemical compounds is given by the following equation:

$$\rho = \frac{1}{\sum_{j=1}^{nc} \frac{w_j}{\rho_j}} \qquad \textit{for an ideal mixture}$$

The composition for a mixture of non-reacting chemical compounds is defined by the chemical components (*j-th's*) and their mass fractions (w_j's), of which there are "*nc*" of them. When "*nc* = 1", the density (ρ) of the mixture reduces to the density (ρ_j) of the pure chemical component *j*, because its mass fraction is one.

You should consult Appendix D to see the derivation of this density equation for a mixture, as well as the other important derivations for mixtures that you may need when you are trying to solve material balance problems. An ideal mixture implies that the volumes of the pure chemical components are additive when they are combined to form the liquid or solid mixture, a fairly good assumption for chemical components that have similar molecular structures.

In the above summation, the density (ρ_j) of pure chemical component *j* at the temperature (T) and pressure (P) of the mixture is given by the following functional equation:

$$\rho_j = density\left[T, P, pure\ component\ j\right]$$

The notation *density*[…] is a functional form that means knowing the material state properties within the brackets, one can find the intensive quantity of pure component *j* on the left side of the equation. In general, any functional form can be represented by a graph, table, equations, or computer software tool like the Aspen HYSYS® simulator and the AIChE eLibrary database.

The liquid or solid density of a pure chemical compound is often recorded in tables of various literature sources as a specific gravity (sg_j) value. This value is a ratio of the density of the compound of interest at 20°*C* to the density of pure water at 4°*C*. As an example, the specific gravity of toluene is:

$sg_{TL} = \frac{\rho_{TL}\ at\ 20^\circ C}{\rho_{H_2O}\ at\ 4^\circ C} = 0.866\ \frac{20^\circ}{4^\circ}$ from the Felder and Rousseau textbook [2005] in Table B.1	ρ_{water} @ 4°*C* = 1.000 *g/mL* = 1.000 *kg/L* = 62.428 lb_m/ft^3

After you obtain a specific gravity value from a literature source, be sure you know what the temperature ratio is for that value. For solids and liquids, the denominator temperature is usually zero for pure water.

For toluene at 20°*C*, its density is 0.866·(1.000) *g/mL*, 0.866·(1.000) k*g/L*, or 0.866·(62.428) lb_m/ft^3, depending upon on what units you need in order to solve a particular material balance problem.

For most process applications, the liquid or solid density for a mixture of chemical components is a function of temperature, but it is usually independent of pressure because a liquid or solid is assumed to be incompressible. For liquid mixtures as well as gas mixtures, software tools like the Aspen HYSYS® simulator account for the effect of temperature, pressure, and composition on any mixture density.

Molar Volume of a Chemical Mixture

Molar volume ($\hat{V}$) relates mass-moles and volume. It is an intensive property that is most often associated with gaseous or liquid mixtures of chemical compounds. Molar volume is defined in Table "gotche" above, and its amount and rate forms for a mixture of chemical components are as follows:

$$\hat{V} = \frac{V}{n} \qquad or \qquad \hat{V} = \frac{\dot{V}}{\dot{n}}$$

In general, the molar volume for a mixture of chemical components is a function of temperature (*T*), pressure (*P*), and molar composition ($\bar{x}$), as expressed by the following functional equation:

$$\hat{V} = eos\left[T, P, \bar{x}\right]$$

where the symbol $\bar{x}$ is a short notation for all of the mole fractions ($x_1, x_2, x_3, \cdots, x_{nc}$) in the mixture, of which there are "*nc*" of them. The notation *eos*[…] is a functional form that means knowing the state properties within the brackets, one can find the intensive quantity of molar volume on the left side of the equation. In general, any functional form can be represented by a graph, table, equations, or computer software tool like the Aspen HYSYS® simulator. **The function "*eos*" is called an equation of state.**

Many equations of state can describe the pressure-volume-temperature (PVT) relationship of a chemical mixture for the gas, vapor or supercritical fluid phases, and some of them can predict the liquid phase as well. When "$nc = 1$", the molar volume ($\hat{V}$) of the mixture reduces to the molar volume ($\hat{V}_j$) of pure chemical component *j-th*, because its mole fraction is one. Some example equations of state are described using graphic organizers in the remainder of this chapter. A list of those examples is:

- Ideal Gas Law, the Simplest Equation of State
- Pure Chemical Compounds and Their Physical Properties
- PVT Diagram for Pure Carbon Dioxide based on Experimental Data
- PVT Diagram for Pure Carbon Dioxide based on the Ideal Gas Law
- PVT Diagram for Pure Carbon Dioxide based on the Van der Waals Equation
- PVT Diagram for Pure Carbon Dioxide based on the Redlich-Kwong Equation
- PVT Diagram for Pure Carbon Dioxide based on the Virial Equation
- Benedict-Webb-Rubin Equation and some other Cubic Equations of State
- PVT Diagram for any Substance based on Generalized Compressibility Factor
- Peng-Robinson Equation of State for Pure Compounds and Mixtures
- Two CO_2 PVT Diagrams based on Peng-Robinson and Soave-Redlich-Kwong

Each graphic organizer presents equations and/or a pressure-volume-temperature (or PVT) diagram. The conditions under which an equation of state is applicable are given. Some of these equations of state are limited to the gas, vapor, and fluid phases, and some predict the molar volume in certain phase regions poorly.

An interesting exercise is for you to make paper copies of the seven PVT diagrams for pure carbon dioxide. You can then super-impose one of the PVT diagrams based on an equation of state over the PVT diagram based on experimental data, hold them up to a light, and note the differences.

eLEAPS How To **eLEAPS script**

Simplest Equation of State

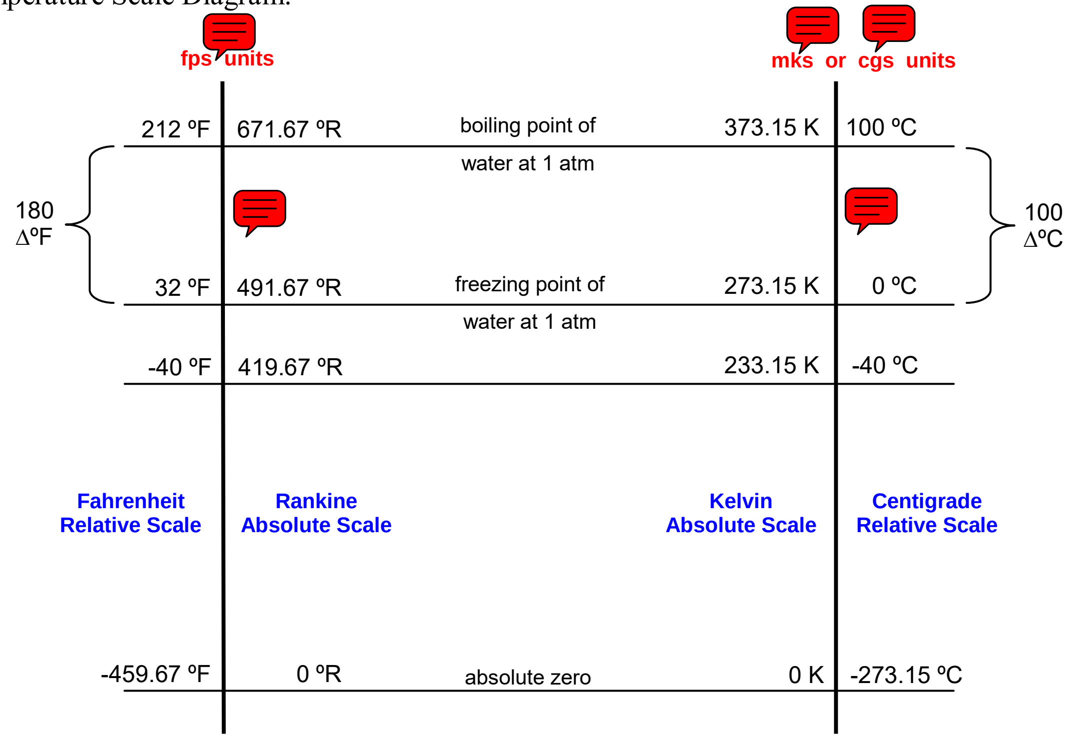
An eLEAPS Session

An equation of state (**EOS**) predicts the relationship between the temperature, pressure, moles, and volume of a single-phase substance, that is, either all-liquid or all-gas mixture of chemical compounds.

Temperature

A. Temperature is a measure of the thermal energy of the random motion of the molecules of a chemical substance at thermal equilibrium. A substance can be pure or a mixture of chemical compounds.

B. Temperature Scale Diagram:



C. Conversion Factors:

$\Delta^\circ F \equiv \Delta R$ $\quad$ $\Delta^\circ C \equiv 1.8\,\Delta^\circ F$ $\quad$ $\Delta^\circ C$ is sometimes expressed as C° or just $^\circ C$.

$\Delta^\circ C \equiv \Delta K$ $\quad$ $\Delta K \equiv 1.8\,\Delta R$ $\quad$ $\Delta^\circ F$ is sometimes expressed as F° or just $^\circ F$.

D. Conversion Equations:

$\left[T_{^\circ F} - 32^\circ F\right] \Delta^\circ F = \left[T_{^\circ C} - 0^\circ C\right] \Delta^\circ C \cdot \left\langle \frac{1.8\,\Delta^\circ F}{\Delta^\circ C} \right\rangle$	$\left[T_{^\circ C} - \left(-273.15^\circ C\right)\right] \Delta^\circ C = \left[T_K - 0\,K\right] \Delta K \cdot \left\langle \frac{\Delta^\circ C}{\Delta K} \right\rangle$
$T_{^\circ F} - 32 = 1.8\,T_{^\circ C}$ *or* $T_{^\circ F} - 32 = \frac{9}{5}\,T_{^\circ C}$	$T_K = T_{^\circ C} + 273.15$
$\left[T_{^\circ R} - 0^\circ R\right] \Delta R = \left[T_K - 0\,K\right] \Delta K \cdot \left\langle \frac{1.8\,\Delta R}{\Delta K} \right\rangle$	$\left[T_{^\circ F} - \left(-459.67^\circ F\right)\right] \Delta^\circ F = \left[T_{^\circ R} - 0^\circ R\right] \Delta R \cdot \left\langle \frac{\Delta^\circ F}{\Delta R} \right\rangle$
$T_{^\circ R} = 1.8\,T_K$	$T_{^\circ R} = T_{^\circ F} + 459.67$

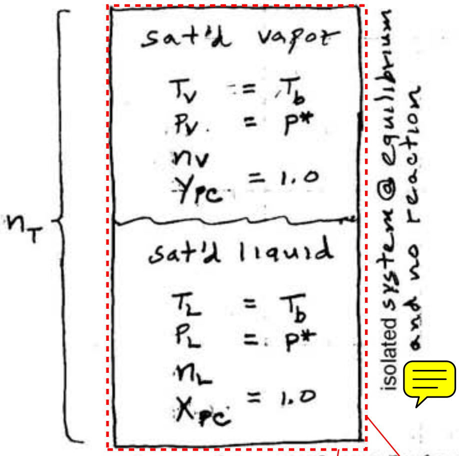
E. In any equation of state, <u>absolute</u> temperature must be used, either K or $^\circ R$, but not $^\circ C$ or $^\circ F$.

Popup notes and/or web links on Pages 3-10 to 3-12 can be accessed through the above web link for the **eLEAPS script**.

Pure Component Phase Equilibrium

1 of 2

Diagram



where pc - pure component

Model

$$n_T = n_V + n_L$$
$$1.0 = n_V/n_T + n_L/n_T$$
$$1.0 = V_f + L_f$$

$$\boxed{\begin{aligned} V_T &= V_{SV} + V_{SL} \\ n_T \hat{V}_T &= n_V \hat{V}_{SV} + n_L \hat{V}_{SL} \\ \hat{V}_T &= V_f \hat{V}_{SV} + L_f \hat{V}_{SL} \end{aligned}}$$

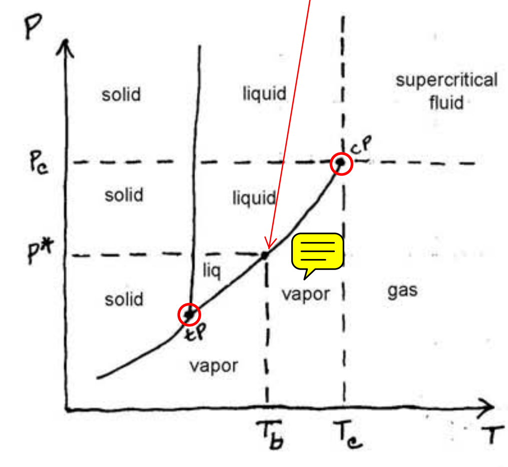
$$U_T = U_{SV} + U_{SL}$$
$$\hat{U}_T = V_f \hat{U}_{SV} + L_f \hat{U}_{SL}$$

$$H_T = H_{SV} + H_{SL}$$
$$\hat{H}_T = V_f \hat{H}_{SV} + L_f \hat{H}_{SL}$$

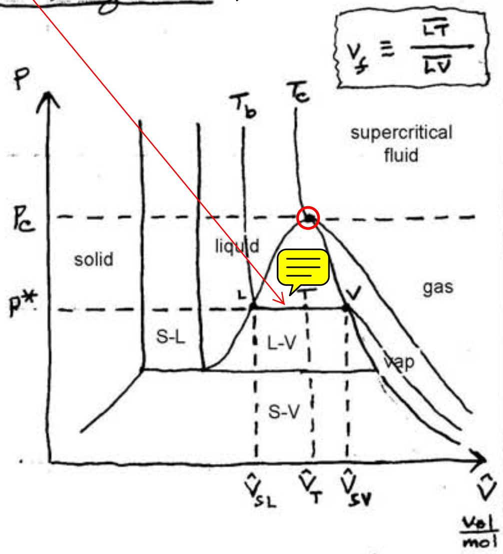
Thermal equil.: $T_V = T_L = T_b$ ← boiling temperature.

Mechanical equil.: $P_V = P_L = P^*$ ← vapor pressure, F&R, 3rd Ed., p. 243

PT Diagram



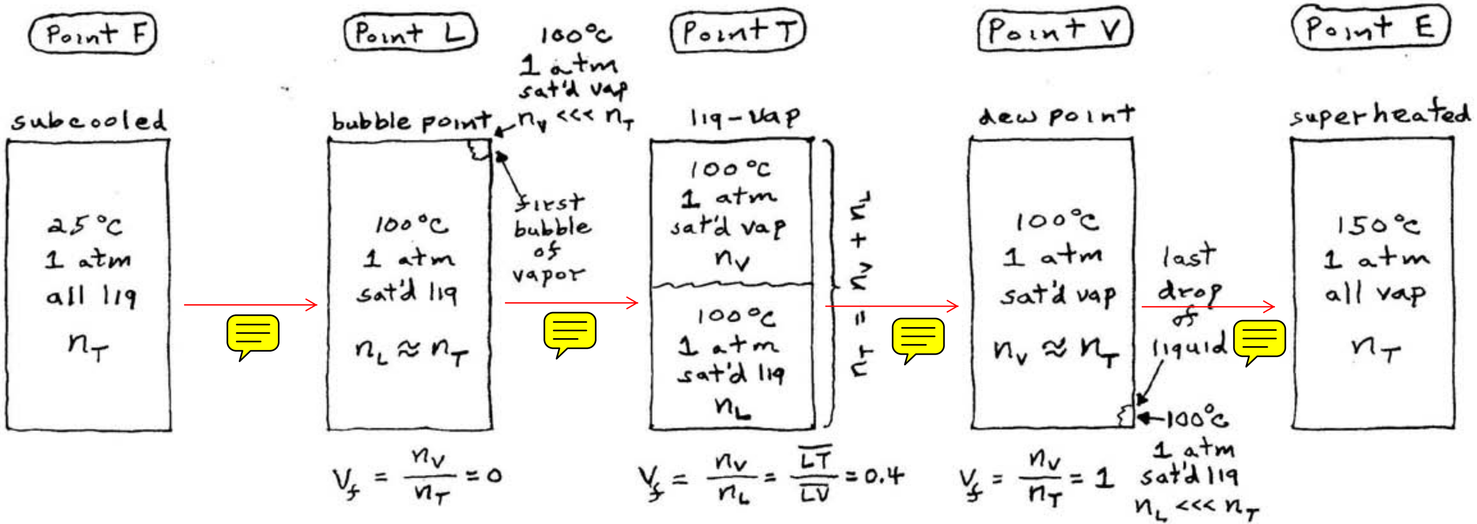
PVT Diagram



For $P^* = 1$ atm, $T_b = T_{NBP}$ found in Table B.1, F&R, 3rd Ed.

For vapor and liquid coexisting at same time, line in PT diagram between triple point and critical point is modeled by the Antoine Equation: $\log_{10} P^* = A - \frac{B}{T + C}$ as given in Table B.4, F&R, 3rd Ed.

Process of Heating Pure Water from 25°C to 150°C at 1 atm



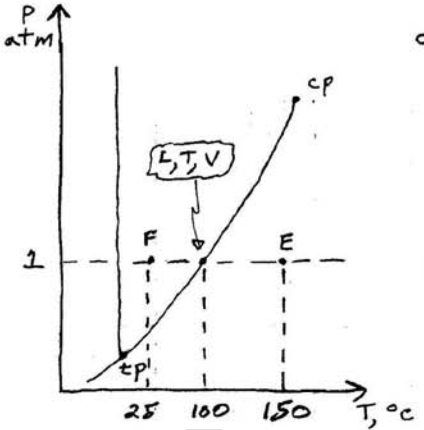
$$V_f = \frac{n_V}{n_T} = 0$$

$$V_f = \frac{n_V}{n_L} = \frac{\overline{LT}}{LV} = 0.4$$

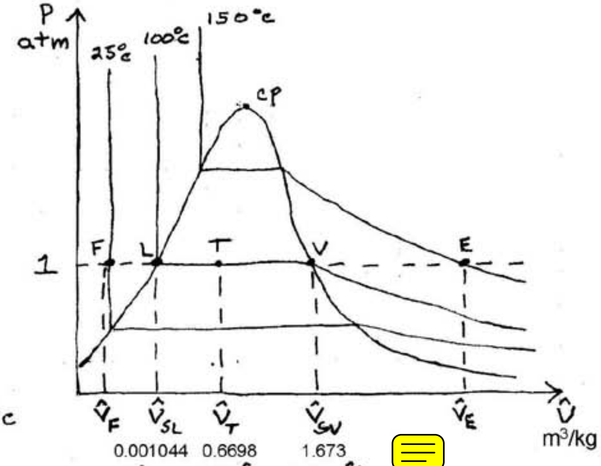
$$V_f = \frac{n_V}{n_T} = 1$$

Click here for a tutorial on sketching property diagrams.

PT Diagram

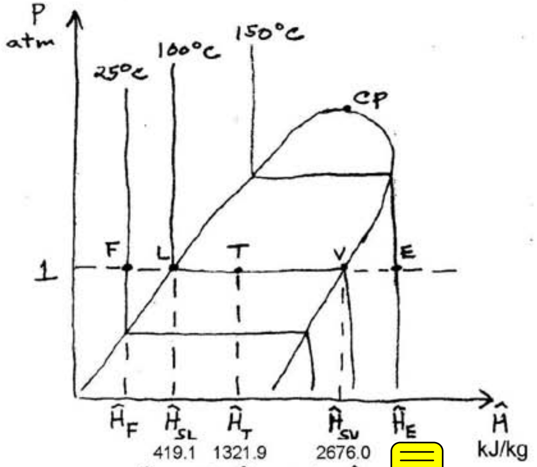


PVT Diagram



$$\hat{V}_T = V_f \hat{V}_{SV} + L_f \hat{V}_{SL}$$

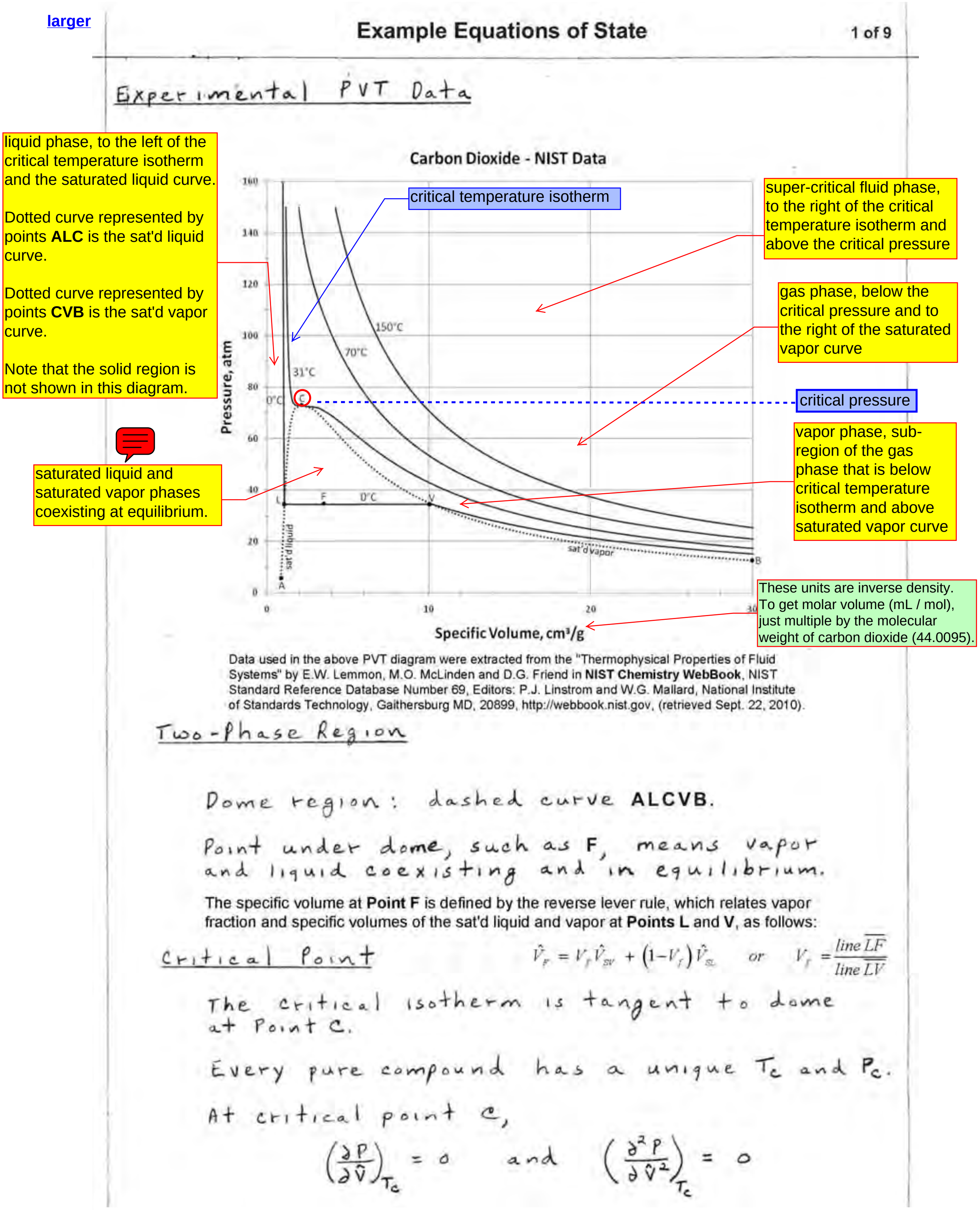
PH Diagram



$$\hat{H}_T = V_f \hat{H}_{SV} + L_f \hat{H}_{SL}$$

Click here to view how to read the steam tables in the Felder and Rousseau (F&R) textbook [2005, pp. 638-639 & 642-651].

larger



Example Equations of State

1 of 9

Experimental PVT Data

Carbon Dioxide - NIST Data

liquid phase, to the left of the critical temperature isotherm and the saturated liquid curve.

Dotted curve represented by points **ALC** is the sat'd liquid curve.

Dotted curve represented by points **CVB** is the sat'd vapor curve.

Note that the solid region is not shown in this diagram.

critical temperature isotherm

super-critical fluid phase, to the right of the critical temperature isotherm and above the critical pressure

gas phase, below the critical pressure and to the right of the saturated vapor curve

critical pressure

vapor phase, sub-region of the gas phase that is below critical temperature isotherm and above saturated vapor curve

saturated liquid and saturated vapor phases coexisting at equilibrium.

These units are inverse density. To get molar volume (mL / mol), just multiple by the molecular weight of carbon dioxide (44.0095).

Data used in the above PVT diagram were extracted from the "Thermophysical Properties of Fluid Systems" by E.W. Lemmon, M.O. McLinden and D.G. Friend in **NIST Chemistry WebBook**, NIST Standard Reference Database Number 69, Editors: P.J. Linstrom and W.G. Mallard, National Institute of Standards Technology, Gaithersburg MD, 20899, http://webbook.nist.gov, (retrieved Sept. 22, 2010).

Two-Phase Region

Dome region: dashed curve **ALCVB**.

Point under dome, such as **F**, means vapor and liquid coexisting and in equilibrium.

The specific volume at **Point F** is defined by the reverse lever rule, which relates vapor fraction and specific volumes of the sat'd liquid and vapor at **Points L** and **V**, as follows:

$$\hat{V}_F = V_f \hat{V}_{SV} + \left(1 - V_f\right)\hat{V}_{SL} \quad or \quad V_f = \frac{line\ \overline{LF}}{line\ \overline{LV}}$$

Critical Point

The critical isotherm is tangent to dome at Point C.

Every pure compound has a unique T_c and P_c.

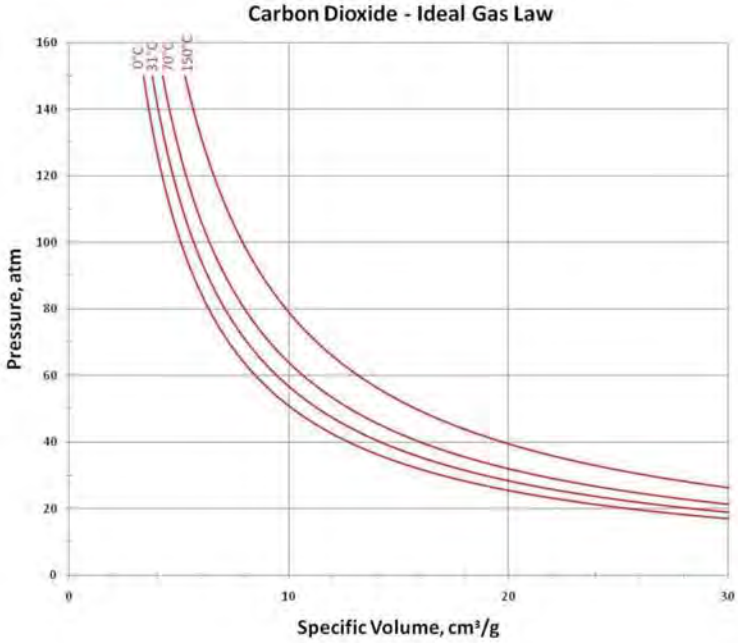
At critical point c,

$$\left(\frac{\partial P}{\partial \hat{V}}\right)_{T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial \hat{V}^2}\right)_{T_c} = 0$$

Click here to view the pressure-temperature (PT), pressure-enthalpy (PH), and pressure-internal-energy (PU) diagrams for pure CO2.

Example Equations of State

Perfect Gas Law



$$P \hat{V} = RT$$

Good at high T and low P.

Yields an error of < 1% if $\hat{V}$ (= RT/P) is:

For carbon dioxide, the limit is greater than 454 cm^3/g.

(1) $\hat{V} > 5$ ℓ/gmol (80 ft^3/lbmol) for diatomic gases

(2) $\hat{V} > 20$ ℓ/gmol (320 ft^3/lbmol) for other gases.

Does not predict two-phase and liquid regions.

To compare the "NIST data" PVT diagram with some example equation-of-state PVT diagrams, **click here** to download, open an Excel file, and view worksheets like "**ig-PVT**" and "**ig-nist**".

Example Equations of State

8 of 9

Molar Volume of a Pure Substance **Peng-Robinson Cubic Equation of State**

$$P = \frac{RT}{\hat{V} - b} - \frac{a\alpha}{\hat{V}^2 + 2b\hat{V} - b^2} \quad or \quad z^3 + (B-1)z^2 + (A - 3B^2 - 2B)z + (B^3 + B^2 - AB) = 0$$

$$a = 0.45724\frac{(RT_c)^2}{P_c} \qquad b = 0.07780\frac{RT_c}{P_c} \qquad z = \frac{P\hat{V}}{RT}$$

$$\alpha = \left[1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)\left(1 - \sqrt{T_r}\right)\right]^2 \qquad T_r = \frac{T}{T_c}$$

Fugacity Coefficient of a Pure Substance

$$\ln\phi = (z-1) - \ln(z-B) - \frac{A}{2.8284B}\ln\left(\frac{z + 2.4142B}{z - 0.4142B}\right)$$

$$A = \frac{a\alpha P}{(RT)^2} \qquad B = \frac{bP}{RT}$$

Vapor-Liquid Equilibrium for a Pure Substance: $\phi^V = \phi^L$

Molar Volume of a Mixture of Substances **Peng-Robinson Cubic Equation of State**

$$P = \frac{RT}{\hat{V} - b} - \frac{a\alpha}{\hat{V}^2 + 2b\hat{V} - b^2} \quad or \quad z^3 + (B-1)z^2 + (A - 3B^2 - 2B)z + (B^3 + B^2 - AB) = 0$$

$$a\alpha = \sum_{j=1}^{nc}\sum_{k=1}^{nc} x_j x_k (a\alpha)_{jk} \qquad b = \sum_{j=1}^{nc} x_j b_j \qquad (a\alpha)_{jk} = \sqrt{(a\alpha)_{jj}(a\alpha)_{kk}}$$

$$a_j = 0.45724\frac{(RT_{c,j})^2}{P_{c,j}} \qquad b_j = 0.07780\frac{RT_{c,j}}{P_{c,j}} \qquad z = \frac{P\hat{V}}{RT}$$

$$\alpha_j = \left[1 + \left(0.37464 + 1.54226\omega_j - 0.26992\omega_j^2\right)\left(1 - \sqrt{T_{r,j}}\right)\right]^2 \qquad T_{r,j} = \frac{T}{T_{c,j}}$$

Fugacity Coefficient of the *i-th* Substance in a Mixture of Substances

$$\ln\hat{\phi}_i = \frac{B_i}{B}(z-1) - \ln(z-B) + \frac{A}{2.8284B}\left[\frac{B_i}{B} - \frac{2}{a\alpha}\sum_{j=1}^{nc} x_j (a\alpha)_{ij}\right]\ln\left(\frac{z + 2.4142B}{z - 0.4142B}\right)$$

$$A = \sum_{j=1}^{nc}\sum_{k=1}^{nc} x_j x_k A_{jk} \qquad A_{jk} = \sqrt{A_{jj}A_{kk}} \qquad A_{jj} = \frac{(a\alpha)_{jj} P}{(RT)^2}$$

$$B = \frac{bP}{RT} \qquad B_i = \frac{b_i P}{RT} \qquad (a\alpha)_{jj} = a_j \alpha_j$$

Vapor-Liquid Equilibrium for the *i-th* Substance in a Mixture: $y_i\hat{\phi}_i^V P = x_i\hat{\phi}_i^L P$

Problem-Solving Strategy

Chapter 2 provided for you an overview of the first principles for material, equilibrium, and energy, which are the important subject matters for this introductory course. By way of an example problem that required the use of the force principle, Chapter 1 illustrated the problem solving methodology that we will use in this course to solve well-defined problems. Because this methodology is more systematic, we will use it instead of the one presented in your required textbook for the course. To refresh your memory, the problem solving methodology illustrated in Chapter 1 is outlined as follows:

Activity	Outcome
1. understand the problem	conceptual model, a.k.a. diagram
2. model the phenomena	mathematical model
3. devise a plan	mathematical algorithm
4. carry out the plan	numerical solution
5. review the problem solution	heuristic observations
6. report the problem solution	formal documentation

This methodology provides a step-by-step structure that will help you to reach the final goal, a single correct answer. Although these steps or stages are sequential, feedback exists between stages. For example, while reviewing the problem solution, you might observe the need to calculate another quantity which was forgotten in the original mathematical model.

The above problem-solving methodology is a critical-thinking strategy called means-ends analysis. It breaks the problem down into smaller sub-problems, each with its own goal, called a sub-goal. The sub-goal of one sub-problem becomes the initial sub-state for the next sub-problem. Each sub-goal moves the engineer closer and closer to the final goal, the correct answer. Sub-problem 1 of "understand the problem" has as its sub-goal a conceptual model. Its initial sub-state is the problem statement, the initial state of the overall problem. Sub-problem 2 of "model the phenomena" has as its sub-goal a mathematical model and as its initial sub-state the conceptual model. Sub-problem 3 of "devise a plan" has as its sub-goal a mathematical algorithm and as its initial sub-state the mathematical model. Sub-problem 5 of "carry out the plan" has as its sub-goal a numerical solution and as its initial sub-state the mathematical algorithm. Sub-problem 4 of "review the problem solution" begins with drafts of the math model, math algorithm, and numerical solution and concludes with the heuristic observations. Finally, Sub-problem 6 of "report the problem solution" begins with the drafts of the first five outcomes and concludes with a formal documentation of the complete problem solution.

Each of the stages in the problem-solving methodology are themselves ill-defined problems. For each of the six-stage sub-problems, how do you "best" draw the problem's conceptual model, develop its math model, construct its math algorithm, do its numerical solution, discover its heuristic observations, and document its solution? What strategy or combination of strategies (i.e., what plan) should be used to solve each sub-problem and why? The remainder of this chapter outlines the strategies (or plans) to solve problems that require the application of the first principles for material, equilibrium, and/or energy.

When applying the problem-solving methodology to the same well-defined problem, each student might produce a different solution path. These differing solutions might have some variations in their diagrams, assumptions, math models, math algorithms, and numerical solutions. Although each solution produces its own correct answer, these answers will be equivalent, only if all solutions are based on the same assumptions.

Before we examine the strategies for the first five stages of the problem solving methodology, you can view the general anatomy for a mathematical model and algorithm as given on the next page. All problems requiring material balances that you will solve in this introductory course will exhibit this anatomy. **Since we have established standard nomenclature for variables in Table "gotche" of Chapter 3, you will not have to write variable descriptions as part of your mathematical models.**

7. List all chemical reactions (if applicable) and label each with a Roman numeral (i.e., I, II, etc.). Balance each chemical reaction so that its stoichoimetric coefficients are expressed with a lowest common denominator of one. For example, $2H_2 + O_2 \rightarrow 2H_2O$ and not $H_2 + ½O_2 \rightarrow H_2O$.
8. List the **Finds** with symbols and units.
9. Start the list of assumptions. Identify the process type and possibly the operation state.

   The assumptions are associated with the mathematical model. Some of these assumptions control what terms are dropped from the first principle equations.

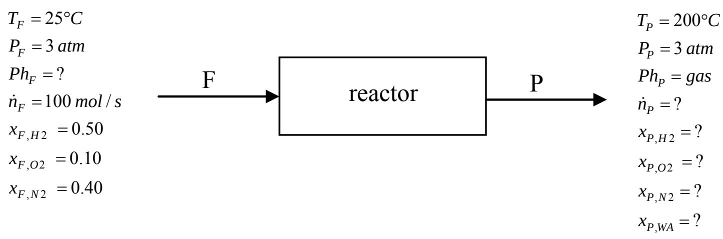
   You only need to state the operation state for a continuous process.

Definitions

System	A spherical boundary (like a balloon) that you imagine exists around the process unit or units. Usually, we represent this boundary by drawing a dashed line around the diagram.
Material	One or more chemical substances being transformed by the process unit. The phase of the material can be gas, liquid, or solid, or combination thereof.
Process Type Click here to see examples of the four process types.	Continuous Process - all chemical substances are continuously flowing across the systems boundary; that is, some may flow into, some may flow out, and some may flow into and out of that imaginary boundary, but none of them are batch. Batch Process - All chemical substances are contained within the system boundary. No chemical substance crosses the system boundary; that is, none of the chemical substances flow into or out of that imaginary boundary. Semi-Batch Process - at least one chemical substance crosses the system boundary. It either flows into or flows out of that imaginary boundary. All remaining chemical substances do not cross the system boundary. Semi-Continuous Process - at least one chemical substance flows into and out of the system boundary. All remaining chemical substances either 1) do not cross that imaginary boundary or 2) one or more of them flow into or flow out of that imaginary boundary and the rest do not. For all remaining chemical substances, they operate in a batch or semi-batch manner.
Operation State	The operational state indicates whether the amount of material within the system boundary is steady with time or changes with time. Steady State - the amount of material within the system boundary is constant with the passing of time. Unless told otherwise, a continuous process will always be assumed to operate at steady state. Unsteady State - the amount of material within the system boundary is changing with the passing of time, either accumulating or depleting. This condition is always true for a batch, semi-batch, or semi-continuous process.
Process State	It is the temperature, pressure, amount, and composition of the material in a process stream or within the system boundary. We use symbols T, P, $\dot{m}\ (or\ \dot{n})$, and $\overline{w}\ (or\ \overline{x})$ to represent the state of the material in process streams, and we use symbols T, P, $m\ (or\ n)$, and $\overline{w}\ (or\ \overline{x})$ to represent the state of the material within the system boundary at the initial time (t_i) and final time (t_f) only.

Continuous Reactor Example { when the chemical reactions are given }

Diagram



Givens:

Rxn I: $2\ H_2 + O_2 \rightarrow 2\ H_2O$

50 mol% conversion of O_2

Finds:

$\dot{V}_P$ in L / h

Assumptions:

1. continuous process
2. steady state
3. Mix P is ideal gas

Mathematical Model

① Total: $\dot{n}_F - \dot{n}_P - 1\ \dot{R}_I = 0$

② H_2: $0.50\ \dot{n}_F - \dot{n}_{P,H2} - 2\ \dot{R}_I = 0$

③ O_2: $0.10\ \dot{n}_F - \dot{n}_{P,O2} - 1\ \dot{R}_I = 0$

④ N_2: $0.40\ \dot{n}_F - \dot{n}_{P,N2} = 0$

⑤ H_2O: $- \dot{n}_{P,WA} + 2\ \dot{R}_I = 0$

✓ Mix P: $\dot{n}_P = \dot{n}_{P,H2} + \dot{n}_{P,O2} + \dot{n}_{P,N2} + \dot{n}_{P,WA}$

# vars = 7
# eqns = 5
DOF = 2

⑥ **Conversion:** $$\frac{0.10\ \dot{n}_F - \dot{n}_{P,O2}}{0.10\ \dot{n}_F} = 0.50$$

⑦ **ideal gas:** $$P_P\ \dot{V}_P = \dot{n}_P\ R\ T_P$$

# vars = 10
# eqns = 7
DOF = 3

Click here to solve this math model using the Excel "EZ Setup"/Solver Add-Ins.

Since three variables [$\dot{n}_F$, T_P, P_P] and a constant [R] are known, the math model can therefore be solved!

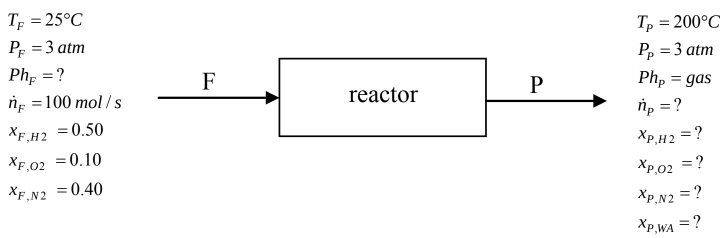
The symbol R without a dot and subscript will *always* represent the *ideal gas constant*. The symbol $\dot{R}_I$ with a dot *and/or* a subscript will always represent the extent of reaction. Example net units for the $\dot{R}_I$ term in the H_2 balance are: $2\ \dot{R}_I\ \ is\ \ \dfrac{2\ g-mol\ of\ H_2}{g-rxns}\left(\dfrac{g-rxns}{s}\right)$. What does $\dot{R}_I$ mean?

If *no reactions* exist in a continuous problem, then the material balances would not contain $\dot{R}$ terms.

Continuous Reactor Example

{ when the chemical reactions are not given }

Diagram



Givens:

50 mol% conversion of O_2

Finds:

$\dot{V}_P$ in L / h

Assumptions:

1. continuous process
2. steady state
3. Mix P is ideal gas

Mathematical Model

✓ Total: $$\dot{m}_F - \dot{m}_P = 0$$

① H atom: $$2\,(0.50\,\dot{n}_F) - 2\,\dot{n}_{P,H2} - 2\,\dot{n}_{P,WA} = 0$$

② O atom: $$2\,(0.10\,\dot{n}_F) - 2\,\dot{n}_{P,O2} - 1\,\dot{n}_{P,WA} = 0$$

③ N atom: $$2\,(0.40\,\dot{n}_F) - 2\,\dot{n}_{P,N2} = 0$$

④ Mix P: $$\dot{n}_P = \dot{n}_{P,H2} + \dot{n}_{P,O2} + \dot{n}_{P,N2} + \dot{n}_{P,WA}$$

# vars = 6
# eqns = 4
DOF = 2

⑤ **Conversion:** $$\frac{0.10\,\dot{n}_F - \dot{n}_{P,O2}}{0.10\,\dot{n}_F} = 0.50$$

⑥ **ideal gas:** $$P_P\,\dot{V}_P = \dot{n}_P\,R\,T_P$$

# vars = 9
# eqns = 6
DOF = 3

Click here to solve this math model using the Excel "EZ Setup"/Solver Add-Ins.

Since three variables [$\dot{n}_F$, T_P, P_P] and a constant [R] are known, the math model can therefore be solved!

In any atom balance, each term has net units of number of atoms per time. For example, the number of H atoms in the feed stream is given by the expression: {note a **mol** and **g-mol** are synonymous}

$$2\,(0.50\,\dot{n}_F)\quad is\quad \frac{2\ g-atoms\ of\ H}{g-mol\ of\ H_2}\left(\frac{g-mol\ of\ H_2}{g-mol\ of\ mix\ F}\cdot\frac{g-mol\ of\ mix\ F}{s}\right)$$

When the flow rate is kg-mol/h or lb-mol/min, the net units are “kg-atoms/h” or “lb-atoms/min”, respectively.

Batch Reactor Example

Diagram

initial time, t_i	final time, t_f
closed container	closed container
$T_i = 25°C$ $P_i = 1\ atm$ $Ph_i = ?$ $n_i = ?$ $x_{i,H2} = 0.50$ $x_{i,O2} = 0.10$ $x_{i,N2} = 0.40$	$T_f = 200°C$ $P_f = 1.5\ atm$ $Ph_f = gas$ $n_f = ?$ $x_{f,H2} = ?$ $x_{f,O2} = ?$ $x_{f,N2} = ?$ $x_{f,WA} = ?$

Givens:

Rxn I: $2\ H_2 + O_2 \rightarrow 2\ H_2O$

50 mol% conversion of O_2

Finds:

V_f in L

Assumptions:

1. batch process
2. unsteady state
3. ideal gas behavior
4. $n_i = 100$ g-mol

Mathematical Model

① Total: $-\ 1\,R_I = n_f - n_i$

② H_2: $-\ 2\,R_I = n_{f,H2} - 0.50\ n_i$

③ O_2: $-\ 1\,R_I = n_{f,O2} - 0.10\ n_i$

④ N_2: $0 = n_{f,N2} - 0.40\ n_i$

⑤ H_2O: $2\,R_I = n_{f,WA}$

✓ Mix P: $n_f = n_{f,H2} + n_{f,O2} + n_{f,N2} + n_{f,WA}$

\# vars = 7
\# eqns = 5
DOF = 2

⑥ **Conversion:** $$\frac{0.10\ n_i - n_{f,O2}}{0.10\ n_i} = 0.50$$

⑦ **ideal gas:** $$P_f\ V_f = n_f\ R\,T_f$$

\# vars = 10
\# eqns = 7
DOF = 3

Click here to solve this math model using the Excel "EZ Setup"/Solver Add-Ins.

Since three variables [n_i, T_f, P_f] and a constant [R] are known, the math model can therefore be solved!

The symbol R without a dot and subscript will *always* represent the *ideal gas constant*. The symbol R_I with a subscript will always represent the extent of reaction. Example net units for the R_I term in the H_2 balance are: $2\ R_I\ \ is\ \ \frac{2\ g-mol\ of\ H_2}{g-rxns}\left(g-rxns\right)$. What does R_I mean, physically?

If *no reactions* exist in a batch problem, then the material balances would not contain R_I terms.

Transformation Process

$$\boxed{\textbf{Mathematical Model}} \xrightarrow[\text{procedure}]{\text{partitioning}} \boxed{\textbf{Mathematical Algorithm}}$$

The mathematical algorithm is a plan (or blueprint) that identifies the independent variables which satisfy the degrees of freedom (DOF) and states the order in which the equations from the mathematical model are to be solved. The systematic partitioning procedure described below moves equations from the mathematical model to the mathematical algorithm.

Partitioning Procedure

1. Define the functional equation for the mathematical algorithm as follows:

   $$[\text{ dependent variables }] = f[\text{ independent variables }]$$

   where the independent variables are those variables in the mathematical model that have known values. The number of independent variables must equal the degrees of freedom (DOF); that is, # of variables minus # of equations.

   The dependent variables are either all of the unknown variables in the mathematical model or just those unknown variables of primary interest. We often just list the “Finds” quantities for the dependent variables.

   The symbol “*f*” implies a function. Basically, a functional equation says that knowing the independent variables you can determine the dependent variables. Often, we replace the symbol “*f*” with a more descriptive name, like “reactor” or “filterPress”.

   The steps in the mathematical algorithm illustrate the order in with the equations must be solved to find the unknown variables. The remainder of this partitioning procedure will help you to develop those steps in the mathematical algorithm.

2. Underline the known variables in the mathematical model using a red pencil or pen. These underlining variables are known in the equations. Some of these known variables could be values that you will look up later in a literature source such as the ideal gas constant or the molecular weights of pure chemical substances.

3. If an algebraic equation contains only one unknown variable, then
   a) Solve algebraically for that unknown variable and simplify its expression.
   b) Remove the resulting equation from the math model, place it as the next step in the math algorithm, and replace its equals sign with a left arrow (←).
   c) Circle this unknown variable in the remaining equations of the math model.
   d) Reapply Step 3.

4. If an unknown variable appears in only one equation, then
   a) Solve algebraically for that unknown variable and simplify its expression.
   b) Remove the resulting equation from the math model, place it before the next-to-the-last step that was placed in the math algorithm, and replace its equals sign with a left arrow (←).

   c) Reapply Step 4.

5. If a linear set of algebraic equations exists (i.e., as many unknown variables as equations), then
   a) Find the smallest set (i.e., 2x2, 3x3, 4x4, etc.) and algebraically rearrange each linear equation in the set into the form: unknown terms = constant(s).
   b) Remove the rearranged set from the math model and place it as the next step in the math algorithm using a **SOLVE** construct. For example, for a (3x3) set:

      SOLVE m_{FH}, m_W, m_{FW} **in**

$$\begin{array}{rcrcrcl} m_{FH} & - & 0.25\,m_W & & & = & m_P \\ & - & 0.45\,m_W & + & m_{FW} & = & 0 \\ x_{FH}\,m_{FH} & & & - & 0.35\,m_{FW} & = & 0 \end{array}$$

      END

      where the unknown terms are lined up vertically in the set of equations. The three unknown variables (m_{FH}, m_W, and m_{FW}) are to be solved simultaneously using the three **coupled linear** equations. The symbol "x_{FH}" and "m_P" are either a known (i.e., given) variable or a calculated variable that appears in an earlier step of the math algorithm.
   c) Circle the to-be-solved variables in the remaining equations of the math model.
   d) Reapply Step 3.

6. If a nonlinear set of algebraic equations exists (as many unknown variables as equations), then
   a) Find the smallest set (i.e., 2x2, 3x3, 4x4, etc.) and algebraically rearrange each equation in the set into the form: unknown terms plus any constant terms = 0.
   b) Remove the rearranged set from the math model and place it as the next step in the math algorithm using a **NSOLVE** construct. For example, for a (3x3) set:

      NSOLVE A, B, V **in**

$$\begin{array}{rcrcl} A & - & 27\,X^2 / V & = & 0 \\ B & - & X / V & = & 0 \\ (m + A / V^2)\,(V - B) & - & 8\,Y & = & 0 \end{array}$$

      END

      The three unknown variables (A, B, and V) are to be solved simultaneously in the **coupled nonlinear** equations. The symbol "m", "X", and "Y" are either a known (i.e., given) variable or a calculated variable that appears in an earlier step of the math algorithm.
   c) Circle the to-be-solved variables in the remaining equations of the math model.
   d) Reapply Step 3.

7. If no additional equations remain in the math model, then stop applying the partitioning procedure. You have moved all equations from the math model to the math algorithm.

eLEAPS How To An eLEAPS Session on the Partitioning Procedure eLEAPS script

SOLVE and NSOLVE Transformations

Click here to view the answers for the eLEAPS session that you accessed at the bottom of Page 4-13.

After completing the above **Partitioning Procedure**, the mathematical algorithm may contain one or more linear SOLVE constructs and/or one or more nonlinear NSOLVE constructs. If a software system like E-Z Solve, Mathcad®, or Mathematica® will be used to solve simultaneously all equations in the mathematical model, then further processing of the SOLVE and NSOLVE constructs is not necessary. When the numerical solution is going to be done manually, each SOLVE and NSOLVE constructs must be further transformed within the mathematical algorithm as described below.

SOLVE Construct

{ transformed only when the numerical solution is going to be done manually }

When the size of a linear SOLVE is greater than (3x3), further processing of this type of construct in the mathematical algorithm is not necessary, because it will be solved by automated means in the numerical solution using a software system like your pocket calculator, Excel®, Matlab®, or E-Z Solve. For a SOLVE with two or three linear algebraic equations, it must to be manually transformed within the mathematical algorithm using the algebraic operations described in Appendix Sections C.4 and C.5. An example of this transformation is shown next.

Symbolic Solution Strategy for a Linear Set

Multiple first two equations, each by a constant:

$$\begin{array}{rrrcll} X & -\,2\,Y & -\,2\,Z & = & 0 & \text{multiple by +2} \\ & -\quad Y & +\,2\,Z & = & 6 & \text{multiple by -4} \\ -2\,X & & +\,4\,Z & = & m_P & \end{array}$$

to get the following:

$$\begin{array}{rrrcll} 2\,X & -\,4\,Y & -\,4\,Z & = & 0 & \\ & +\,4Y & -\,8\,Z & = & -24 & \\ -2\,X & & +\,4\,Z & = & m_P & \text{then add the three equations together} \end{array}$$

to eliminate variables *X* and *Y*:

$$-\,8\,Z = m_P - 24 \quad \Rightarrow \quad Z = \frac{24 - m_P}{8}$$

Back substitute into the 3rd and 2nd equations to find *X* and *Y*:

$$-2\,X + 4\left(\frac{24 - m_P}{8}\right) = m_P \quad \Rightarrow \quad X = 6 - \frac{3}{4}m_P$$

$$-\,Y + 2\left(\frac{24 - m_P}{8}\right) = 6 \quad \Rightarrow \quad Y = -\frac{1}{4}m_P$$

Check the symbolic solution using the first equation:

$$\left(6 - \frac{3}{4}m_P\right) - 2\left(-\frac{1}{4}m_P\right) - 2\left(\frac{24 - m_P}{8}\right) = 0 \quad \Rightarrow \quad OK$$

The above transformation process, called Gaussian Elimination, is to be worked out manually on a separate piece of scrap paper. Then, the yellow-highlighted symbolic equations in the above example

A false solution can occur when the *f(x)* curve is relatively flat with the *x-axis* within some range of *x* values and crosses over the *x-axis* within that range of *x* values. To guard against a false solution, you should not only see how close *f(x)* is to zero, but you should also see if the last two guesses for the unknown variable *x* are close in value too.

How do you transform a NSOLVE construct into an ITERATE construct for a <u>vector unknown variable</u>? This type of ITERATE construct is where you would be simultaneously iterating on a vector of similar quantities like mole fractions or distribution coefficients. You apply the below transformation process <u>only</u> if all unknown variables in the NSOLVE are vector quantities.

As an example, consider the rigorous mathematical model for the vapor-liquid equilibrium of a multi-component mixture of chemical compounds. The fugacity coefficient functions (*phiV* and *phiL*) can be determined from an equation of state like the Peng-Robinson or the Soave-Redlich-Kwong. The mathematical algorithm below shows how to find the equilibrium temperature (*T*), liquid composition ($\overline{x}$), and vapor composition ($\overline{y}$) for a given pressure (*P*), vapor fraction (V_f), and total composition ($\overline{z}$), Vectors $\overline{x}$, $\overline{y}$, and $\overline{z}$ each represent mole fractions, with *nc* chemical components in the mixture.

Mathematical Model

$$
\begin{aligned}
1.0 &= V_f + L_f \\
z_j &= V_f\, y_j + L_f\, x_j && \textit{for } j = 1, 2, \ldots, nc \\
y_j &= K_j\, x_j && \textit{for } j = 1, 2, \ldots, nc \\
K_j &= \hat{\phi}_j^L / \hat{\phi}_j^V && \textit{for } j = 1, 2, \ldots, nc \\
\hat{\phi}_j^L &= phiL[T, P, \overline{x}] && \textit{for } j = 1, 2, \ldots, nc \\
\hat{\phi}_j^V &= phiV[T, P, \overline{y}] && \textit{for } j = 1, 2, \ldots, nc \\
\sum_{j=1}^{nc} x_j - \sum_{j=1}^{nc} y_j &= 0
\end{aligned}
$$

$\overline{x}$ *is vector elements* $x_1, x_2, \cdots, x_{nc}$

$\overline{y}$ *is vector elements* $y_1, y_2, \cdots, y_{nc}$

$\overline{z}$ *is vector elements* $z_1, z_2, \cdots, z_{nc}$

$\overline{K}$ *is vector elements* $K_1, K_2, \cdots, K_{nc}$

Degrees-of-Freedom Analysis:

$$
\begin{aligned}
\#\,\text{vars} &= 6\cdot nc + 4 \\
\#\,\text{eqns} &= \underline{5\cdot nc + 2} \\
dof &= 1\cdot nc + 2
\end{aligned}
$$

Mathematical Algorithm A

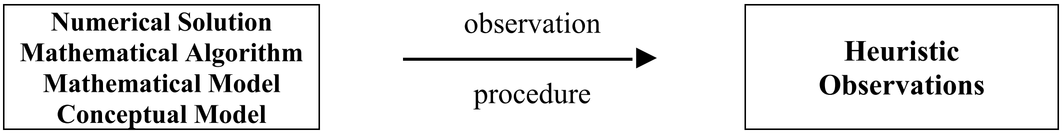
```
$[\,T,\ \overline{x},\ \overline{y}\,] = vlet[\,P,\ V_f,\ \overline{z}\,]$
  1. $L_f \leftarrow 1.0 - V_f$
  2. NSOLVE  $T,\ \overline{x},\ \overline{y},\ \overline{K},\ \hat{\phi}_j^L\text{'s},\ \hat{\phi}_j^V\text{'s}$  in
         $z_j - V_f\, y_j - L_f\, x_j = 0$   $\textit{for } j = 1, 2, \ldots, nc$
         $y_j - K_j\, x_j = 0$   $\textit{for } j = 1, 2, \ldots, nc$
         $K_j - \hat{\phi}_j^L / \hat{\phi}_j^V = 0$   $\textit{for } j = 1, 2, \ldots, nc$
         $\hat{\phi}_j^L - phiL[T, P, \overline{x}] = 0$   $\textit{for } j = 1, 2, \ldots, nc$
         $\hat{\phi}_j^V - phiV[T, P, \overline{y}] = 0$   $\textit{for } j = 1, 2, \ldots, nc$
         $\sum_{j=1}^{nc} x_j - \sum_{j=1}^{nc} y_j = 0$
     END
```

When **Steps 1 to 7** of the above **Partitioning Algorithm** are applied to the mathematical model, the mathematical algorithm to the left is the result of that transformation.

It produces one direct calculation and a nonlinear solve with (5·*nc* + 1) unknown variables. The scalar unknown is *T*, while the other five unknowns are vector quantities with *nc* elements each.

Since the mathematical algorithm to the left contains a NSOLVE construct, it must be further transformed as shown in **Mathematical Algorithm B** below.

Transformation Process



From your experience of solving the well-defined problem, what heuristic observations can you make that will give you a better understanding of both the technical subject matter and the application of the problem-solving methodology? These observations are to be general conclusions and/or recommendations that you could apply to the solution of any well-defined problem. The systematic observation procedure is described below.

Observation Procedure

1. Numerical Solution

Primarily the check equation: total flow = sum of component flows.
Decide to use the "*standard form*" or "*normalized form*" of this equation.
See the **Numerical Solution** guidelines for a description of these two forms.
If there is no check equation, then use a simpler assumption to approximate solution.
Apply the total mass balance when applicable, provided it was not used in the mathematical model.

2. Mathematical Algorithm

The key is to look at the list of known variables.
How would the algorithm change if you knew a different DOF variable?
That is, you did not know a given, but knew a calculated variable instead.
Pick a new known variable that would lead to a realistic problem.
Will the new algorithm be less complex, more complex, or the same as the original algorithm?
Document the new algorithm so that you can review it at a later time.

3. Mathematical Model

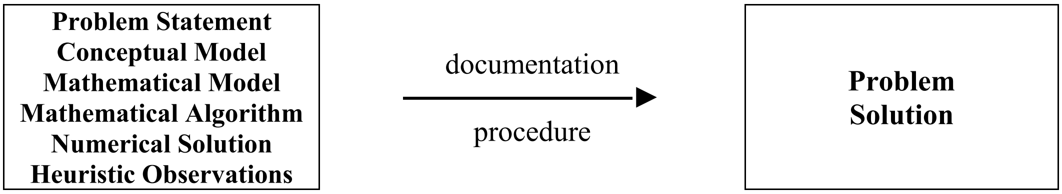
The key is to look at the list of assumptions, and change one of them.
How would the math model differ if you changed one of the assumptions?
Pick an assumption to change that would lead to a realistic problem.
What if other types of flow rates or amounts were given or asked to be found?

4. Conceptual Model

State why the process type listed in the assumptions can not be any of the other types; that is, continuous, semi-continuous, batch, and semi-batch.
How might the problem change if you had extra or less input streams (2, 3, etc.)?
How might the problem change if you had extra or less output streams (2, 3, etc.)?
How might the problem change if you had extra chemical reactions?

The development of the heuristic observations is a "What If" analysis; that is, how would the problem and its solution have to change if this or that were different? This creative analysis serves as good preparation for the exams.

Transformation Process



When you apply the six-stage problem-solving methodology, you are exercising your technical responsibilities as a problem solver and your rhetorical responsibilities as a report writer. You are a problem solver in the first five problem-solving stages and a report writer in the last problem-solving stage. Since writing is an evolutionary process, you are also a report writer during the first five problem-solving stages, because you are drafting segments of the final problem solution—the problem statement, conceptual model, mathematical model, mathematical algorithm, numerical solution, and heuristic observations.

Once you have done all drafting activities, you complete the rhetorical process of formally documenting the solution to the well-defined problem. As you become more proficient doing all stages of the problem-solving methodology, you will partially merge the activities of drafting and formal documentation. The procedure and standards listed below will help you to produce a professional-looking problem solution, one of which is illustrated in "A Well-Defined Problem" at the end of Chapter 1.

Documentation Procedure

The problem solution is to contain the six segments listed below, where each segment name is to appear as a heading on the beginning of a new page. The next problem segment can appear at the end of the previous segment provided that all of that next segment can fit on the last page of the previous segment; otherwise, that next segment should begin on a new page. The content items for each segment are listed below, and that content must follow the documentation standards also listed below.

1. Problem Statement

Manually print it, copy and paste (or tape) it, or computer print it on engineering paper. Engineering paper is a pastel green and translucent paper with grid lines on the back side of each page that show through faintly to the front side. When photocopied or scanned, the grid lines typically do not show up in the resulting copy, which often gives your work a professional appearance.

Provide an **Assumptions** heading and list the assumptions as you develop the problem solution. Optionally, the assumptions can appear under the **Conceptual Model**, instead of here, when they are few in number and only require short descriptions.

2. Conceptual Model (is the preferred heading, but **Diagram** could be used instead)

For a continuous process, provide a diagram for the process unit or set of process units and draw a dashed system boundary around that diagram. Label each process stream entering and leaving the system boundary with its temperature, pressure, phase, flow rate, and composition, providing symbols and values with units, or question marks when no value is given in the problem statement.

Introduction

This chapter on material balances has four major objectives. First, the general material balance discussed in Chapter 2 is used to present the first principle equations for material balances. You should review this material in Chapter 2 before continuing to read here. Second, chemical process classifications are presented for continuous, batch, semi-batch, and semi-continuous system. Third, two key examples that show how to use the first principle equations are given in the form of graphic organizers. Fourth, example material balance problems are provided, whose solutions were generated using the problem solving strategy described in Chapter 4. Most of these examples are worked-out problems found in various editions of the Felder and Rousseau textbook [2005] entitled "*Elementary Principles of Chemical Processes*." Once you understand the solution to an example in this *CinChE* chapter, you should compare it to its counterpart in the appropriate edition of the Felder and Rousseau textbook and analyze the differences. The information on material balances and process classifications, as well as the graphic organizers, will help you to understand the example problems.

General Material Balance

As presented in Chapter 2, the material balance accounts for the amount of material associated with a system, a process unit or set of process units. When no nuclear reactions occur, its general form is:

$$\begin{matrix}\textit{amount}\text{ rates}\\\text{flowing in}\end{matrix} \;-\; \begin{matrix}\textit{amount}\text{ rates}\\\text{flowing out}\end{matrix} \;\pm\; \begin{matrix}\textit{amount}\text{ rates}\\\text{of change}\\\text{by reactions}\end{matrix} \;=\; \frac{d(amount)_{sys}}{dt}$$

where the "amount" is the quantity variable for either mass, moles (i.e., molecules), or atoms.

Index and Limit Conventions

A. Index i denotes a process stream; Limit nt is the total number of streams.
B. Index j denotes a chemical component; Limit nc is the total number of components.
C. Index k denotes a chemical element; Limit ne is the total number of elements.
D. Index l denotes a chemical reaction; Limit nr is the total number of reactions.

Chemical Reactions

A. **Stoichiometric Equations:** example, $1\ CH_4 + 2\ O_2 \rightarrow 1\ CO_2 + 2\ H_2O$

$$\sum_{reactants} \upsilon_{l,j}\, C_{j,l} \rightarrow \sum_{products} \upsilon_{l,j}\, C_{j,l} \qquad for \quad l = 1, 2, \cdots, nr$$

B. **Stoichiometric Balances:** { conservation of total mass for a chemical reaction }

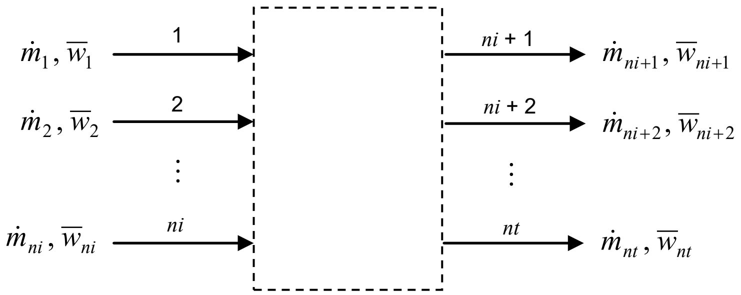
$$\sum_{j=1}^{nc} \upsilon_{l,j}\, M_j = 0 \qquad for \quad l = 1, 2, \cdots, nr$$

where	$\upsilon_{l,j}$	is	the stoichiometric coefficient for the *j-th* component in the *l-th* reaction. In any balance equation, it is positive (+) for a product and negative (−) for a reactant. It has units of (mass-mole of *j-th*) per (mass-reaction of *l-th*). Example units are (g-mol *j-th*)/(g-rxn *l-th*), (kg-mol *j-th*)/(kg-rxn *l-th*), and (lb-mol *j-th*)/(lb-rxn *l-th*).
	$C_{j,l}$	is	the chemical formula for *j-th* component in the *l-th* reaction.
	M_j	is	molecular weight of the *j-th* component in units of mass/mass-mole.

The stoichiometric balance equation is written "*nr*" times, once for each chemical reaction.

Material Balances with Mass Quantities (integral form) {see Integral Form Derivations below}

A. Diagram of a System Boundary



B. Total Mass Balance:

$$\sum_{i=1}^{ni} m_i - \sum_{i=ni+1}^{nt} m_i = (m)_{sys,f} - (m)_{sys,i} \qquad \textbf{(5.1i)}$$

C. Component Mass Balances:

$$\sum_{i=1}^{ni} m_{i,j} - \sum_{i=ni+1}^{nt} m_{i,j} + \sum_{l=1}^{nr} M_j\, \upsilon_{l,j}\, R_l = \left(m_j\right)_{sys,f} - \left(m_j\right)_{sys,i} \quad for \quad j = 1, 2, \cdots, nc \qquad \textbf{(5.2i)}$$

where $m_{i,j} = m_i\, w_{i,j}$ { composition equations }

The component mass balance is written "*nc*" times, once for each chemical component, while the composition equation is written for each component *j* in those process streams where the mass fraction of that component is not known and is to be found. This same rule also applies to the system states (*i* and *f*).

D. Mixture Equations: { By definition, a mixture is chemically inert; that is, no chemical reactions are occurring }

$$m_i = \sum_{j=1}^{nc} m_{i,j}$$

standard form

or

$$\sum_{j=1}^{nc} w_{i,j} = 1.0$$

normalized form

for those applicable process stream *i*'s

The "*standard form*" of the mixture equation is written only for those process streams where each has at least one unknown component mass fraction. This same rule also applies to the system states (*i* and *f*). The "*normalized form*" of the mixture equation is often used as a check equation whenever you need to determine mass fractions.

E. Atom Balances: { examples of an element are C, H, O, and N }

$$\sum_{i=1}^{ni}\left(\sum_{j=1}^{nc}\frac{m_{i,j}}{M_j}\,a_{j,k}\right) - \sum_{i=ni+1}^{nt}\left(\sum_{j=1}^{nc}\frac{m_{i,j}}{M_j}\,a_{j,k}\right) = \sum_{j=1}^{nc}\frac{\left(m_j\right)_{sys,f}}{M_j}\left(a_{j,k}\right)_{sys,f} - \sum_{j=1}^{nc}\frac{\left(m_j\right)_{sys,i}}{M_j}\left(a_{j,k}\right)_{sys,i} \quad for \quad k = 1, 2, \cdots, ne \qquad \textbf{(5.3i)}$$

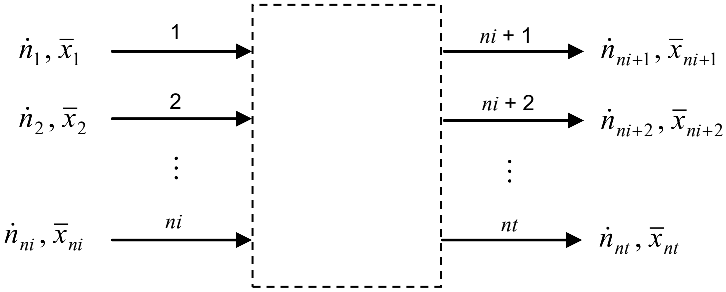
The atom balance is written "*ne*" times, once for each element within the system boundary. The net units for the atom balance (Eq. 5.3i) are mass-atom, while the net units for the total and component mass balances (Eqs. 5.1i and 5.2i) are mass.

F. Variable Definitions:

where	ni	is	the number of process streams flowing into the system boundary.
	nt	is	the total number of process streams around the system boundary.
	nr	is	the number of chemical reactions within the system boundary.
	nc	is	the number of chemical components within the system boundary.
	ne	is	the number of chemical elements in all of the chemical components.
	m_i	is	the total mass of the *i-th* process stream over the time period ($t_f - t_i$) in units of (mass of *i*). If the mass flow rate of the *i-th* process stream ($\dot{m}_i$) is constant with time over the period ($t_f - t_i$), then variable m_i can be replaced with $\dot{m}_i \Delta t$, or $\dot{m}_i (t_f - t_i)$.
	$m_{i,\,j}$	is	the component mass of the *j-th* component in the *i-th* stream over the time period ($t_f - t_i$) in units of (mass of *j*). If the mass flow rate of the *j-th* chemical component in the *i-th* process stream ($\dot{m}_{i,j}$) is constant with time over the period ($t_f - t_i$), then variable $m_{i,\,j}$ can be replaced with $\dot{m}_{i,j} \Delta t$, or $\dot{m}_{i,\,j} (t_f - t_i)$.
	$w_{i,\,j}$	is	the mass fraction of the *j-th* component in the *i-th* stream in units of (mass of *j*)/(mass of *i*). The vector variable of $\overline{w}_i$ is a short notation for all mass fractions ($w_{i,1}, w_{i,2}, w_{i,3}, \cdots, w_{i,\,nc}$) in the *i-th* stream.
	$\upsilon_{l,\,j}$	is	the stoichiometric coefficient for the *j-th* component in the *l-th* reaction. In any balance equation, it is positive (+) for a product and negative (−) for a reactant. It has units of (mass-mole of *j*)/(mass-reaction of *l*).
	R_l	is	the number of reaction events for the *l-th* reaction in units of (mass-reaction of *l*). Some example units are: **g-rxn**, **kg-rxn**, and **lb-rxn**. The number of reaction events, often called the extent of reaction, is always positive and the same in value for all component balances. A **g-rxn** is by definition Avogadro's number (N_A) of *l-th* chemical reactions. A **kg-rxn** is ($1000 \cdot N_A$) number of *l-th* chemical reactions. A **lb-rxn** is ($453.592 \cdot N_A$) number of *l-th* chemical reactions.
	$a_{j,\,k}$	is	the number of mass-atoms of the *k-th* element in a mass-mole of the *j-th* component in units of (mass-atom of *k*)/(mass-mole of *j*).
	M_j	is	the molecular weight of the *j-th* component in units of (mass of *j*)/(mass-mole of *j*).
	$(m)_{sys,\,i}$	is	the total mass within the system boundary initially in units of (total mass at t_i). Note: $(m)_{sys,\,i} = (m_1)_{sys,\,i} + (m_2)_{sys,\,i} + \cdots + (m_{nc})_{sys,\,i}$
	$(m)_{sys,\,f}$	is	the total mass within the system boundary finally in units of (total mass at t_f). Note: $(m)_{sys,\,f} = (m_1)_{sys,\,f} + (m_2)_{sys,\,f} + \cdots + (m_{nc})_{sys,\,f}$
	$(m_j)_{sys,\,i}$	is	the mass of the *j-th* component within the system boundary initially in units of (mass of *j* at t_i).
	$(m_j)_{sys,\,f}$	is	the mass of the *j-th* component within the system boundary finally in units of (mass of *j* at t_f).
	$(a_k)_{sys,\,i}$	is	the mass-atoms for the *k-th* element within the system boundary initially in units of (mass-atoms of *k* at t_i).
	$(a_k)_{sys,\,f}$	is	the mass-atoms for the *k-th* element within the system boundary finally in units of (mass-atoms of *k* at t_f).

Material Balances with Molar Quantities (integral form) {see Integral Form Derivations below}

A. Diagram of a System Boundary



B. Total Mole Balance:

$$\sum_{i=1}^{ni} n_i - \sum_{i=ni+1}^{nt} n_i + \sum_{l=1}^{nr}\left(\sum_{j=1}^{nc}\upsilon_{l,j}\right)R_l = (n)_{sys,f} - (n)_{sys,i} \qquad \textbf{(5.4i)}$$

C. Component Mole Balances:

$$\sum_{i=1}^{ni} n_{i,j} - \sum_{i=ni+1}^{nt} n_{i,j} + \sum_{l=1}^{nr}\upsilon_{l,j}R_l = (n_j)_{sys,f} - (n_j)_{sys,i} \qquad for \quad j = 1, 2, \cdots, nc \qquad \textbf{(5.5i)}$$

where $n_{i,j} = n_i \, x_{i,j}$ { composition equations }

The component mole balance is written "*nc*" times, once for each chemical component, while the composition equation is written for each component *j* in those process streams where the mole fraction of that component is not known and is to be found. This same rule also applies to the system states (*i* and *f*).

D. Mixture Equations: { By definition, a mixture is chemically inert; that is, no chemical reactions are occurring }

$$n_i = \sum_{j=1}^{nc} n_{i,j} \qquad \text{or} \qquad \sum_{j=1}^{nc} x_{i,j} = 1.0$$

standard form *normalized form* for those applicable process stream *i*'s

The "*standard form*" of the mixture equation is written only for those process streams where each has at least one unknown component mole fraction. This same rule also applies to the system states (*i* and *f*). The "*normalized form*" of the mixture equation is often used as a check equation whenever you need to determine mole fractions.

E. Atom Balances: { examples of an element are C, H, O, and N }

$$\sum_{i=1}^{ni}\left(\sum_{j=1}^{nc} n_{i,j}\, a_{j,k}\right) - \sum_{i=ni+1}^{nt}\left(\sum_{j=1}^{nc} n_{i,j}\, a_{j,k}\right) = \sum_{j=1}^{nc}(n_j)_{sys,f}(a_{j,k})_{sys,f} - \sum_{j=1}^{nc}(n_j)_{sys,i}(a_{j,k})_{sys,i} \qquad \textbf{(5.6i)}$$

$$for \quad k = 1, 2, \cdots, ne$$

The atom balance is written "*ne*" times, once for each element within the system boundary. The net units for the atom balance (Eq. 5.6i) are mass-atom, while the net units for the total and component mole balances (Eqs. 5.4i and 5.5i) are mass-mole.

F. Variable Definitions:

where	ni	is	the number of process streams flowing into the system boundary.
	nt	is	the total number of process streams around the system boundary.
	nr	is	the number of chemical reactions within the system boundary.
	nc	is	the number of chemical components within the system boundary.
	ne	is	the number of chemical elements in all of the chemical components.
	n_i	is	the total moles of the *i-th* process stream over the time period ($t_f - t_i$) in units of (mass-mole of *i*). If the molar flow rate of the *i-th* process stream ($\dot{n}_i$) is <u>constant</u> with time over the period ($t_f - t_i$), then variable n_i can be replaced with $\dot{n}_i \Delta t$, or $\dot{n}_i (t_f - t_i)$.
	$n_{i,j}$	is	the component moles of the *j-th* component in the *i-th* stream over the time period ($t_f - t_i$) in units of (mass-mole of *j*). If the molar flow rate of the *j-th* chemical component in the *i-th* process stream ($\dot{n}_{i,j}$) is <u>constant</u> with time over the period ($t_f - t_i$), then variable $n_{i,j}$ can be replaced with $\dot{n}_{i,j} \Delta t$, or $\dot{n}_{i,j} (t_f - t_i)$.
	$x_{i,j}$	is	the mole fraction of the *j-th* component in the *i-th* stream in units of (mass-mole of *j*)/(mass-mole of *i*). The vector variable of $\overline{x}_i$ is a short notation for all mass fractions ($x_{i,1}, x_{i,2}, x_{i,3}, \cdots, x_{i,nc}$) in the *i-th* stream.
	$\upsilon_{l,j}$	is	the stoichiometric coefficient for the *j-th* component in the *l-th* reaction. In any balance equation, it is positive (+) for a product and negative (−) for a reactant. It has units of (mass-mole of *j*)/(mass-reaction of *l*).
	R_l	is	the number of reaction events for the *l-th* reaction in units of (mass-reaction of *l*). Some example units are: **g-rxn**, **kg-rxn**, and **lb-rxn**. The number of reaction events, often called the <u>extent of reaction</u>, is always positive and the same in value for all component balances. A **g-rxn** is by definition Avogadro's number (N_A) of *l-th* chemical reactions. A **kg-rxn** is ($1000 \cdot N_A$) number of *l-th* chemical reactions. A **lb-rxn** is ($453.592 \cdot N_A$) number of *l-th* chemical reactions.
	$a_{j,k}$	is	the number of mass-atoms of the *k-th* element in a mass-mole of the *j-th* component in units of (mass-atom of *k)*/(mass-mole of *j*).
	$(n)_{sys,i}$	is	the total mass-moles within the system boundary initially in units of (total mass-mole at t_i). $(n)_{sys,i} = (n_1)_{sys,i} + (n_2)_{sys,i} + \cdots + (n_{nc})_{sys,i}$
	$(n)_{sys,f}$	is	the total mass-moles within the system boundary finally in units of (total mass-mole at t_f). $(n)_{sys,f} = (n_1)_{sys,f} + (n_2)_{sys,f} + \cdots + (n_{nc})_{sys,f}$
	$(n_j)_{sys,i}$	is	the mass-moles of the *j-th* component within the system boundary initially in units of (mass-mole of *j* at t_i).
	$(n_j)_{sys,f}$	is	the mass-moles of the *j-th* component within the system boundary finally in units of (mass-mole of *j* at t_f).
	$(a_k)_{sys,i}$	is	the mass-atoms for the *k-th* element within the system boundary initially in units of (mass-atoms of *k* at t_i).
	$(a_k)_{sys,f}$	is	the mass-atoms for the *k-th* element within the system boundary finally in units of (mass-atoms of *k* at t_f).

toast some bread, spread some jam on the toast, and eat a treat. From time t_i to t_f, you heat the pot on the stove to boil off some of the water and thus make jam. Considering the pot as your system boundary, this evaporation process is a semi-batch operation. The solids and sugar do not cross the imaginary boundary, but steam (i.e., water vapor) leaves through that boundary. Can you think of a semi-batch cooking example where some material exists within the system boundary and some material enters through that boundary, but no material leaves through that boundary?

A **semi-continuous** process is similar to a continuous operation because some material continuously flows into and out of the system boundary, while other material operates in a batch and/or semi-batch manner. For example, you love to have a fresh cup of coffee in the morning that is made using your automatic coffee maker. Before some initial time (t_i), you will place coffee grounds into a filter, place that filter into the coffee maker, place an empty glass carafe under the filter, and add water to the reservoir in the coffee maker. After some final time (t_f), you will remove the carafe, pour yourself a hot cup of java, and begin reading the daily newspaper. From time t_i to t_f, you start the coffee maker to let it brew some java. Considering the filter to be your system boundary, this brewing process is a semi-continuous operation. The water flows continuously into and out of the imaginary boundary. The coffee flavor that is extracted from the ground coffee by the hot water leaves through the boundary in a semi-batch manner. Finally, the coffee grounds operate in a batch manner since they do not cross the system boundary. If you had considered the system boundary to be around the coffee maker, then the brewing process would be a batch operation, instead of a semi-batch operation. This example illustrates that placement of your system boundary can effect what the processing type will be.

How do you develop the mathematical model for each of these four types of chemical processes, starting with the first principles for material balances? For a continuous process operating at steady state, you begin with the differential forms for mass, moles, or atoms (Eqs. 5.1d and 5.2d for mass, 5.4d and 5.5d for moles, or 5.3d or 5.6d for atoms). For batch, semi-batch, and semi-continuous processes which by their nature are unsteady state, you begin with the integral forms for mass, moles, or atoms (Eqs. 5.1i and 5.2i for mass, 5.4i and 5.5i for moles, or 5.3i or 5.6i for atoms). We conclude this section with some important guidelines on applying the first principles for material balances to the four types of process operations. As you solve material balance problems, you should consult these guidelines often to begin the math model development.

B. Continuous Process

Click here to view some illustrations.

In this type of process, all chemical substances must continuously flow across the system boundary; that is, they flow into and/or out of that imaginary boundary. The table below identifies the first principles and applicable conditions to account for material in a continuous process.

Continuous Process Guidelines

Most Data	Applicable Material Balances	Condition
molar units	Mole Balances, Eqs. 5.4d and 5.5d	no rxn's or know rxn's
	Atom Balances, Eq. 5.6d	do not know rxn's
mass units	Mass Balances, Eqs. 5.1d and 5.2d	no rxn's or know rxn's
	Atom Balances, Eq. 5.3d	do not know rxn's

In your math model development, you will begin with the appropriate material balances—mass, moles, or atoms. Unless you are told otherwise, assume steady-state operation for a continuous process, and you will write "steady state" as part of the "List of Assumptions" in your problem solution. The steady-state assumption implies that the term on the right-hand side of the equal sign is zero in the differential forms for the material balances. If you write the assumption of "no reactions", you are indicating that the "$\dot{R}_l$" term has been dropped in the applicable differential material balances.

C. Batch Process

Click here to view some illustrations.

In this type of process, all chemical substances must be contained within the system boundary. No chemical substance crosses the system boundary; that is, none of the chemical substances flow into or out of that imaginary boundary while the process is operating. Before some initial time (t_i), material will have been put into the system boundary, and after some final time (t_f), material will have been removed from the system boundary. However from time t_i to t_f, no material within the system will cross the imaginary boundary in a batch process. The table below identifies the first principles and applicable conditions to account for material in a batch process.

Batch Process Guidelines

Most Data	Applicable Material Balances	Condition
molar units	Mole Balances, Eqs. 5.4i and 5.5i	no rxn's or know rxn's
	Atom Balances, Eq. 5.6i	do not know rxn's
mass units	Mass Balances, Eqs. 5.1i and 5.2i	no rxn's or know rxn's
	Atom Balances, Eq. 5.3i	do not know rxn's
no "flows in" terms and no "flows out" terms in any of the balances.		

In your math model development, you will begin with the appropriate material balances—mass, mole, or atom. When you write "batch process" as part of the "List of Assumptions," you are implying that no material flows into and out of the system boundary. If you write the assumption of "no reactions", then you are indicating that the "R_l" term has been dropped in the applicable integral material balances.

The material balances for a batch process and their counterparts for a continuous process operating at steady state have similar structures. For the continuous case, the general structure is:

$$\text{in} \quad - \quad \text{out} \quad \pm \quad \text{reactions} \quad = \quad 0$$

For the batch case, the general structure is as follows:

$$\text{initial} \quad - \quad \text{final} \quad \pm \quad \text{reactions} \quad = \quad 0$$

This general structure is a helpful learning aid for writing the balances. The Felder and Rousseau textbook [2005, p. 87] exploits this general structure for their approach to drawing one diagram for a batch process that looks similar to one for a continuous process unit, but they do not explain why they can do it that way. We will use a different approach for the diagramming of a batch process; that is, we will drawn two diagrams—one for the initial time and one for the final time—that is, two "snapshots" in time. In this approach, we will be looking at the state of the system at two different points in time.

D. Semi-Batch Process

Click here to view some illustrations.

In this type of process, at least one chemical substance crosses the system boundary. It either flows into or flows out of that imaginary boundary; it can not do both. All remaining chemical substances do not cross the system boundary; they are contained within the system boundary. The one or more chemical substances that cross the system boundary are the "*semi*" part of a semi-batch process. The remaining chemical substances are the "*batch*" part of a semi-batch process.

The table below identifies the first principles and applicable conditions to account for material in a semi-batch process.

Semi-Batch Process Guidelines

Most Data	Applicable Material Balances	Condition
molar units	Mole Balances, Eqs. 5.4i and 5.5i	no rxn's or know rxn's
	Atom Balances, Eq. 5.6i	do not know rxn's
mass units	Mass Balances, Eqs. 5.1i and 5.2i	no rxn's or know rxn's
	Atom Balances, Eq. 5.3i	do not know rxn's

Total Amount: no "flows out" terms, but "flows in" terms in total balance; or no "flows in" terms, but "flows out" terms in total balance.
Batch Components: no "flows in" terms and no "flows out" terms in component balance.
Semi-Batch Components: no "flows out" terms, but "flows in" terms in component balance; or no "flows in" terms, but "flows out" terms in component balance.

When the total flow rate for any process stream entering or leaving the system boundary is constant with time over the period $(t_f - t_i)$, its total amount term in a total integral balance can be replaced with its total flow rate times Δt. For that same process stream, each of its component amounts appearing in their component integral balances can be replaced with their component flow rate times Δt. For a further explanation about these substitutions, see the "Variable Definitions" section under the applicable integral forms for mole or mass balances.

In your math model development, you will begin with the appropriate material balances—mass, mole, or atom. When you write "semi-batch process" as part of the "List of Assumptions," you are implying that material flows either into or out of the system boundary. If you write the assumption of "no reactions", then you are indicating that the "R_l" term has been dropped in the applicable integral material balances.

E. Semi-Continuous Process

Click here to view some illustrations.

In this type of process, at least one chemical substance flows into and out of the system boundary. All remaining chemical substances either 1) do not cross that imaginary boundary or 2) one or more of them flow into or flow out of that imaginary boundary and the rest do not. The one or more chemical substances that flow both into and out of the system boundary represent the "*continuous*" part of a semi-continuous process. The remaining chemical substances are the "*semi-*" part of a semi-continuous process, because they are processed either in a batch and/or

Semi-Continuous Process Guidelines

Most Data	Applicable Material Balances	Condition
molar units	Mole Balances, Eqs. 5.4i and 5.5i	no rxn's or know rxn's
	Atom Balances, Eq. 5.6i	do not know rxn's
mass units	Mass Balances, Eqs. 5.1i and 5.2i	no rxn's or know rxn's
	Atom Balances, Eq. 5.3i	do not know rxn's

Total Amount: "flows in" terms and "flows out" terms in total balance.
Continuous Components: "flows in" terms and "flows out" terms in component balance, but the terms for the system amount initially and finally are dropped because that component is assumed to operate at steady state within the system.
Batch Components: no "flows in" terms and no "flows out" terms in component balance.
Semi-Batch Components: no "flows out" terms, but "flows in" terms in component balance; or no "flows in" terms, but "flows out" terms in component balance.

semi-batch manner. The table above identifies the first principles and applicable conditions to account for material in a semi-continuous process. When the total flow rate for any process stream entering and/or leaving the system boundary is constant with time over the period ($t_f - t_i$), its total amount term in a total integral balance can be replaced with its total flow rate times Δt. For that same process stream, each of its component amounts appearing in their component integral balances can be replaced with their component flow rate times Δt. For a further explanation about these substitutions, see the "Variable Definitions" section under the applicable integral forms for mole or mass balances.

In your math model development, you will begin with the appropriate material balances—mass, mole, or atom. When you write "semi-continuous process" as part of the "List of Assumptions," you are implying that some material flows both into and out of the system boundary. As one of your assumptions, you would write "steady state for X, Y, etc." where "X, Y, etc." are the names of the chemical compounds that flowing continuously into and out of the system boundary. If you write the assumption of "no reactions", then you are indicating that the "R_l" term has been dropped in the applicable integral material balances.

Example Problems

When you begin to develop the mathematical model for any material balance problem, you will start with the differential principles given in Eqs. 5.1d to 5.6d for continuous processes, and with the integral principles given in Eqs. 5.1i to 5.6i for batch, semi-batch, and semi-continuous processes.

The list below summarizes the graphic organizers (**go**) and example problems (**ep**) that appear in the remainder of this chapter. The example problems require the application of material balance principles, and they were solved using the problem solving strategy outlined in Chapter 4. The example problems in the two graphic organizers were also solved using the same problem solving strategy.

If you have any questions about the graphic organizers or example problem solutions, please consult with one of your teammates or contact the instructor. The instructor is very willing to help you, if you ask.

Mathematical Algorithm Development

Click here for an illustration.

Based on the procedure in Chapter 4 for developing a mathematical algorithm, you start by writing the functional equation for that algorithm. In this case, it is as follows:

$$[n_i] = reactor\left[n_{f,SM}\right] \qquad or \qquad n_i = reactor\left[n_{f,SM}\right]$$

where "*reactor*" is the name assigned to the function. The brackets on the right side of the functional equation contain those variables that satisfy the degrees of freedom (DOF). The number of variables listed within these brackets must equal the DOF. The brackets on the left side of the functional equation contain those calculated variables that are of interest, namely the "Finds" in the conceptual model. When the list of variables within these brackets is only one, we usually drop the brackets.

The rest of the development process for the mathematical algorithm is left as an exercise for you to try, following the procedure given in Chapter 4. The correct order of the math model equations in the mathematical algorithm is as follows: ④, ⑦, {⑧ and ⑨ simultaneously}, ②, ⑥, ⑤, ③ and ①. A dimensional consistency analysis of the mathematical algorithm reveals that no unit conversion factors are needed in any of its equations.

Once you have developed the steps in the mathematical algorithm, you should check to make sure that you have gotten them in the right order. An easy way to do that is by looking at the arithmetic expression on the right hand side of a step, starting with the first step and working your way to the last step. Each variable that appears in the arithmetic expression must be either specified or was calculated in a previous step. A specified variable is one that appears in the right-hand brackets of the functional equation for the mathematical algorithm. Variable names that are constants, like the ideal gas constant and molecular weight, are presumed to be known since they can be found in the technical literature.

Numerical Solution Development

Click here for an illustration.

Based on the procedure in Chapter 4 for developing a numerical solution, you start by writing the base system of units for the calculation and the basis for the amount or flow rate on which the solution is based. For the semi-batch reactor above, the system of units is "**mks**", and the basis is $n_{f,SM} = 150$ *kg-mol*, or any other value like 100 *kg-mol*. The rest of the development process for the numerical solution is left as an exercise for you to try, following the procedure given in Chapter 4.

Heuristic Observations Development

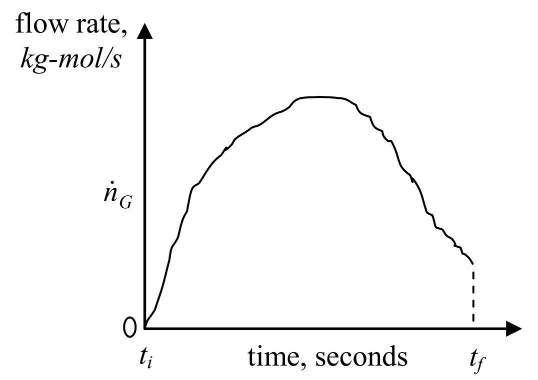
Click here for an illustration.

Based on the procedure in Chapter 4 for developing the heuristic observation, you are to do a "what if" analysis on the generated numerical solution, mathematical algorithm, mathematical model, and conceptual model, in that order. We will examine only one observation here about the mathematical model. The rest of the development process for the heuristic observation is left as an exercise for you to try, following the procedure given in Chapter 4.

What if you were asked to find the volume amount of the hydrogen gas that was produced in the semi-batch reactor? Based on the solution above, the moles of hydrogen gas (n_G) would be determined through the material balance equations. You need to find a way to relate moles (n_G) to volume (V_G). Since the pressure for the semi-batch reactor is 1 atm, you could use the ideal gas law for that relationship; that is, $P_G \cdot V_G = n_G \cdot R \cdot T_G$, and add it to the mathematical model.

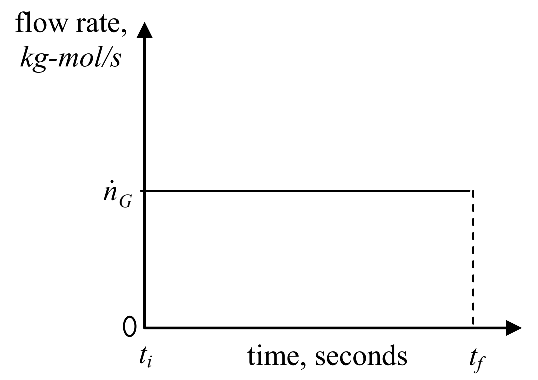
What is the difference between the variable $\dot{n}_G$ in the conceptual model and the variable n_G in the mathematical model? The former has units of mass-mole/time like *kg-mol/s*, while the latter has units of mass-mole like *kg-mol*. In the plot below, the curve is the flow rate of Stream G at different points in time. The area under the example curve for the flow rates is the integral or n_G (see the integral form derivations on Pages 5-10 to 5-12). In a batch reactor, the reactions will start slow, progress to a maximum rate, and then decrease as the reactants are consumed. The example curve represents the flow rate of the hydrogen as the reactions progress.

$$n_G = \int_{t_i}^{t_f} \dot{n}_G \, dt$$



If the flow rate ($\dot{n}_G$) leaving the batch reactor were, however, constant with time, then the curve in the diagram below would be a horizontal line from times t_i to t_f, and the area under the curve would be that of a rectangle. This area is expressed mathematically as $n_G = \dot{n}_G \Delta t$.

$$n_G = \dot{n}_G \Delta t$$



Problem Solution Variability

For a specific problem statement, the application of the steps in the problem-solving methodology, found in Chapter 4 of the *CinChE* manual, could produce variability in the problem solution; that is, the conceptual model, mathematical model, mathematical algorithm, numerical solution, and the heuristic observations. Therefore, no two solutions to a specific problem statement will be exactly alike in their documentation. **Click here** to examine six example scenarios that demonstrate the kinds of variability one might encounter when comparing one problem solution to another problem solution for the same problem statement.

larger

eLEAPS How To

Continuous Reactor

An eLEAPS Session

eLEAPS script

1 of 6

Problem Statement

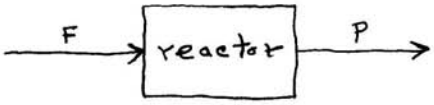
Chemists in our Research and Development Department have discovered a catalyst, which will produce styrene monomer from toluene and methanol in one step by the reaction pathway:

$$\underset{\text{toluene}}{C_7H_8} + \underset{\text{methanol}}{CH_3OH} \rightarrow \underset{\textbf{styrene}}{C_8H_8} + \underset{\textbf{water}}{H_2O} + \underset{\textbf{hydrogen}}{H_2}$$

Based on their experimental reactor studies, our chemists report that **80** mole % of the toluene is converted to styrene monomer when an **equimolar** mixture of methanol and toluene are fed to a small-scale reactor at **520°C** and **300 kPa**. For a feed rate of **610.6 L/s**, our company needs to know what the molar flow rate and composition would be for the product stream, which exits the adiabatic reactor as a gas at **337°C** and **270 kPa**. The mass flow of this gas stream is also needed in kilograms per hour. As a sophomore chemical engineer in our company, please provide a **well-document** solution to this problem using our standard problem-solving methodology.

Diagram

$T_F = 520°C$
$P_F = 300$ kPa
$Ph_F =$ gas
$\dot{n}_F = ?$
$x_{F,TL} = 0.5$
$x_{F,ME} = 0.5$



$T_P = 337°C$
$P_P = 270$ kPa
$Ph_P =$ gas
$\dot{n}_P = ?$
$x_{P,TL} = ?$
$x_{P,ME} = ?$
$x_{P,SM} = ?$
$x_{P,WA} = ?$
$x_{P,H2} = ?$

other Givens:

Rxn I: $C_7H_8 + CH_3OH \rightarrow C_8H_8 + H_2O + H_2$

$\dot{V}_F = 610.6$ L/s

80 mol % conversion of toluene

Finds:

$\dot{n}_P$ in kg-mol/h
$x_{P,j}$'s in mol. frac.
$\dot{m}_P$ in kg/h

Assumptions

1. continuous process
2. steady state
3. Stream F is ideal gas

Popup notes and/or web links on Pages 5-25 to 5-28 can be accessed through the above web link for the **eLEAPS script**.

larger

ChE 200
Hanyak

Example 4.2-2
in F&R, 2nd Ed.

9/18/90
1 of 2

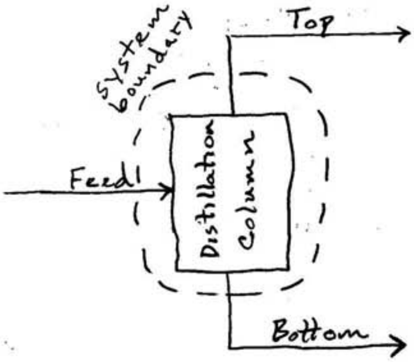
Similar to Example 4.2-2 in F&R, 3rd Ed.

Example 4.2-2 — A Continuous Process

A client of our Bison Engineering and Evaluation Firm (BEEF, Inc.) uses the "BTX (Benzene-Toluene-Xylenes)" process to catalytic reform aliphatic (i.e., straight chain) hydrocarbons into the aromatic (i.e., ring) compounds of benzene and toluene. For our client, benzene is the primary product of the BTX process, and it is sold as an intermediate to make styrene monomer from ethylbenzene. The incoming feed condition to our client's distillation column is 55°C, 1 atm, and 1000 kg/h of 50 wt% benzene and 50 wt% toluene. Based on some operating conditions at the BTX plant, the outgoing flow rate of benzene at the top of the distillation column is 450 kg/h, and that of toluene at the bottom is 475 kg/h. Our client wants BEEF, Inc. to determine the unknown total flow rates, component flow rates, and mass compositions of the two process streams leaving the distillation column.

Diagram

T_F = 55°C
P_F = 1 atm
$\dot{m}_F = 1000$ kg/h
$\omega_{F,BZ} = 0.5$
$\omega_{F,TL} = 0.5$
$Ph_F = ?$



$T_T = ?$
$P_T = ?$
$\dot{m}_T = ?$
$\omega_{T,BZ} = ?$
$\omega_{T,TL} = ?$
$Ph_T = ?$

$T_B = ?$
$P_B = ?$
$\dot{m}_B = ?$
$\omega_{B,BZ} = ?$
$\omega_{B,TL} = ?$
$Ph_B = ?$

BZ - benzene
TL - toluene

Assumptions

1. open system for BZ
2. open system for TL
3. steady state
4. no reaction

Given

$\dot{m}_{T,BZ} = 450$ kg/h
$\dot{m}_{B,TL} = 475$ kg/h

Find

$\dot{m}_T$, $\dot{m}_{T,TL}$, $\overline{\omega}_T$
$\dot{m}_B$, $\dot{m}_{B,BZ}$, $\overline{\omega}_B$

cm 200
Hanyak

Example 4.2-2
in F+R, 2nd Ed.

9/18/90
2 of 2

Math. Model

check Total: $\underline{\dot{m}}_F - \dot{m}_T - \dot{m}_B = 0$

① BZ: $0.5\,\underline{\dot{m}}_F - \underline{\dot{m}}_{T,BZ} - \dot{m}_{B,BZ} = 0$

② TL: $0.5\,\underline{\dot{m}}_F - \dot{m}_{T,TL} - \underline{\dot{m}}_{B,TL} = 0$

③ Mix. T: $\dot{m}_T = \underline{\dot{m}}_{T,BZ} + \dot{m}_{T,TL}$

④ Mix. B: $\dot{m}_B = \dot{m}_{B,BZ} + \underline{\dot{m}}_{B,TL}$

check for linear independence

⑤ $\underline{\dot{m}}_{T,BZ} = \omega_{T,BZ}\,\dot{m}_T$

⑥ $\dot{m}_{T,TL} = \omega_{T,TL}\,\dot{m}_T$

⑦ $\dot{m}_{B,BZ} = \omega_{B,BZ}\,\dot{m}_B$

⑧ $\underline{\dot{m}}_{B,TL} = \omega_{B,TL}\,\dot{m}_B$

\# vars = 11
\# eqns = 8
D.O.F. = 3

Math. Algorithm

Solution

[unknowns] = f [$\dot{m}_F$, $\dot{m}_{T,BZ}$, $\dot{m}_{B,TL}$]

Basis: $\dot{m}_F = 1000$ kg/h, $\dot{m}_{T,BZ} = 450$ kg/h, $\dot{m}_{B,TL} = 475$ kg/h

①: 1. $\dot{m}_{B,BZ} \leftarrow 0.5\,\dot{m}_F - \dot{m}_{T,BZ}$ $\dot{m}_{B,BZ} = 0.5(1000) - 450 = 50$ kg/h

②: 2. $\dot{m}_{T,TL} \leftarrow 0.5\,\dot{m}_F - \dot{m}_{B,TL}$ $\dot{m}_{T,TL} = 0.5(1000) - 475 = 25$ kg/h

③: 3. $\dot{m}_T \leftarrow \dot{m}_{T,BZ} + \dot{m}_{T,TL}$ $\dot{m}_T = 450 + 25 = 475$ kg/h

④: 4. $\dot{m}_B \leftarrow \dot{m}_{B,BZ} + \dot{m}_{B,TL}$ $\dot{m}_B = 50 + 475 = 525$ kg/h

⑤: 5. $\omega_{T,BZ} \leftarrow \dot{m}_{T,BZ} / \dot{m}_T$ $\omega_{T,BZ} = 450/475 = 0.9474$

⑥: 6. $\omega_{T,TL} \leftarrow \dot{m}_{T,TL} / \dot{m}_T$ $\omega_{T,TL} = 25/475 = 0.0526$

⑦: 7. $\omega_{B,BZ} \leftarrow \dot{m}_{B,BZ} / \dot{m}_B$ $\omega_{B,BZ} = 50/525 = 0.0952$

⑧: 8. $\omega_{B,TL} \leftarrow \dot{m}_{B,TL} / \dot{m}_B$ $\omega_{B,TL} = 475/525 = 0.9048$

Check: $1000 - 475 - 525 \overset{\text{Yes}}{=} 0$

larger

CM 200
Hanyak

Example 4.2-3
in F+R, 2nd Ed.

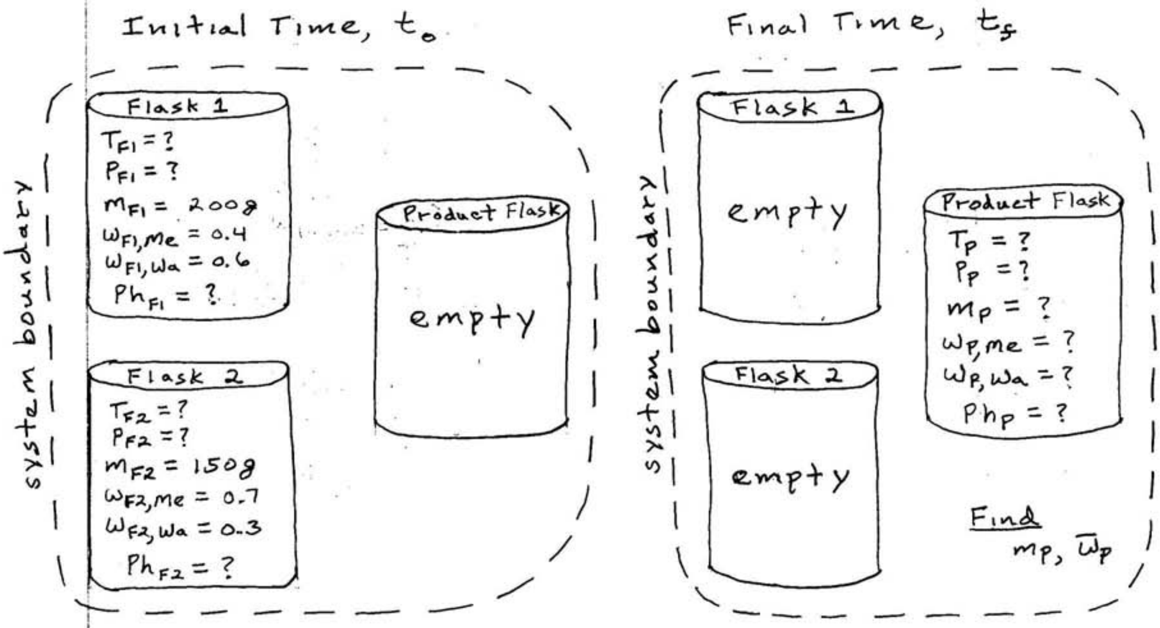
9/18/90
1 of 2

Similar to Example 4.2-3 in F&R, 3rd Ed.

Example 4.2-3 A Batch Process

As a summer intern at the Bison Engineering and Evaluation Firm (BEEF, Inc.), your project supervisor tests your technical abilities on the first day of work by asking to report to the chemist in the laboratory. On the lab table, you find a beaker labeled with 200 grams of a liquid mixture containing 40 mass% methanol and 60 mass% water. A second beaker contains 150 grams of a second liquid mixture containing 70 mass% methanol and the rest water. The chemist instructs you to mix the contents of the two beakers into an empty third beaker on the lab table. She then asks what are the total mass and mass fractions of the methanol-water mixture in the third beaker?

Diagram



Assumptions

1. Closed system for both methanol and water
2. unsteady state
3. no reactions
4. At time t_o, product flask is empty.
5. At time t_f, first and second flask are empty.
6. Temperatures and pressures are at ambient conditions and all phases are liquids.

CM 200
Hanyak

Example 4.2.3
in F+R, 2nd Ed.

9/18/90
2 of 2

Mass Balances { on any batch process, no rxn }

Total: $\int_{t_0}^{t_f} 0 \, dt = \int_{m_{sys}|_{t_0}}^{m_{sys}|_{t_f}} d\, m_{sys}$

$$m_{sys}|_{t_f} - m_{sys}|_{t_0} = 0$$

Comp. j: $\int_{t_0}^{t_f} 0 \, dt = \int_{m_{j,sys}|_{t_0}}^{m_{j,sys}|_{t_f}} d\, m_{j,sys}$

$$m_{j,sys}|_{t_f} - m_{j,sys}|_{t_0} = 0 \quad \therefore \text{ for each } j$$

This presentation in the red box begins with the differential forms and derives the integral forms for this particular batch problem.

This derivation is not part of the solution, but is presented here for clarity. See Eqs. 5.1i and 5.2i in the "Introduction" section of this chapter.

Math Model

check Total: $m_P - m_{F1} - m_{F2} = 0$

① Me: $m_{P,Me} - 0.4\, m_{F1} - 0.7\, m_{F2} = 0$

② Wa: $m_{P,Wa} - 0.6\, m_{F1} - 0.3\, m_{F2} = 0$

③ Mix P: $m_P = m_{P,Me} + m_{P,Wa}$

check for linear independence

④ $m_{P,Me} = \omega_{P,Me}\, m_P$

⑤ $m_{P,Wa} = \omega_{P,Wa}\, m_P$

# vars = 7
# eqns = 5
D.O.F. = 2

Math. Algorithm

$[m_P, \bar{\omega}_P] = f\,[m_{F1}, m_{F2}]$

Solution

Basis: $\{ m_{F1} = 200\,g ,\; m_{F2} = 150\,g$

①: 1. $m_{P,Me} \leftarrow 0.4\, m_{F1} + 0.7\, m_{F2}$ — $m_{P,Me} = 0.4(200) + 0.7(150) = 185\,g$

②: 2. $m_{P,Wa} \leftarrow 0.6\, m_{F1} + 0.3\, m_{F2}$ — $m_{P,Wa} = 0.6(200) + 0.3(150) = 165\,g$

③: 3. $m_P \leftarrow m_{P,Me} + m_{P,Wa}$ — $m_P = 185 + 165 = 350\,g$

④: 4. $\omega_{P,Me} \leftarrow m_{P,Me} / m_P$ — $\omega_{P,Me} = 185/350 = 0.5286$

⑤: 5. $\omega_{P,Wa} \leftarrow m_{P,Wa} / m_P$ — $\omega_{P,Wa} = 165/350 = 0.4714$

Check: $350\,g - 200\,g - 150\,g \overset{Yes}{=} 0$

larger

CM 200
Hanyak

Example 4.2-4
in F+R, 2nd Ed.

9/18/90
1 of 3

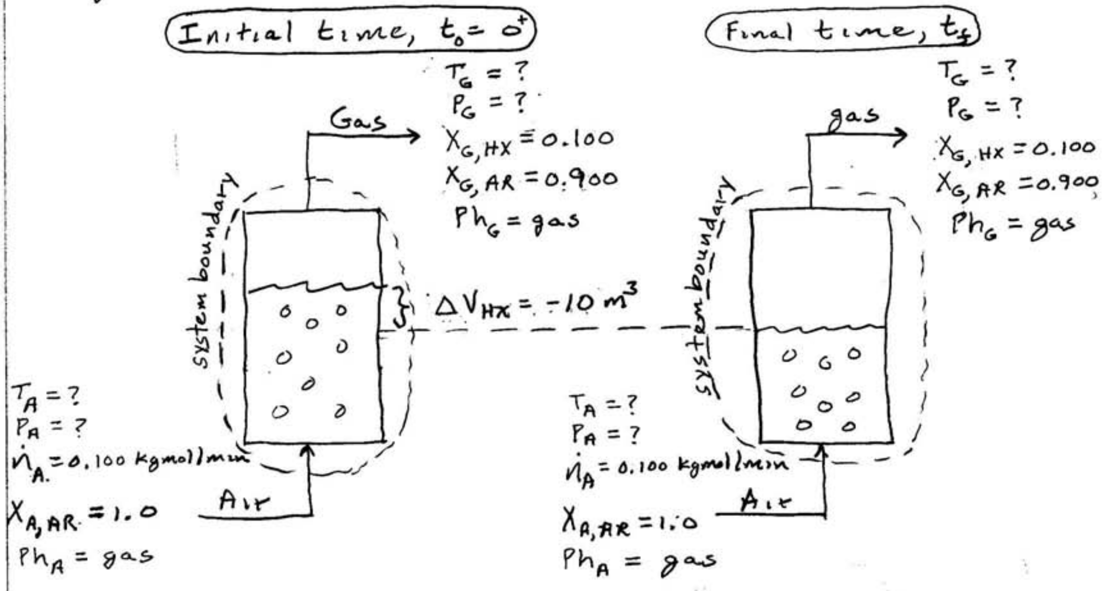
Similar to Example 4.2-4 in F&R, 3rd Ed.

Example 4.2-4

A Semi-Continuous Process

As a chemical engineer at the Bison Engineering and Evaluation Firm (BEEF, Inc.), you are supervising a technician who is feeding a chemical mixture of 10 mole percent n-hexane and 90 mole percent air to a production line. This mixture is generated by bubbling air through a 55-gallon drum of liquid n-hexane at a rate of 0.100 kg-mol/min. Since you were recently assigned to the production line, your technician with 10 years of experience wants to test your abilities as a chemical engineer. He asks you how much time would be required to vaporize 10.0 m^3 of the hexane in the drum, assuming the air is insoluble in liquid hexane?

Diagram



Assumptions

1. Open system for both air and hexane.
2. Component air flows continuously and reaches steady state instantaneously.
3. Component hexane flows semi-continuously; its an unsteady-state operation.
4. no reaction
5. Air is insoluble in liquid hexane.
6. Liquid hexane is at 20°C and 1 atm.

CM 200
Hanyak

Example 4.2-4
in F+R, 2nd Ed.

9/18/90
2 of 3

Mole Balances

{on this semibatch process, no rxn}

This presentation in the red box begins with the differential forms and derives the integral forms for this particular semi-continuous problem.

This derivation is not part of the solution, but is presented here for clarity. See Eqs. 5.4i and 5.5i in the "Introduction" section of this chapter.

Hexane:
$$-0.100\,\dot{n}_G = \frac{d\,n_{HX,sys}}{dt}$$

$$\int_{t_o=0^+}^{t_f} -0.100\,\dot{n}_G\,dt = \int_{n_{HX,sys}|_{t_o}}^{n_{HX,sys}|_{t_f}} d\,n_{HX,sys}$$

$$-0.100\,\dot{n}_G\,t_f = \underbrace{n_{HX,sys}\big|_{t_f} - n_{HX,sys}\big|_{t_o}}_{\Delta n_{HX}}$$

$\underline{\Delta n_{HX}}$ is kgmoles of hexane vaporized.

Total:
$$\dot{n}_A - \dot{n}_G = \frac{d\,n_{sys}}{dt}$$

but $n_{sys} = n_{A,sys} + n_{H,sys}$

and $d\,n_{sys} = d\,\cancelto{0}{n_{A,sys}} + d\,n_{H,sys}$

$$\dot{n}_A - \dot{n}_G = \frac{d\,n_{H,sys}}{dt}$$

$$\int_{t_o=0^+}^{t_f} (\dot{n}_A - \dot{n}_G)\,dt = \int_{n_{HX,sys}|_{t_o}}^{n_{HX,sys}|_{t_f}} d\,n_{HX,sys}$$

$$(\dot{n}_A - \dot{n}_G)\,t_f = \Delta n_{HX}$$

CM 200
Hanyak

Example 4.2-4
in F&R, 2nd Ed.

9/18/90
3 of 3

Math Model

(check) Total: $(\dot{n}_A - \dot{n}_G)\, t_f = \Delta n_{HX}$

① Air: $\dot{n}_A - 0.900\, \dot{n}_G = 0$

② Hexane: $-0.100\, \dot{n}_G\, t_f = \Delta n_{HX}$

check for linear independence

③ $\rho_{HX} = m_{HX} / \Delta V_{HX}$

④ $sg_{HX} = \dfrac{\rho_{HX} \text{ @ } 20°C}{\rho_{H_2O} \text{ @ } 4°C}$

⑤ $M_{HX} = \dfrac{m_{HX}}{\Delta n_{HX}}$

\# vars = 10
\# eqns = 5
D.O.F. = 5

Math Algorithm

$[t] = f[\dot{n}_A, \Delta V_{HX}, sg_{HX}, \rho_{H_2O}, M_{HX}]$

①: 1. $n_G \leftarrow \dot{n}_A / 0.900$

④: 2. $\rho_{HX} \leftarrow sg_{HX}\, \rho_{H_2O}$

③: 3. $m_{HX} \leftarrow \rho_{HX}\, \Delta V_{HX}$

⑤: 4. $\Delta n_{HX} \leftarrow m_{HX} / M_{HX}$

②: 5. $t_f \leftarrow -\Delta n_{HX} / (0.100\, \dot{n}_G)$

Additional Data

$M_{HX} = 86.17$
$sg_{HX} = 0.659 \, \frac{20°}{4°}$
} Table B.1 in F&R

$\rho_{H_2O} = 1.000 \text{ g/cm}^3 \text{ @ } 4°C$
↑ p. 44 in F&R

Solution

Basis: $\dot{n}_A = 0.100$ kgmol/min

$$n_G = \left(\frac{0.100 \text{ kgmol}}{\text{min}}\right)\left(\frac{1}{0.9}\right) = 0.111\,111 \frac{\text{kgmol}}{\text{min}}$$

$$\rho_{HX} = (0.659)\left(\frac{1.0 \text{ g}}{\text{cm}^3}\right)\left\langle\frac{\text{kg}}{10^3 \text{ g}}\right\rangle\left\langle\frac{10^6 \text{ cm}^3}{\text{m}^3}\right\rangle$$
$$= 659. \text{ kg/m}^3$$

$$m_{HX} = \left(\frac{659 \text{ kg}}{\text{m}^3}\right)(-10.0 \text{ m}^3) = -6590 \text{ kg}$$

$$\Delta n_{HX} = (-6590 \text{ kg})\left(\frac{\text{kgmol}}{86.17 \text{ kg}}\right)$$
$$= -76.4767 \text{ kgmol}$$

$$t_f = (76.4767 \text{ kgmol})\left(\frac{\text{min}}{0.100(0.111\,111 \text{ kgmol})}\right)$$

$$\boxed{t_f = 6882.91 \text{ min} \quad (6880 \text{ min})}$$

check

$$(\dot{n}_A - \dot{n}_G)\, t_f \overset{?}{=} \Delta n_{HX}$$

$$(0.100 - 0.111\,111)(6882.91) \overset{?}{=} -76.4767 \text{ kgmol}$$

$$\underline{\underline{-76.4760 = -76.4767}}$$

larger

CM 200
Hanyak

Problem 5.17
in F&R, 1st Ed.

9/20/90
1 of 3

Problem 5.17 {similar to Prob. 4.19 in F&R, 2nd Ed.}

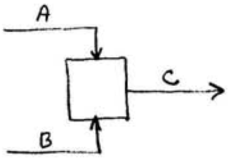
This problem is not in F&R, 3rd Ed.

As a sophomore majoring in chemical engineering, your chemistry professor in the analytical laboratory provides you with two carboys: 1) a 10-molar aqueous solution of sodium hydroxide with a specific gravity of 1.37 (20°/4°), and 2) a 5-molar aqueous solution of sodium hydroxide with a specific gravity of 1.18 (20°/4°). The professor instructs you to mix 50 mL/min of the first solution with 4 L/hr of the second solution. He then asks you what is the composition of the final mixture on a mass and molar basis, and what are the mole fractions of the two incoming streams?

Diagram

$\dot{n}_A = ?$
$x_{A,N} = ?$
$x_{A,w} = ?$

$\dot{n}_B = ?$
$x_{B,N} = ?$
$x_{B,w} = ?$



$\dot{n}_C = ?$
$x_{C,N} = ?$
$x_{C,w} = ?$

Assumptions

1. Continuous process
2. steady state
3. no rxn
4. sg's reference to H_2O at 4 °C
5. Temp. and pressures of streams A, B, & C are the same.

Given:

$\dot{V}_A = 50 \text{ mL/min}$
$\hat{C}_{A,N} = 10 \text{ g-mol NaOH/L soln}$
$sg_A = 1.37$
$\dot{V}_B = 4 \text{ L/hr}$
$\hat{C}_{B,N} = 5 \text{ g-mol NaOH/L soln}$
$sg_B = 1.18$

Find:

$x_{C,N}$ & $x_{C,w}$
$w_{C,N}$ & $w_{C,w}$
$x_{A,N}$ & $x_{A,w}$
$x_{B,N}$ & $x_{B,w}$

Additional Data

$\rho_r = 1.000 \text{ g/ml}$ for H_2O @ 4 °C ; p. 28 in F&R Text.

$M_N = 40.00$ for NaOH
$M_w = 18.016$ for H_2O
} Table B.1 in Appendix B of F&R Text.

$\dot{V}_B = 4 \text{ L/hr}$

$\dot{V}_A = (50 \text{ mL/min}) \{60 \text{ min/hr} \times \text{L}/1000 \text{ mL}\} = 3 \text{ L/hr}$

ChM 200 Hanyak

Problem 5.17
in F&R, 1st Ed.

9/20/90
2 of 3

Math. Model

① TM: $\dot{n}_A + \dot{n}_B - \dot{n}_c = 0$

② NaOH: $\dot{n}_{A,N} + \dot{n}_{B,N} - \dot{n}_{c,N} = 0$

③ H_2O: $\dot{n}_{A,w} + \dot{n}_{B,w} - \dot{n}_{c,w} = 0$

④ $\dot{n}_A = \dot{n}_{A,N} + \dot{n}_{A,w}$

⑤ $\dot{n}_B = \dot{n}_{B,N} + \dot{n}_{B,w}$

check: $\dot{n}_c = \dot{n}_{c,N} + \dot{n}_{c,w}$

⑥ $\dot{n}_{A,N} = \dot{n}_A x_{A,N}$

⑦ $\dot{n}_{A,w} = \dot{n}_A x_{A,w}$

⑧ $\dot{n}_{B,N} = \dot{n}_B x_{B,N}$

⑨ $\dot{n}_{B,w} = \dot{n}_B x_{B,w}$

⑩ $\dot{n}_{c,N} = \dot{n}_c x_{c,N}$

⑪ $\dot{n}_{c,w} = \dot{n}_c x_{c,w}$

12

⑫ $\dot{n}_A = \underline{\dot{V}_A}\, \rho_A / M_A$

~~⑬~~ $\rho_A = \underline{sg_A}\, \underline{\rho_r}$

What is Eq. 12? density plus mol. wt.

⑭ $\dot{n}_B = \underline{\dot{V}_B}\, \rho_B / M_B$

~~⑮~~ $\rho_B = \underline{sg_B}\, \underline{\rho_r}$

What is sg? See Page 3-7 in *CinChE.*

⑯ $M_A = x_{A,N}\, \underline{M_N} + x_{A,w}\, \underline{M_w}$

⑰ $M_B = x_{B,N}\, \underline{M_N} + x_{B,w}\, \underline{M_w}$

What is Eq. 16? See Page D-2 in *CinChE.*

~~⑱~~ $\dot{n}_{A,N} = \underline{\hat{c}_{A,N}}\, \underline{\dot{V}_A}$

~~⑲~~ $\dot{n}_{B,N} = \underline{\hat{c}_{B,N}}\, \underline{\dot{V}_B}$

What is Eq. 18?

molar concentration
"gotche" table, p. 3-5

⑳ $w_{c,N} = x_{c,N}\, \underline{M_N} / M_c$

㉑ $w_{c,w} = x_{c,w}\, \underline{M_w} / M_c$

What is Eq. 20?

CinChE, Page D-3

㉒ $M_c = x_{c,N}\, \underline{M_N} + x_{c,w}\, \underline{M_w}$

DOF = # vars − # eqns

DOF = 31 − 22 = 9

CM 200
Hanyak

Problem 5.17
in F&R, 1st Ed.

9/20/90
3 of 3

Math Algorithm

$$[\bar{x}_A, \bar{x}_B, \bar{x}_c, \bar{\omega}_c] = f\,[\dot{V}_A, \dot{C}_{A,N}, \dot{V}_B, \dot{C}_{B,N}, \underbrace{sg_A, sg_B, \rho_r, M_N, M_w}_{\text{5 physical constants}}]$$

⑬ 1. $\rho_A \leftarrow sg_A\,\rho_r$

⑮ 2. $\rho_B \leftarrow sg_B\,\rho_r$

⑱ 3. $\dot{n}_{A,N} \leftarrow \hat{C}_{A,N}\,\dot{V}_A$

⑲ 4. $\dot{n}_{B,N} \leftarrow \hat{C}_{B,N}\,\dot{V}_B$

② 5. $\dot{n}_{c,N} \leftarrow \dot{n}_{A,N} + \dot{n}_{B,N}$

6. **NSOLVE** for $\dot{n}_A, \dot{n}_{A,w}, x_{A,N}, x_{A,w}, M_A$ in

④ $\dot{n}_A = \dot{n}_{A,N} + \dot{n}_{A,w}$

⑥ $\dot{n}_{A,N} = \dot{n}_A\,x_{A,N}$

⑦ $\dot{n}_{A,w} = \dot{n}_A\,x_{A,w}$

⑫ $\dot{n}_A = \dot{V}_A\,\rho_A / M_A$

⑯ $M_A = x_{A,N}\,M_N + x_{A,w}\,M_W$

END

Why NSOLVE here? Eq'ns 4 and 16 are linear; Eqn's 6, 7, 12 are non-linear. Why?

7. **NSOLVE** for $\dot{n}_B, \dot{n}_{B,w}, x_{B,N}, x_{B,w}, M_B$ in

⑤ $\dot{n}_B = \dot{n}_{B,N} + \dot{n}_{B,W}$

⑧ $\dot{n}_{B,N} = \dot{n}_B\,x_{B,N}$

⑨ $\dot{n}_{B,w} = \dot{n}_B\,x_{B,w}$

⑭ $\dot{n}_B = \dot{V}_B\,\rho_B / M_B$

⑰ $M_B = x_{B,N}\,M_N + x_{B,w}\,M_w$

END

What's unique here? All unknowns are for Stream B.

A similar observations is true for Stream A in Step 6 above.

① 8. $\dot{n}_c \leftarrow \dot{n}_A + \dot{n}_B$

③ 9. $\dot{n}_{c,w} \leftarrow \dot{n}_{A,w} + \dot{n}_{B,w}$

⑪ 10. $x_{c,w} \leftarrow \dot{n}_{c,w} / \dot{n}_c$

⑩ 11. $x_{c,N} \leftarrow \dot{n}_{c,N} / \dot{n}_c$

㉒ 12. $M_c \leftarrow x_{c,N}\,M_N + x_{c,w}\,M_w$

㉑ 13. $w_{c,w} \leftarrow x_{c,w}\,M_w / M_c$

⑳ 14. $w_{c,N} \leftarrow x_{c,N}\,M_N / M_c$

Click here to view the Excel "**EZ Setup**"/**Solver** solution.

larger

CM 200 Hanyak | Example 4.5-1 in F&R, 2nd Ed. | 9/27/90 1 of 4

Similar to Example 4.5-2 in F&R, 3rd Ed.

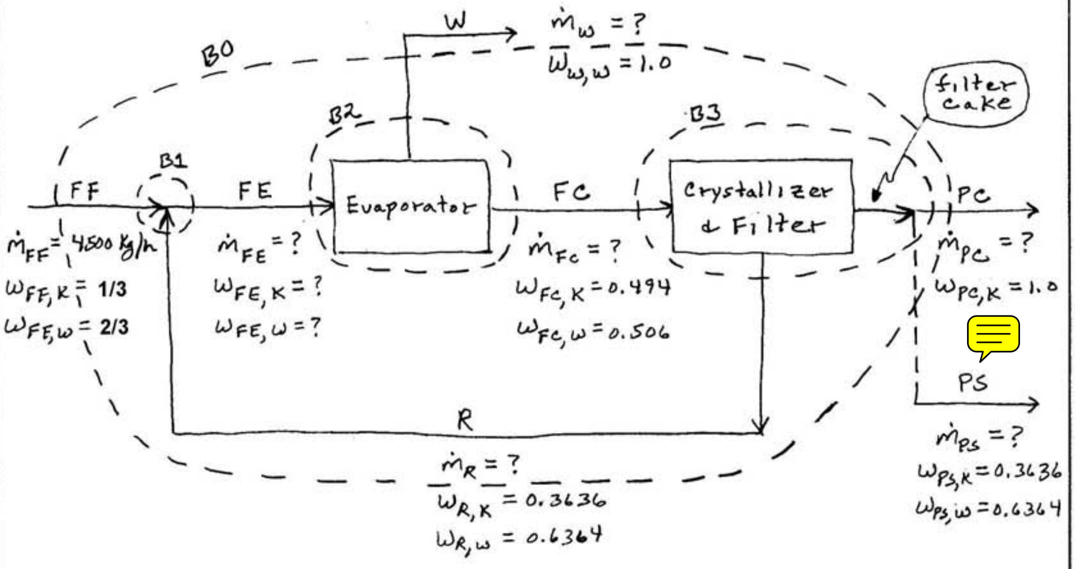
Example 4.5-1

One of our clients has asked our Bison Engineering and Evaluation Firm (BEEF, Inc.) to evaluate a multi-unit chemical process that recovers solid potassium chromate salt from an aqueous solution. The client has provide a description of the chemical process, as given in the next paragraph.

A feed stream of potassium chromate solution is sent to an evaporator where heat boils off some water as steam and produces a concentrated solution containing 49.4 wt% K_2CrO_4. This concentrated stream is fed into a crystallizer in which the solution is cooled causing potassium chromate crystals to form, and then the solution with suspended crystals is filtered. The filter cake contains solid crystals with an entrapped solution of 36.36 wt% dissolved K_2CrO_4. The crystals account for 95% of the total mass of the filter cake. The solution that passes through the filter is recycled back to the beginning of the multi-unit process. This recycle stream containing 36.36 wt% K_2CrO_4 is mixed with 4.500×10^3 kg/h of a fresh aqueous solution to the multi-unit process that contains one-third potassium chromate by mass. The resulting stream from the mixing is then fed into the evaporator.

Your project supervisor has asked you to complete the material balances on this multi-unit process. You are to determine the flow rate of the steam leaving the evaporator, the rate of production of crystalline K_2CrO_4, the feed rates that the evaporator and crystallizer must be designed to handle, and the ratio (kg recycle per kg fresh feed). Also, what is the composition of the feed to the evaporator?

Diagram



Find: $\dot{m}_W$, $\dot{m}_{PC}$, $\dot{m}_{FE}$, $\dot{m}_{FC}$, $R = \frac{\dot{m}_R}{\dot{m}_{FF}}$, $\bar{\omega}_{FE}$

cm 200
Hanyak

Example 4.5-1
in F+R, 2nd Ed.

9/27/90
2 of 4

Assumptions

1. continuous process
2. steady state
3. no rxn

Additional Data

none

Mathematical Model

Overall Balance B0

① Total: $\underline{\dot{m}}_{FF} - \dot{m}_{W} - \dot{m}_{PC} - \dot{m}_{PS} = 0$

② K_2CrO_4: $1/3\ \underline{\dot{m}}_{FF} - \dot{m}_{PC} - 0.3636\ \dot{m}_{PS} = 0$

not indep. H_2O: $2/3\ \underline{\dot{m}}_{FF} - \dot{m}_{W} - 0.6364\ \dot{m}_{PS}$

{no mixture equations}

③ $m_{PC} = 0.95\,(\dot{m}_{PC} + \dot{m}_{PS})$

\# vars = 4
\# eqns = 3
D.O.F. = 1

Know: $\dot{m}_{FF}$

Find: $\dot{m}_{W}$, $\dot{m}_{PC}$, $\dot{m}_{PS}$

Unit Balance B3

④ Total: $\dot{m}_{FC} - \dot{m}_{R} - \dot{m}_{PC} - \dot{m}_{PS}$

⑤ K_2CrO_4: $0.494\ \dot{m}_{FC} - 0.3636\,\dot{m}_{R} - \dot{m}_{PC} - 0.3636\ \dot{m}_{PS} = 0$

not indep. H_2O: $0.506\ \dot{m}_{FC} - 0.6364\,\dot{m}_{R} - 0.6364\ \dot{m}_{PS} = 0$

{no mixture equations}

\# vars = 4
\# eqns = 2
D.O.F. = 2

Know: $\dot{m}_{PC}$, $\dot{m}_{PS}$

Find: $\dot{m}_{FC}$, $\dot{m}_{R}$

Unit Balance B2

⑥ Total: $\dot{m}_{FE} - \dot{m}_{W} - \dot{m}_{FC} = 0$

⑦ K_2CrO_4: $\dot{m}_{FE,K} - 0.494\ \dot{m}_{FC} = 0$

⑧ H_2O: $\dot{m}_{FE,W} - \dot{m}_{W} - 0.506\ \dot{m}_{FC} = 0$

not indep. $\dot{m}_{FE} = \dot{m}_{FE,K} + \dot{m}_{FE,W}$

\# vars = 5
\# eqns = 3
D.O.F. = 2

Know: $\dot{m}_{W}$, $\dot{m}_{FC}$

Find: $\dot{m}_{FE}$, $\dot{m}_{FE,K}$, $\dot{m}_{FE,W}$

Unit Balance B1

Not independent; therefore, can not write it.

cm 200
Hanyak

Example 4.5-1
in F&R, 2nd Ed.

9/27/90
3 of 4

Additional Equations

⑨ $R = \dot{m}_R / \dot{m}_{FF}$

⑩ $\dot{m}_{FE,K} = \omega_{FE,K}\, \dot{m}_{FE}$

⑪ $\dot{m}_{FE,w} = \omega_{FE,w}\, \dot{m}_{FE}$

Overall

\# var = 12
\# eqn = 11
D.O.F. = 1

Math Algorithm

$[\dot{m}_w, \dot{m}_{pe}, \dot{m}_{FE}, \dot{m}_{Fc}, R, \bar{\omega}_{FE}] = f\,[m_{FF}]$

1. SOLVE for $\dot{m}_w, \dot{m}_{pe}, \dot{m}_{ps}$ in

① $\dot{m}_w + \dot{m}_{pe} + \dot{m}_{ps} = \dot{m}_{FF}$

② $\dot{m}_{pe} + 0.3636\, \dot{m}_{ps} = 1/3\ \dot{m}_{FF}$

③ $0.05\, \dot{m}_{pe} - 0.95\, \dot{m}_{ps} = 0$

END

2. SOLVE for $\dot{m}_{Fc}, \dot{m}_R$ in

④ $\dot{m}_{Fc} - \dot{m}_R = \dot{m}_{pe} + \dot{m}_{ps}$

⑤ $0.494\, \dot{m}_{Fc} - 0.3636\, \dot{m}_R = \dot{m}_{pe} + 0.3636\, \dot{m}_{ps}$

END

⑧ 3. $\dot{m}_{FE,w} \leftarrow 0.506\, \dot{m}_{Fc} + \dot{m}_w$

⑦ 4. $\dot{m}_{FE,K} \leftarrow 0.494\, \dot{m}_{Fc}$

⑥ 5. $\dot{m}_{FE} \leftarrow \dot{m}_w + \dot{m}_{Fc}$

⑪ 6. $\omega_{FE,w} \leftarrow \dot{m}_{FE,w} / \dot{m}_{FE}$

⑩ 7. $\omega_{FE,K} \leftarrow \dot{m}_{FE,K} / \dot{m}_{FE}$

⑨ 8. $R \leftarrow \dot{m}_R / \dot{m}_{FF}$

Click here to view the Excel "**EZ Setup**"/ **Solver** file containing solutions of several mathematical models and a mathematical algorithm. This file also demonstrates the financial benefit of recycling materials.

Solution Check

$$\dot{m}_{FE} \overset{?}{=} \dot{m}_{FE,K} + \dot{m}_{FE,w}$$

or

$$1.0 \overset{?}{=} \omega_{FE,K} + \omega_{FE,w}$$

CM200
Hanyak

Example 4.5-1
in F&R, 2nd Ed.

9/27/90
4 of 4

Mathematical Model 2

Unit Balance B1

① Total: $\underline{\dot{m}}_{FF} + \dot{m}_R - \dot{m}_{FE} = 0$

② K_2CrO_4: $1/3\ \underline{\dot{m}}_{FF} + 0.3636\ \dot{m}_R - \dot{m}_{FE,K} = 0$

③ H_2O: $2/3\ \underline{\dot{m}}_{FF} + 0.6364\ \dot{m}_R - \dot{m}_{FE,w} = 0$

not indep Mix FE: $\dot{m}_{FE} = \dot{m}_{FE,K} + \dot{m}_{FE,w}$

\# vars = 5
\# eqns = 3
DOF = 2

Know: $\dot{m}_{FF}$, $\dot{m}_R$

Unit Balance B2

④ Total: $\dot{m}_{FE} - \dot{m}_w - \dot{m}_{Fc} = 0$

⑤ K_2CrO_4: $\dot{m}_{FE,K} - 0.494\ \dot{m}_{Fc} = 0$

not indep H_2O: $\dot{m}_{FE,w} - \dot{m}_w - 0.506\ \dot{m}_{Fc} = 0$

not indep Mix FE: $\dot{m}_{FE} = \dot{m}_{FE,K} + \dot{m}_{FE,w}$

\# vars = 4
\# eqns = 2
DOF = 2

Know: $\dot{m}_{FE}$, $\dot{m}_{FE,K}$

Unit Balance B3

⑥ Total: $\dot{m}_{Fc} - \dot{m}_R - \dot{m}_{Pc} - \dot{m}_{PS} = 0$

⑦ K_2CrO_4: $0.494\ \dot{m}_{Fc} - 0.3636\ \dot{m}_R - \dot{m}_{Pc} - 0.3636\ \dot{m}_{PS} = 0$

not indep H_2O: $0.506\ \dot{m}_{Fc} - 0.6364\ \dot{m}_R - 0.6364\ \dot{m}_{PS} = 0$

⑧ $\dot{m}_{Pc} = 0.95\ (\dot{m}_{Pc} + \dot{m}_{RS})$

\# vars = 4
\# eqns = 3
DOF = 1

Know: $\dot{m}_{Fc}$

Additional Equations

⑨ $\dot{m}_{FE,K} = \omega_{FE,K}\ \dot{m}_{FE}$

⑩ $\dot{m}_{FE,w} = \omega_{FE,w}\ \dot{m}_{FE}$

⑪ $R = \dot{m}_R / \dot{m}_{FF}$

overall

\# vars = 12
\# eqns = 11
DOF = 1

larger

cm 200
Hanyak

Example 4.7-3
in F&R, 2nd Ed.

10/4/90
1 of 3

Similar to Example 4.8-3 in F&R, 3rd Ed.

Example 4.7-3

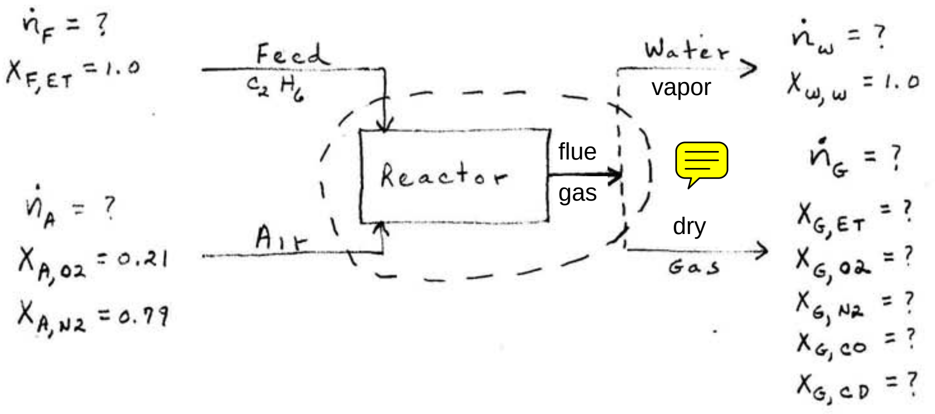
You were heating your home using natural gas, which is mostly pure methane. You have just signed a contract with a new gas supplier, BuyLo, to supply you with ethane (C_2H_6) at a cheaper price than natural gas. BuyLo has tested your home furnace and found you get a 90% molar conversion of the ethane when it is burned with 50% excess air on a molar basis. Of the ethane burned, 25% reacts to form carbon monoxide (CO) and the balance to form carbon dioxide (CO_2). Being that you just graduated with a bachelor degree in chemical engineering, you have decided to calculate the molar composition on a dry basis of the gas going up the flue and the molar ratio of water to dry flue gas. You also want to calculate the selectivity and the three forms of yield, as define in the 2nd Edition of the Felder and Rousseau textbook.

Additional Data

Rxn I : $2\,C_2H_6 + 7\,O_2 \rightarrow 4\,CO_2 + 6\,H_2O$

Rxn II : $2\,C_2H_6 + 5\,O_2 \rightarrow 4\,CO + 6\,H_2O$

Diagram



Assumptions

1. Basis: $\dot{n}_F$ = 100 gmol/hr
2. Steady state
3. Air contains only 79 mole % N_2 and 21 % O_2

CM 200
Hanyak

Example 4.7-3
in F&R, 2nd Ed.

10/4/90
2 of 3

Mathematical Model

Total: ① $\underline{\dot{n}}_F + \dot{n}_A - \dot{n}_w - \dot{n}_G + \dot{R}_I + 3\dot{R}_{II} = 0$

C_2H_6: ② $\underline{\dot{n}}_F - \dot{n}_{G,ET} - 2\dot{R}_I - 2\dot{R}_{II} = 0$

O_2: ③ $0.21\dot{n}_A - \dot{n}_{G,O2} - 7\dot{R}_I - 5\dot{R}_{II} = 0$

N_2: ④ $0.79\dot{n}_A - \dot{n}_{G,N2} = 0$

CO: ⑤ $-\dot{n}_{G,CO} + 4\dot{R}_{II} = 0$

CO_2: ⑥ $-\dot{n}_{G,CD} + 4\dot{R}_I = 0$

H_2O: ⑦ $-\dot{n}_w + 6\dot{R}_I + 6\dot{R}_{II} = 0$

⑧ $\dot{n}_{G,ET} = \dot{n}_G X_{G,ET}$

⑨ $\dot{n}_{G,O2} = \dot{n}_G X_{G,O2}$

⑩ $\dot{n}_{G,N2} = \dot{n}_G X_{G,N2}$

⑪ $\dot{n}_{G,CO} = \dot{n}_G X_{G,CO}$

⑫ $\dot{n}_{G,CD} = \dot{n}_G X_{G,CD}$

Check: $\dot{n}_G = \dot{n}_{G,ET} + \dot{n}_{G,O2} + \dot{n}_{G,N2} + \dot{n}_{G,CO} + \dot{n}_{G,CD}$

⑬ $$\frac{\underline{\dot{n}}_F - \dot{n}_{G,ET}}{\underline{\dot{n}}_F} = 0.9$$

Click here for a definiton of % excess air.

⑭ + ⑮ $0.21\dot{n}_A = 1.5\,\dot{n}^t_{O2}$ $\dot{n}^t_{O2} = \left(\frac{7 \text{ mol } O_2}{2 \text{ mol ET}}\right)\underline{\dot{n}}_F$

F&R, 2nd Ed., p. 144

⑯ $\dot{n}_{G,CO} = 0.25\,(\underline{\dot{n}}_F - \dot{n}_{G,ET})\left(\frac{4 \text{ mol CO}}{2 \text{ mol ET}}\right)$

dep. eq'n $\dot{n}_{G,CD} = 0.75\,(\underline{\dot{n}}_F - \dot{n}_{G,ET})\left(\frac{4 \text{ mol CD}}{2 \text{ mol ET}}\right)$

⑱ $R = \dot{n}_w / \dot{n}_G$

$\leftarrow$ # vars = 18
# eqns = 17
D.O.F = 1

⑲ $S = \dot{n}_{G,CD} / \dot{n}_{G,CO}$

⑳ $$Y_{100\%} = \frac{\dot{n}_{G,CD}}{2\,\underline{\dot{n}}_F}$$ $\leftarrow$ $\boxed{\dot{n}'_{G,CD} = \left(\frac{4 \text{ mol CD}}{2 \text{ mol ET}}\right)\dot{n}_F}$

㉑ $$Y_F = \frac{\dot{n}_{G,CD}}{\underline{\dot{n}}_F}$$

㉒ $$Y_{RC} = \frac{\dot{n}_{G,CD}}{\underline{\dot{n}}_F - \dot{n}_{G,ET}}$$

# vars = 22
# eqns = 21
D.O.F. = 1

F&R, 2nd p. 127

larger

cm 200 Example 2-3 (Thomspon & Ceckler) Dr. Hanyak

Application of Atom Balances

A client of the Bison Engineering and Evaluation Firm (BEEF, Inc.) is involved in the refining and petrochemical business. They are producing hydrogen by reacting methane and ethane in the presence of a nickel catalyst. Our client has asked BEEF, Inc. to determine the molar ratio of methane to ethane in the feed to the reactor based on an analysis of the gases leaving the reactor. Our Analytical Department has taken samples of the exiting gas stream and used gas chromatography to determine the following composition of that stream on a dry basis:

CH_4	methane	4.6 mol%
$C2H_6$	ethane	2.3 mol%
CO	carbon monoxide	18.6 mol%
CO_2	carbon dioxide	4.6 mol%
H_2	hydrogen	69.7 mol%

Although steam is present in the exiting gas mixture, it is not included in the analytical analysis because the analytical technique does not detect the presence of water vapor. Note that the feed to the reactor only contains methane and ethane.

Our client would also like to know how many pounds of steam react in the reactor per 1000 standard cubic feet (SCF) of hydrocarbon feed gas.

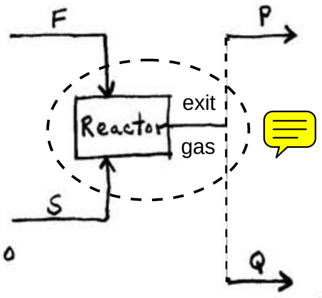
Since chemical reactions are not given in the above problem statement, you are to use atom balances to solve the problem.

CM 200 | Example 2-3 (Thomspon & Ceckler) | Dr. Hanyak

Diagram

$\dot{n}_F = ?$
$X_{F,CH_4} = ?$
$X_{F,C_2H_6} = ?$

$\dot{n}_S = ?$
$X_{S,H_2O} = 1.0$



$\dot{n}_P = ?$
$X_{P,CH_4} = 0.046$
$X_{P,C_2H_6} = 0.023$
$X_{P,CO} = 0.186$
$X_{P,CO_2} = 0.046$
$X_{P,H_2} = 0.697$

$\dot{n}_Q = ?$
$X_{Q,H_2O} = 1.0$

Assumptions

1. steady state
2. stream F is an ideal gas at 60°F and 1atm, s.c.
3. Basis: $\dot{n}_P = 100$ lbmol/min

Find:

1. Molar ratio of CH_4 to C_2H_6 in Ⓕ.
2. $\dot{n}'_{SR}$ per 1000 scf of Ⓕ.
3. $V'_F = 1000\ ft^3$ @ s.c.

Math. Model

see Page 5-6 to write the atom balances

① C: $1\,\dot{n}_{F,CH_4} + 2\,\dot{n}_{F,C_2H_6} - 1(0.046)\underline{\dot{n}_P} - 2(0.023)\underline{\dot{n}_P} - 1(0.186)\underline{\dot{n}_P} - 1(0.046)\underline{\dot{n}_P} = 0$

② H: $4\,\dot{n}_{F,CH_4} + 6\,\dot{n}_{F,C_2H_6} + 2(1.0)\,\dot{n}_S - 4(0.046)\underline{\dot{n}_P} - 6(0.023)\underline{\dot{n}_P}$
$- 2(0.697)\underline{\dot{n}_P} - 2(1.0)\,\dot{n}_Q = 0$

③ O: $1(1.0)\,\dot{n}_S - 1(0.186)\underline{\dot{n}_P} - 2(0.046)\underline{\dot{n}_P} - 1(1.0)\,\dot{n}_Q = 0$

④ $R = \dot{n}_{F,CH_4} / \dot{n}_{F,C_2H_6}$

⑤ $\underline{P_F}\,\underline{V'_F} = \dot{n}'_F\ R\,\underline{T_F}$

⑥ $\dfrac{\dot{n}'_{SR}}{\dot{n}_{SR}} = \dfrac{\dot{n}'_F}{\dot{n}_F}$

Click here to learn about scaling.

⑦ $\dot{n}_F = \dot{n}_{F,CH_4} + \dot{n}_{F,C_2H_6}$

⑧ $\dot{n}_{SR} = \overbrace{(\dot{n}_S - \dot{n}_Q)}^{\text{Treat as } \Delta\dot{n}_{SQ}}$

# vars = 13
# eqns = 8
D.O.F = 5 ?

Math. Algorithm

$[R, \dot{n}'_S] = f[T_F, P_F, V'_F, \dot{n}_P]$

③: 1. $\Delta\dot{n}_{SQ} = (\dot{n}_S - \dot{n}_Q) \leftarrow 0.278\,\dot{n}_P$

2. SOLVE $\dot{n}_{F,CH_4}$ & $\dot{n}_{F,C_2H_6}$;

①: $1\,\dot{n}_{F,CH_4} + 2\,\dot{n}_{F,C_2H_6} = 0.324\,\dot{n}_P$

②: $4\,\dot{n}_{F,CH_4} + 6\,\dot{n}_{F,C_2H_6} = 1.716\,\dot{n}_P - 2\,\Delta\dot{n}_{SQ}$

END;

larger

ChE 200
Dr. Hanyak

Problem 5.26
F&R, 2nd Ed.

10/16/91
1 of 4

Similar to Problem 5.38 in F&R, 3rd Ed.

Problem Statement

A client of of the Bison Engineering and Evaluation Firm (BEEF, Inc.) is in the business of making propane from propylene and hydrogen. The propane is marketed in fuel tanks for barbecues, portable stove, and residential central heating. In the client's plant, equal molar amounts of propylene and hydrogen are fed into the batch reactor at 25°C and a total absolute pressure of 32.0 atm. After the reactor has been charged, the hydrogenation reaction of C_3H_6 (g) + H_2 (g) ==> C_3H_8 (g) starts and is allowed to take place for a time until the temperature reaches 250°C. Your project supervisor has asked you to analyze the following two cases for this batch reactor:

1) determine the final pressure when the reaction goes to completion at 250°C.
2) determine the mole percentage of propylene that reacts if the final conditions are 250°C and 35.1 atm.

Since an equation of state is required to solve this problem, your project supervisor wants you to produce a table for these two cases based on using different equations of state, namely ideal gas law and the Lee-Kesler-Plocker (LKP), Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), and Peng-Robinson Stryjek-Vera (PRSV) in HYSYS.

Diagram

@ $t_i = 0$

$T_i = 25°C$
$P_i = 32.0$ atm
$n_i = ?$
$x_{i,PY} = 0.5$
$x_{i,H2} = 0.5$
$V_i = ?$

$\Longrightarrow$

@ t_f

$T_f = 250°C$
$P_f = ?$
$n_f = ?$
$x_{f,PY} = ?$
$x_{f,H2} = ?$
$x_{f,PR} = ?$
$V_f = ?$

Assumptions

1. closed batch reactor, i.e. $V_i = V_f$
2. ideal gas behavior
3. Basis of $n_i = 100$ mol

Model

Total: ① $-R_I = n_f - \underline{n_i}$

Propylene: ② $-R_I = n_{f,PY} - 0.5\,\underline{n_i}$ ⑤ $n_{f,PY} = n_f\, x_{f,PY}$

Hydrogen: ③ $-R_I = n_{f,H2} - 0.5\,\underline{n_i}$ ⑥ $n_{f,H2} = n_f\, x_{f,H2}$

Propane: ④ $R_I = n_{f,PR}$ ⑦ $n_{f,PR} = n_f\, x_{f,PR}$

check: $n_f = n_{f,PY} + n_{f,H2} + n_{f,PR}$

# vars = 18
# eqns = 13
DOF = 5

⑧ $V_i = V_f$

⑨ $\eta = \dfrac{0.5\,\underline{n_i} - n_{f,PY}}{0.5\,\underline{n_i}}$

⑩ $\hat{V}_i = \hat{V}[\underline{T_i}, \underline{P_i}, \underline{\bar{X}_i}]$ ⑫ $\hat{V}_i = V_i / \underline{n_i}$

⑪ $\hat{V}_f = \hat{V}[\underline{T_f}, \underline{P_f}, \underline{\bar{X}_f}]$ ⑬ $\hat{V}_f = V_f / n_f$

CM 200
Dr. Hanyak

Problem 5.26
F&R, 2nd Ed.

10/16/91
2 of 4

Algorithm A for ideal or real gas mixture

$$[P_f, \bar{X}_f] = f_A[T_i, P_i, n_i, \bar{X}_i, T_f, \eta]$$

Answers for Algorithm A and B are given using the ideal gas law. You should check if they are correct.

Try in Algorithm A to use several fluid packages in Aspen HYSYS to find the molar volume. The equations of state to try are SRK, PRSV, MBWR, and Lee-Kesler-Plocker. See Pages 3-23 to 3-24 in Chapter 3 of CinChE.

⑨ 1. $n_{f,PY} \leftarrow 0.5(1-\eta)\,n_i$
② 2. $R_I \leftarrow 0.5\,n_i - n_{f,PY}$
① 3. $n_f \leftarrow n_i - R_I$
③ 4. $n_{f,H2} \leftarrow 0.5\,n_i - R_I$
④ 5. $n_{f,PR} \leftarrow R_I$

⑤ 6. $X_{f,PY} \leftarrow n_{f,PY}/n_f$
⑥ 7. $X_{f,H2} \leftarrow n_{f,H2}/n_f$
⑦ 8. $X_{f,PR} \leftarrow n_{f,PR}/n_f$

⑩ 9. $\hat{V}_i \leftarrow \hat{V}[T_i, P_i, \bar{X}_i] = RT_i/P_i$
⑫ 10. $V_i \leftarrow \hat{V}_i\,n_i$
⑧ 11. $V_f \leftarrow V_i$

⑬ 12. $\hat{V}_f \leftarrow V_f/n_f$
⑪ 13. $P_f \leftarrow P[T_f, \hat{V}_f, \bar{X}_f] = RT_f/\hat{V}_f$

↑ 28.1 atm for ideal gas

For ideal gas only,

$$\frac{P_f V_f}{P_i V_i} = \frac{n_f R T_f}{n_i R T_i}$$

which gives

$$P_f = \frac{n_f\,T_f}{n_i\,T_i}\,P_i$$

In Aspen HYSYS for real gas, you would guess pressure and then calculate its molar volume. You will continue the iteration until the calculated molar volume match that in Step 12.

Algorithm B for ideal gas mixture only

$$[\eta, \bar{X}_f] = f_B[T_i, P_i, n_i, \bar{X}_i, T_f, P_f]$$

⑩ 1. $\hat{V}_i \leftarrow \hat{V}[T_i, P_i] = RT_i/P_i$
⑫ 2. $V_i \leftarrow \hat{V}_i\,n_i$
⑧ 3 $V_f \leftarrow V_i$
⑪ 4. $\hat{V}_f \leftarrow \hat{V}[T_f, P_f] = RT_f/P_f$
⑬ 5. $n_f \leftarrow V_f/\hat{V}_f$

① 6. $R_I \leftarrow n_i - n_f$
② 7. $n_{f,PY} \leftarrow 0.5\,n_i - R_I$
③ 8. $n_{f,H2} \leftarrow 0.5\,n_i - R_I$
④ 9. $n_{f,PR} \leftarrow R_I$

⑤ 10. $X_{f,PY} \leftarrow n_{f,PY}/n_f$
⑥ 11. $X_{f,H2} \leftarrow n_{f,H2}/n_f$
⑦ 12. $X_{f,PR} \leftarrow n_{f,PR}/n_f$

⑨ 13. $\eta \leftarrow [(0.5n_i - n_{f,py})/(0.5n_i)](100)$

↑ 75 % conversion of propylene for the ideal gas law

For ideal gas only,

$$\frac{P_f V_f}{P_i V_i} = \frac{n_f R T_f}{n_i R T_i}$$

which gives

$$n_f = \frac{P_f}{P_i}\cdot\frac{T_i}{T_f}\cdot n_i$$

For ideal gas mixture ONLY, the molar volume is only a function of temperature and pressure and NOT composition.

CM 200
Dr. Hanyak

Problem 5.26
F&R, 2nd Ed.

10/16/91
3 of 4

Algorithm C

not an ideal gas

For real gas mixture, the molar volume is always a function of temperature, pressure, and composition.

$$[\eta, \bar{X}_f] = f_c[T_i, P_i, n_i, \bar{X}_i, T_f, P_f]$$

```
⑩  1.  $\hat{V}_i \leftarrow \hat{V}[T_i, P_i, \bar{X}_i]$
⑫  2.  $V_i \leftarrow \hat{V}_i n_i$
⑧  3.  $V_f \leftarrow \hat{V}_i$

    4.  Iterate on $\eta$ in
⑨          $n_{f,PY} \leftarrow 0.5(1-\eta) n_i$
②          $R_I \leftarrow 0.5 n_i - n_{f,PY}$
①          $n_f \leftarrow n_i - R_I$
③          $n_{f,H2} \leftarrow 0.5 n_i - R_I$
④          $n_{f,PR} \leftarrow R_I$

⑤          $x_{f,PY} \leftarrow n_{f,PY} / n_f$
⑥          $x_{f,H2} \leftarrow n_{f,H2} / n_f$
⑦          $x_{f,PR} \leftarrow n_{f,PR} / n_f$

⑬          $\hat{V}_f \leftarrow V_f / n_f$
⑪          $\hat{V}_f' \leftarrow \hat{V}[T_f, P_f, \bar{X}_f]$
        until $f(\eta) = \hat{V}_f - \hat{V}_f' = 0$
```

For this "eos" function, use SRK, PRSV, MBWR, of Lee-Kesler-Plocker in HYSYS.

Consult the "Development of a Math Algorithm" in Chapter 4 of the CinChE manual to see how an ITERATE construct is developed, starting on Page 4-16.

For this "eos" function, use SRK, PRSV, MBWR, of Lee-Kesler-Plocker in HYSYS.

Using various equations of state in Aspen HYSYS for the "eos" function, one can solve Algorithms A and C for a real gas mixture and not an ideal gas mixture. The next page tabulates the solutions for each algorithm using the Lee-Kesler-Plocker (LKP), Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), and Peng-Robinson Stryjek-Vera (PRSV) in HYSYS. The percent deviation from the PRSV equation of state is given for each solution, including the one for the ideal gas law.

Algorithms A, B, and C were programmed into an Excel file, and all of the "eos" functions, except for the ideal gas cases, were solved using Aspen HYSYS.

Click here to download the Excel file

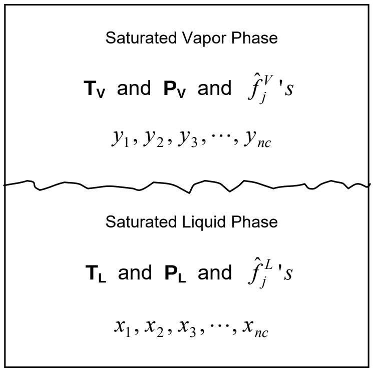
Click here to download the HYSYS file

Introduction

This chapter on phase equilibrium has three major objectives. First, vapor-liquid equilibrium, environmental equilibrium, and solubility are examined using the first principle of the distribution coefficient discussed in Chapter 2. You should review this material in Chapter 2 before continuing to read here. Second, several key concepts are described in the form of graphic organizers. Third, example phase equilibrium problems are provided, whose solutions were generated using the problem solving strategy described in Chapter 4. Most of these examples are worked-out problems found in various editions of the Felder and Rousseau textbook [2005] entitled "*Elementary Principles of Chemical Processes*." Once you understand the solution to an example in this *CinChE* chapter, you should compare it to its counterpart in the appropriate edition of the Felder and Rousseau textbook and analyze the differences. The information on vapor-liquid equilibrium, environmental equilibrium, and solubility, as well as the graphic organizers, will help you to understand the example problems.

Vapor-Liquid Equilibrium

Based on the presentation in Chapter 2, the criteria for phase equilibrium are that the temperature in all phases is the same, the pressure in all phases is the same, and the fugacity for each chemical component in all phases is the same. When the fugacity of each component in each phase is the same, the composition in each phase has its own set of fixed values. For example, consider the following isolated system for vapor-liquid equilibrium:



where "*nc*" is the number of chemical components in the system, and the temperature, pressure, and composition of each phase are measurable properties. An isolated system is a hypothetical construct that has neither material nor energy crossing the system boundary. Each of the chemical components (*j-th* = 1, 2, 3, …, *nc*) is distributed in both phases and no chemical reactions are occurring. The vapor mole fractions ($y_1, y_2, y_3, \cdots, y_{nc}$) have fixed values, while the liquid mole fractions ($x_1, x_2, x_3, \cdots, x_{nc}$) have fixed but different values. If the temperature or pressure in the above diagram were to increase (or decrease) slightly, the compositions in the vapor and liquid phases would adjust to a new state of equilibrium, so that the fugacity of each *j-th* component ($\hat{f}_j$) becomes the same in both phases. In this hypothetical system, its boundary is flexible and, thus, allows for expansion or contraction of its volume, in order to account for changes in temperature or pressure.

As was defined in Chapter 2, the first principle for phase equilibrium is called the distribution coefficient, or sometimes it is also know as the partitioning coefficient or the equilibrium vaporization ratio. This first principle is expressed as follows for the *j-th* component in the equilibrium system:

$$K_j = \frac{\textit{composition of component j in one phase}}{\textit{composition of component j in another phase}}$$

oxygen and give off carbon dioxide, while algae performing photosynthesis consume carbon dioxide and emit oxygen.

The second simplified model to represent vapor-liquid equilibrium is **Raoult's Law**. It is used for chemical compounds that will condense from a vapor phase. The saturated vapor behaves as an ideal gas ($\hat{\phi}_j^V = 1$) and the saturated liquid behaves as ideal solution because the *j-th* component has similar intermolecular interactions with other molecules (including itself) in the mixture ($\hat{\phi}_j^L = P_j^* / P$). With these assumptions the rigorous chemical criterion for vapor-liquid equilibrium ($\hat{\phi}_j^V y_j P = \hat{\phi}_j^L x_j P$) can be reduced to the following, which is known as Raoult's Law:

Subcritical Components:

$$y_j P = P_j^* x_j \qquad \Rightarrow \qquad K_j = \frac{y_j}{x_j} = \frac{P_j^*}{P}$$

$$P_j^* = psat[T, pure\ j]$$

where T and P are the temperature and pressure of the equilibrium system, respectively, and the variable P_j^* is called the vapor pressure of pure component *j-th* at the temperature of the equilibrium system. The notation of $psat[T, pure\ j]$ is a functional form for the saturation pressure of a pure chemical compound. This functional form can be represented by a graph, table, equation, or software tool like the Aspen HYSYS® simulator or *ThermoSolver*. The equation most often used to represent the relationship between the temperature and saturation pressure of a pure chemical substance ($psat[T, pure\ j]$) is the Antoine equation. Your textbook defines this equation and provides a table of its coefficients for various chemical substances (i.e. compounds). These coefficients also can be found in Aspen HYSYS®, *ThermoSolver*, and the *AIChE eLibrary* database.

Raoult's Law is an approximation that is generally valid when x_j is close to 1—that is, when the liquid is almost pure component *j-th*. It is also valid over the entire range of compositions (zero to one) for mixtures of similar substances, such as hydrocarbons of similar molecular weights. These mixtures are usually ideal solutions, like the benzene-toluene system or the hexane-octane system, as we will see later in some of the example problems. In a vapor-liquid system at a specific temperature and pressure, Raoult's Law will primarily be used to represent the equilibrium for those chemical components that are subcritical; that is, the equilibrium temperature is below their critical temperature.

If the vapor phase behaves like an ideal gas mixture, then **Dalton's Law** states that the partial pressures of the chemical components (p_j's) add up to the total pressure of the vapor phase. It is expressed mathematically as follows:

Dalton's Law:

$$P = p_1 + p_2 + \cdots + p_{nc} \qquad where \qquad p_j = y_j P \quad for\ j = 1, 2, 3, \cdots, nc$$

If you substitute the expression $y_j P$ for the partial pressure into Dalton's Law and then divide by the total pressure, the resulting equation states that the vapor mole fractions of the chemical components add to one. The assumption of an ideal gas is a good approximation when $P \le 3\ atm$. Also, mole fractions and volume fractions are equivalent for an ideal gas mixture. Click here for a proof of this equivalence.

The above form of Raoult's Law is for a vapor-liquid equilibrium system where each chemical component condenses and thus distributes itself in both phases. Special forms of this law exist for a one-condensable component and a pure-component equilibrium system. In a **one-condensable component** system, "$nc \ge 2$" in the vapor phase and "$nc = 1$" in the liquid phase; that is, only one chemical component various chemical compounds are available from the Environmental Protection Agency (EPA) as a program download called the EPI Suite.

In the environmental graphical organizer on the next page, the water solubility quantity appears not to be the ratio of two compositions. The actual definition for water solubility is

$$K_j = S_j = \frac{\text{mass fraction of } j \text{ in the liquid solution}}{\text{mass fraction of } j \text{ in the pure solid}} = \frac{m_j / m_{\text{soln}}}{1.0}$$

Since the solid phase contains only pure component *j-th*, then its mass fraction is always one. For very dilute solutions, water solubility is often expressed with units of *moles j per liter* of solution, as follows:

$$S_j = \frac{m_j}{m_{\text{soln}}} = \frac{M_j n_j}{\rho_{\text{soln}} V_{\text{soln}}} \quad \Rightarrow \quad S_{w,j} = \frac{S_j \cdot \rho_{\text{soln}}}{M_j} = \frac{n_j}{V_{\text{soln}}}$$

where M_j is the molecular weight of the solute *j*, and ρ_{soln} is the mass density of the solution, which is composed of solute *j* and water. When the solution is very dilute, we often approximate ρ_{soln} to be equal to ρ_{water} at the temperature and pressure of the solution.

Example Problems

When you begin to develop the mathematical model for any chemical process problem, you will start with the first principles presented in Chapter 5 for the material balances of a continuous, batch, semi-batch, or semi-continuous system. When multiple phases coexist within the system boundary, you will assume phase equilibrium, and you will need to apply the appropriate equilibrium equations to solve the problem. These equations are Raoult's Law for vapor-liquid equilibrium, Henry's Law for non-condensables dissolved in a liquid, partitioning coefficient relationships for environmental equilibrium, solubility for water-solid systems, and/or any other equilibrium models not discussed here but found in your textbook for this introductory course on chemical engineering.

The list below summarizes the graphic organizers (**go**) and example problems (**ep**) that appear in the remainder of this chapter. The example problems require the application of material balance and phase equilibrium principles, and they were solved using the problem solving strategy outlined in Chapter 4.

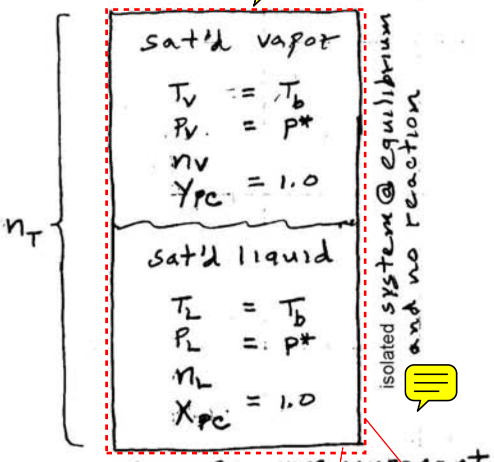
If you have any questions about the graphic organizers or example problem solutions, please consult with one of your teammates or contact the instructor. The instructor is very willing to help you, if you ask.

larger

Pure Component Phase Equilibrium

Page 1 of 4

Diagram



where PC - pure component

Model

$$n_T = n_V + n_L$$
$$1.0 = n_V/n_T + n_L/n_T$$
$$1.0 = V_f + L_f$$

$$\boxed{\begin{aligned} V_T &= V_{SV} + V_{SL} \\ n_T \hat{V}_T &= n_V \hat{V}_{SV} + n_L \hat{V}_{SL} \\ \hat{V}_T &= V_f \hat{V}_{SV} + L_f \hat{V}_{SL} \end{aligned}}$$

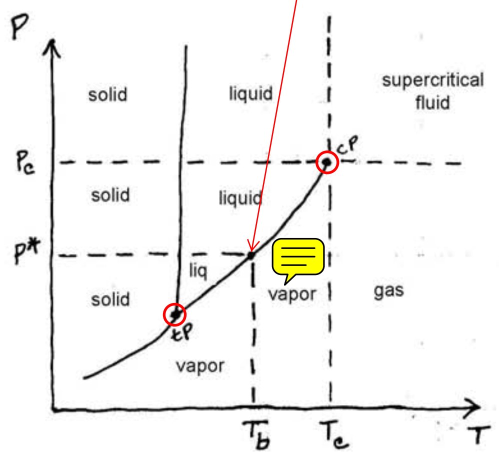
$$U_T = U_{SV} + U_{SL}$$
$$\hat{U}_T = V_f \hat{U}_{SV} + L_f \hat{U}_{SL}$$

$$H_T = H_{SV} + H_{SL}$$
$$\hat{H}_T = V_f \hat{H}_{SV} + L_f \hat{H}_{SL}$$

Thermal equil.: $T_V = T_L = T_b$ ← boiling temperature.

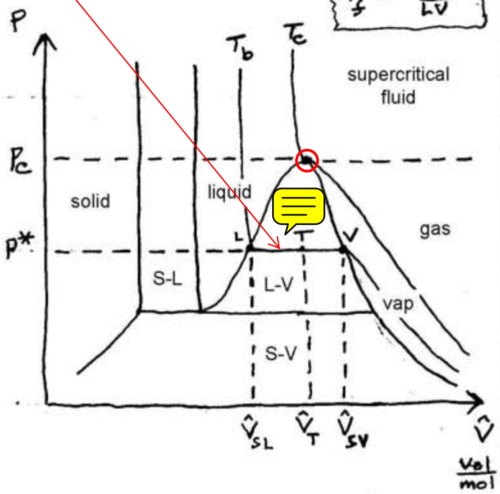
Mechanical equil.: $P_V = P_L = P^*$ ← vapor pressure, F+R, 3rd Ed., p. 243

PT Diagram



PVT Diagram

$$\boxed{V_f \equiv \frac{\overline{LT}}{\overline{LV}}}$$



For $P^* = 1$ atm, $T_b = T_{NBP}$ found in Table B.1, F+R, 3rd Ed.

For vapor and liquid coexisting at same time, line in PT diagram between triple point and critical point is modeled by the Antoine Equation: $\log_{10} P^* = A - \frac{B}{T + C}$ as given in Table B.4, F+R, 3rd Ed.

Pure Component
Phase Equilibrium

Page 2 of 4

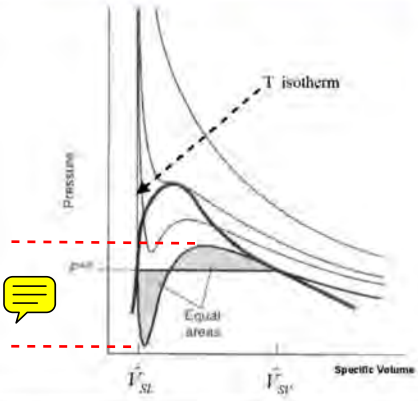
Equation-of-State Method

As stated on the previous page, the vapor-liquid coexistence curve on the PT diagram is usually represented by the Antoine equation. Although this equation is a curve fit of experimental data, it is applicable over a limited range of saturation temperatures. The Antoine equation for water is:

$$\log_{10} P^{sat} = 7.96681 - \frac{1668.210}{T + 228} \qquad \text{range of 60 to 150°C}$$

where the saturation pressure P^{sat} is in mm Hg and the saturation temperature T is in °C. Sometimes the symbol P^{sat} is written as P^{*}. Cubic equations of state that predict both the liquid and vapor regions can be used to predict the coexistence curve over its whole range from the triple point to the critical point. Some examples are Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), and Peng-Robinson Stryjek-Vera (PRSV). The general mathematical model for vapor-liquid equilibrium (VLE) of a pure component system is given next, along with two mathematical algorithms for the coexistence curve in the PT diagram and the dome region in the PVT diagram.

VLE Mathematical Model

PVT Diagram for a Pure Compound	**Pure-Component VLE**
 	$\phi^{SL} = \phi^{SV}$ for the equal areas $[\phi^{SL}, \hat{V}_{SL}] = phiL[T, P^{sat}]$ 2 eqn's $[\phi^{SV}, \hat{V}_{SV}] = phiV[T, P^{sat}]$ 2 eqn's # vars = 6 $\underline{\text{\# eqns} = 5}$ $d.o.f. = 1$ Gibbs Phase Rule: $d.o.f. = 2 + nc - \pi = 1$

VLE Mathematical Algorithms

{ see CinChE, Ch. 4, p. 4-16, for the formulation of these algorithms }

```
$[T, \hat{V}_{SL}, \hat{V}_{SV}] = tsat[P^{sat}]$
    ITERATE  $T$  in
        $[\phi^{SL}, \hat{V}_{SL}] \leftarrow phiL[T, P^{sat}]$
        $[\phi^{SV}, \hat{V}_{SV}] \leftarrow phiV[T, P^{sat}]$
        $f(T) \leftarrow \phi^{SL} - \phi^{SV}$
    UNTIL  $f(T) = 0$
```

```
$[P^{sat}, \hat{V}_{SL}, \hat{V}_{SV}] = psat[T]$
    ITERATE  $P^{sat}$  in
        $[\phi^{SL}, \hat{V}_{SL}] \leftarrow phiL[T, P^{sat}]$
        $[\phi^{SV}, \hat{V}_{SV}] \leftarrow phiV[T, P^{sat}]$
        $f(P^{sat}) \leftarrow \phi^{SL} - \phi^{SV}$
    UNTIL  $f(P^{sat}) = 0$
```

Using the E-Z Solve software tool, the above "*tsat*" math algorithm is illustrated on the next page for pure water and the Peng-Robinson (PR) equation of state, which is given in Chapter 3 on Page 3-25.

Pure Component
Phase Equilibrium

Page 3 of 4

E-Z Solve:

```
//   Peng-Robinson Equation of State in M. D. Koretsky's ThermoSolver, 2004
//        Vapor-liquid equilibrium temperature for water at 1 atm

//   [ Vsv ] = PReos [ T, P ]    and    [ Vsl ] = PReos [ T, P ]

        P = R * T / (Vsv - b) - alpha * a / (Vsv^2 + 2* b* Vsv - b^2)     // molar volume for saturated vapor
        P = R * T / (Vsl - b)  - alpha * a / (Vsl^2  + 2* b* Vsl  - b^2)    // molar volume for saturated liquid

        a = 0.45724 * (R*Tc)^2 / Pc
        b = 0.07780 * R * Tc / Pc

        alpha = ( 1 + (0.37464 + 1.54226*omega - 0.26992*omega^2) * (1 - Tr^0.5) )^2

        Tr = T / Tc
        R = 0.0820574587             //  L atm / mol K

//   [ FCsv ] = PReos [ T, P ]    and    [ FCsl ] = PReos [ T, P ]      // for saturated vapor and liquid

        ln(FCsv) = (Zsv - 1) - ln(Zsv - B) - A * ln( (Zsv + 2.4142*B) / (Zsv - 0.4142*B) ) / (2.8284*B)
        ln(FCsl)  = (Zsl  - 1) - ln(Zsl  - B) - A * ln( (Zsl  + 2.4142*B) / (Zsl  - 0.4142*B) ) / (2.8284*B)

        Zsv = P * Vsv / (R * T)
        Zsl  = P * Vsl  / (R * T)

        A    = a * alpha * P / (R*T)^2
        B    = b * P / (R*T)

        fT   =  FCsv - FCsl
        t    = 100

//   Specfic volume for the saturated liquid and saturated vapor phases

        SV_sv = Vsv / MW     //  m^3 / kg,       Vsv    in   L / mol
        SV_sl  = Vsl  / MW     //  m^3 / kg,       Vsl    in   L / mol

//   Given saturation pressure P, iterating for saturation temperature T

        Pbar = 1.01325              //  bar
        P     = Pbar / 1.01325      //  atm
        T     = t + 273.15          //  K,      t  in  C

//   Physical Constants for water

        Tc      = 647.3             //  K
        Pc      = 217.6             //  atm
        omega = 0.344
        MW     = 18.016             //  g / mol
```

The E-Z Solve solution of the PR equation of state says that water at 1 atm boils at 101.477°C, as given below for f(T) = -0.0000122.

This value differs from the HYSYS PR solution which gives 99.96°C. HYSYS's PR includes a special interaction parameter for the water molecule, thus giving a better result compared to 100°C.

An alternate way to solve this problem is to use the calculator at the website of of P.J. Barrie. See *Journal of Chemical Education*, **82**, 958-959 (2005).

E-Z Solve Solution

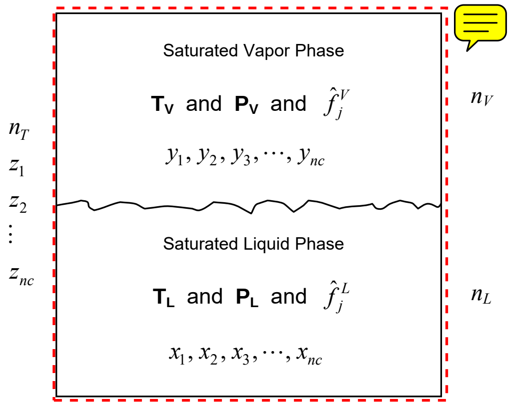
t, °C	P, atm	SVsl, m^3/kg	SVsv, m^3/kg	FCsl	FCsv	fT
101.470	1	0.00125196	1.691580	0.991217	0.991455	0.000237551
101.471	1	0.00125197	1.691590	0.991253	0.991455	0.000201874
101.472	1	0.00125197	1.691590	0.991289	0.991455	0.000166195
101.473	1	0.00125197	1.691600	0.991324	0.991455	0.000130516
101.474	1	0.00125197	1.691600	0.991360	0.991455	9.48E-05
101.475	1	0.00125197	1.691610	0.991396	0.991455	5.92E-05
101.476	1	0.00125197	1.691610	0.991432	0.991455	2.35E-05
101.477	1	0.00125197	1.691620	0.991467	0.991455	-1.22E-05
101.478	1	0.00125197	1.691620	0.991503	0.991455	-4.79E-05
101.479	1	0.00125197	1.691630	0.991539	0.991455	-8.36E-05
101.480	1	0.00125198	1.691630	0.991575	0.991455	-0.000119271

Rigorous VLE Mathematical Model

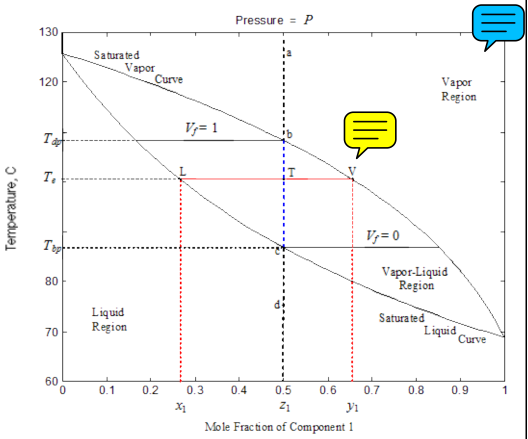
Page 1 of 3

larger

Multicomponent Vapor-Liquid Equilibrium



TXY Diagram for a Binary Mixture



Mathematical Model

$$1.0 = V_f + L_f$$

$$z_j = V_f\, y_j + L_f\, x_j \qquad \textit{for } j = 1, 2, ..., nc$$

$$y_j = K_j\, x_j \qquad \textit{for } j = 1, 2, ..., nc$$

$$K_j = \hat{\phi}_j^L \,/\, \hat{\phi}_j^V \qquad \textit{for } j = 1, 2, ..., nc$$

$$\hat{\phi}_j^L = phiL[T, P, \bar{x}] \qquad \textit{for } j = 1, 2, ..., nc$$

$$\hat{\phi}_j^V = phiV[T, P, \bar{y}] \qquad \textit{for } j = 1, 2, ..., nc$$

$$\sum_{j=1}^{nc} x_j - \sum_{j=1}^{nc} y_j = 0$$

$\bar{x}$ *is vector elements* $x_1, x_2, \cdots, x_{nc}$

$\bar{y}$ *is vector elements* $y_1, y_2, \cdots, y_{nc}$

$\bar{z}$ *is vector elements* $z_1, z_2, \cdots, z_{nc}$

$\bar{K}$ *is vector elements* $K_1, K_2, \cdots, K_{nc}$

Degrees-of-Freedom Analysis:

$$\begin{array}{rcl} \#\text{ vars} & = & 6 \cdot nc + 4 \\ \#\text{ eqns} & = & \underline{5 \cdot nc + 2} \\ dof & = & 1 \cdot nc + 2 \end{array}$$

Gibbs Phase Rule Model

$$y_j = K_j\, x_j \qquad \textit{for } j = 1, 2, ..., nc$$

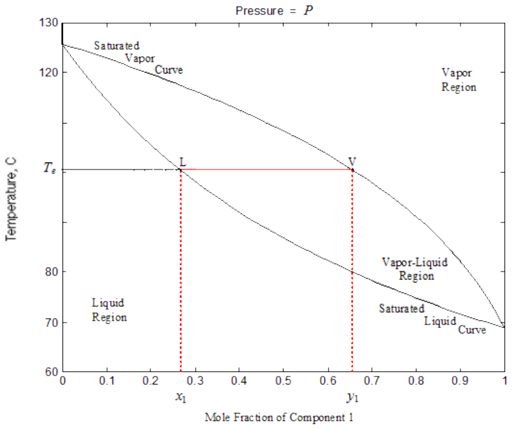
$$K_j = \hat{\phi}_j^L \,/\, \hat{\phi}_j^V \qquad \textit{for } j = 1, 2, ..., nc$$

$$\hat{\phi}_j^L = phiL[T, P, \bar{x}] \qquad \textit{for } j = 1, 2, ..., nc$$

$$\hat{\phi}_j^V = phiV[T, P, \bar{y}] \qquad \textit{for } j = 1, 2, ..., nc$$

$$\sum_{j=1}^{nc} x_j = 1 \qquad \textit{and} \qquad \sum_{j=1}^{nc} y_j = 1$$

$$\begin{array}{rcl} \#\text{ vars} & = & 5 \cdot \text{nc} + 2 \\ \#\text{ eqns} & = & \underline{4 \cdot \text{nc} + 2} \\ dof & = & 1 \cdot \text{nc} \end{array}$$



Gibbs Phase Rule: $dof = 2 + nc - \pi$

The Gibbs model is a partial subset of the VLE model, and it represents the solid red line from Points L to V in the above TXY diagram. The VLE model depicts not only the solid red line but also the vertical dotted blue line from Points "b" to "c" in its TXY diagram above.

Rigorous Mathematical Algorithm VLET

Page 2 of 3

```
$[\,T,\ \bar{x},\ \bar{y}\,] = vlet[\,P,\ V_f,\ \bar{z}\,]$
  1. $L_f \leftarrow 1.0 - V_f$
  2. ITERATE $T$ in
       ITERATE $\bar{K}$ in
           $x_j \leftarrow z_j \,/\, \left(V_f\, K_j + L_f\right)$    $for\ j = 1, 2, ..., nc$
           $y_j \leftarrow K_j\, x_j$    $for\ j = 1, 2, ..., nc$
           $\hat{\phi}_j^L \leftarrow phiL[T, P, \bar{x}]$    $for\ j = 1, 2, ..., nc$
           $\hat{\phi}_j^V \leftarrow phiV[T, P, \bar{y}]$    $for\ j = 1, 2, ..., nc$
           $K'_j \leftarrow \hat{\phi}_j^L \,/\, \hat{\phi}_j^V$    $for\ j = 1, 2, ..., nc$
       UNTIL $\bar{K} = \bar{K}'$
       $f(T) = \sum_{j=1}^{nc} x_j - \sum_{j=1}^{nc} y_j$
     UNTIL $f(T) = 0$
```

The “Development of a Mathematical Algorithm” in Chapter 4 (pp. 4-15 to 4-20) presents the procedure to generate an ITERATE construct from a NSOLVE construct.

Algorithm VLET has an outer iteration loop on temperature (T, a scalar quantity) and an inner iteration loop on the distribution coefficients ($\bar{K}$, a vector quantity).

An initial estimate for T can be found with:

$$T = \sum_{j=1}^{nc} z_j\, T_j^{sat} \quad where \quad T_j^{sat} = tsat[P,\ pure\ j]$$

The *tsat* function is the Antoine equation.

An initial estimate for $\bar{K}$ can be found with:

$$K_j = P_j^* \big/ P \quad where \quad P_j^* = psat[T,\ pure\ j]$$

The *psat* function is the Antoine equation.

Rigorous Mathematical Algorithm VLEVF

```
$[\,V_f,\ \bar{x},\ \bar{y}\,] = vlevf[\,T,\ P,\ \bar{z}\,]$
  1. ITERATE $V_f$ in
       $L_f \leftarrow 1.0 - V_f$
       ITERATE $\bar{K}$ in
           $x_j \leftarrow z_j \,/\, \left(V_f\, K_j + L_f\right)$    $for\ j = 1, 2, ..., nc$
           $y_j \leftarrow K_j\, x_j$    $for\ j = 1, 2, ..., nc$
           $\hat{\phi}_j^L \leftarrow phiL[T, P, \bar{x}]$    $for\ j = 1, 2, ..., nc$
           $\hat{\phi}_j^V \leftarrow phiV[T, P, \bar{y}]$    $for\ j = 1, 2, ..., nc$
           $K'_j \leftarrow \hat{\phi}_j^L \,/\, \hat{\phi}_j^V$    $for\ j = 1, 2, ..., nc$
       UNTIL $\bar{K} = \bar{K}'$
       $f(V_f) = \sum_{j=1}^{nc} x_j - \sum_{j=1}^{nc} y_j$
     UNTIL $f(V_f) = 0$
```

The “Development of a Mathematical Algorithm” in Chapter 4 (pp. 4-15 to 4-20) presents the procedure to generate an ITERATE construct from a NSOLVE construct.

Algorithm VLEVF has an outer iteration loop on vapor fraction (V_f, a scalar quantity) and an inner iteration loop on the distribution coefficients ($\bar{K}$, a vector quantity).

An initial estimate for V_f is bounded by

$$0 \le V_f \le 1$$

Start with a value of 0.5.

An initial estimate for $\bar{K}$ can be found with:

$$K_j = P_j^* \big/ P \quad where \quad P_j^* = psat[T,\ pure\ j]$$

The *psat* function is the Antoine equation

Rigorous Mathematical Algorithm VLEP

Page 3 of 3

```
$[\,P,\ \overline{x},\ \overline{y}\,] = vlet[\,T,\ V_f,\ \overline{z}\,]$
  1. $L_f \leftarrow 1.0 - V_f$
  2. ITERATE  $P$  in
       ITERATE  $\overline{K}$  in
         $x_j \leftarrow z_j / \left(V_f\, K_j + L_f\right)$      $for\ j = 1, 2, ..., nc$
         $y_j \leftarrow K_j\, x_j$                        $for\ j = 1, 2, ..., nc$
         $\hat{\phi}_j^L \leftarrow phiL[T, P, \overline{x}]$        $for\ j = 1, 2, ..., nc$
         $\hat{\phi}_j^V \leftarrow phiV[T, P, \overline{y}]$        $for\ j = 1, 2, ..., nc$
         $K_j' \leftarrow \hat{\phi}_j^L / \hat{\phi}_j^V$               $for\ j = 1, 2, ..., nc$
       UNTIL  $\overline{K} = \overline{K}'$
       $f(P) = \sum_{j=1}^{nc} x_j - \sum_{j=1}^{nc} y_j$
     UNTIL  $f(P) = 0$
```

The "Development of a Mathematical Algorithm" in Chapter 4 (pp. 4-15 to 4-20) presents the procedure to generate an ITERATE construct from a NSOLVE construct.

Algorithm VLEP has an outer iteration loop on pressure (P, a scalar quantity) and an inner iteration loop on the distribution coefficients ($\overline{K}$, a vector quantity).

An initial estimate for P can be found with:

$$P = \sum_{j=1}^{nc} z_j\, P_j^{sat} \quad where \quad P_j^{sat} = psat[T,\ pure\ j]$$

The *psat* function is the Antoine equation.

An initial estimate for $\overline{K}$ can be found with:

$$K_j = P_j^* \big/ P \quad where \quad P_j^* = psat[T,\ pure\ j]$$

The *psat* function is the Antoine equation

The above **rigorous** mathematical model for vapor-liquid equilibrium of a multicomponent system has three mathematical algorithms as given above and summarized below.

$$[\,T,\ \overline{x},\ \overline{y}\,] = vlet[\,P,\ V_f,\ \overline{z}\,]$$
$$[\,V_f,\ \overline{x},\ \overline{y}\,] = vlevf[\,T,\ P,\ \overline{z}\,]$$
$$[\,P,\ \overline{x},\ \overline{y}\,] = vlep[\,T,\ V_f,\ \overline{z}\,]$$

Because the above mathematical algorithms use fugacity coefficient functions (*phiV* and *phiL*) that are rigorously represented by equations of state and activity coefficient models, a software tool like the Aspen HYSYS® simulator and ThermoSolver are needed to automate their solution. Manually solving the rigorous versions of these algorithms is a complex and often error prone task, and it is never done.

The three functional equations highlighted above for *vlet*, *vlevf*, and *vlep* are the first principles that we will write in the mathematical models of problems that involve vapor-liquid equilibrium. However, we will assume that Raoult's law is applicable for all chemical components in most equilibrium problems. This assumption simplifies the three rigorous mathematical algorithms by eliminating the inner iteration loop on the distribution coefficients. The K_j*'s* are not dependent upon the vapor and liquid mole fractions under Raoult's law, as they are for the rigorous mathematical algorithms above.

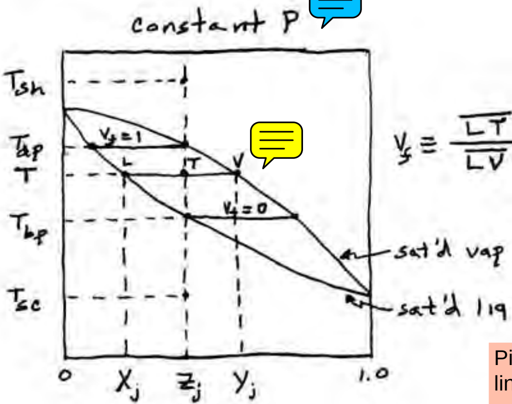
The mathematical model and its three mathematical algorithms for multicomponent vapor-liquid equilibrium (VLE) based on Raoult's law are presented on the next three pages. Whenever you need to solve one of mathematical algorithms, you would enter the VLE mathematical model into "**EZ Setup**" for a **binary** system and have the Excel **Solver** tool do the iterative calculations. Alternately, you will use Aspen **HYSYS**® for system with greater than two chemical components. You will need to provide Excel "**EZ Setup**"/**Solver** or **HYSYS** printouts as part of your solution documentation.

larger

Raoult's Law Model
Multicomponent VLE

Page 1 of 6

Diagram



$$V_f \equiv \frac{\overline{LT}}{\overline{LV}}$$

Assumptions

1. vapor-liquid equil.
2. Raoult's law; i.e., both liquid and vapor phases behave as ideal solutions.
3. Saturation pressure P_j^* is given by the Antoine equation.

Pictorially, the math model represents each horizontal line in the TXY diagram that can be drawn from the saturated liquid curve to the saturated vapor curve, and that line must cross or touch the vertical line somewhere from the dew-point temperature to the bubble-point temperature; that is, from a vapor fraction of one to zero for a given pressure P and any total composition (Z_j's) on the x-axis from zero to one.

Mathematical Model

total bal. $1.0 = V_f + L_f$

comp. bal. $z_j = V_f y_j + L_f x_j$

Raoult's Law $\left\{ \begin{array}{l} y_j = K_j x_j \\ K_j = P_j^* / P \end{array} \right.$

Antoine eqn $P_j^* = \text{PSAT}[T, \text{pure } j]$

for $j = 1, 2, \ldots, nc$

end points of horizontal line connecting the sat'd liquid curve to the sat'd vapor curve.

K_j is called the equilibrium distribution coefficient

$$\sum_{j=1}^{nc} x_j - \sum_{j=1}^{nc} y_j = 0$$

\# vars = 5 nc + 3
\# eqns = 4 nc + 1
d.o.f. = nc + 2

Mathematical Algorithms

A. $[T, \bar{x}, \bar{y}] = \text{vlet}[P, V_f, \bar{z}]$

B. $[V_f, \bar{x}, \bar{y}] = \text{vlevf}[T, P, \bar{z}]$

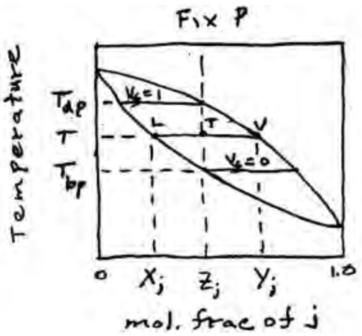
C. $[P, \bar{x}, \bar{y}] = \text{vlep}[T, V_f, \bar{z}]$

where $\bar{x} \equiv x_1, x_2, \ldots, x_{nc}$; $\bar{y} \equiv y_1, y_2, \ldots, y_{nc}$; $\bar{z} \equiv z_1, z_2, \ldots, z_{nc}$

Find VLE Temperature

Click here to view info on the "**EZ Setup**" function for "**vlet**".

```
$[T, \bar{x}, \bar{y}] = \text{vlet}[P, V_f, \bar{z}]$
  1.  $L_f \leftarrow 1.0 - V_f$
  2.  Iterate on $T$ in
        $p_j^* \leftarrow \text{psat}[T, \text{pure } j]$            }
        $K_j \leftarrow p_j^* / P$                                  }
        $x_j \leftarrow z_j / (V_f K_j + L_f)$                      }  for $j = 1, 2, \ldots, nc$
        $y_j \leftarrow K_j x_j$                                    }
      $f(T) \leftarrow \sum x_j - \sum y_j$
      Until $f(T)$ is 0.0
```



Find VLE Vapor Fraction

Click here to view info on the "**EZ Setup**" function for "**vlevf**".

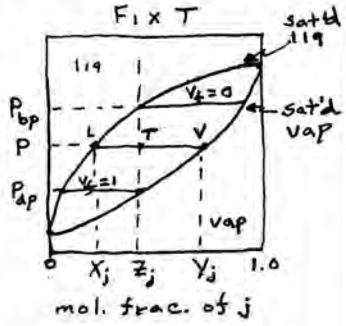
```
$[V_f, \bar{x}, \bar{y}] = \text{vlevf}[T, P, \bar{z}]$
  1.  $p_j^* \leftarrow \text{psat}[T, \text{pure } j]$        for $j = 1, 2, \ldots, nc$
  2.  $K_j \leftarrow p_j^* / P$                              for $j = 1, 2, \ldots, nc$
  3.  Iterate on $V_f$ in
        $L_f \leftarrow 1.0 - V_f$
        $x_j \leftarrow z_j / (V_f K_j + L_f)$                for $j = 1, 2, \ldots, nc$
        $y_j \leftarrow K_j x_j$                              for $j = 1, 2, \ldots, nc$
      $f(V_f) \leftarrow \sum x_j - \sum y_j$
      Until $f(V_f)$ is 0.0
```

Click here for a tidbit.

Click here to view info on the "**EZ Setup**" function for "**vlep**".

Find VLE Pressure

```
$[P, \bar{x}, \bar{y}] = vlep[T, V_f, \bar{z}]$        for $0 < V_f < 1.0$
    1. $L_f \leftarrow 1.0 - V_f$
    2. $P_j^* \leftarrow psat[T, pure\ j]$             for $j = 1, 2, \dots, nc$
    3. Iterate on $P$ in
           $K_j \leftarrow P_j^* / P$
           $x_j \leftarrow z_j / (V_f K_j + L_f)$      for $j = 1, 2, \dots, nc$
           $y_j \leftarrow K_j x_j$
           $f(P) \leftarrow \sum x_j - \sum y_j$
       Until $f(P)$ is 0.0
```

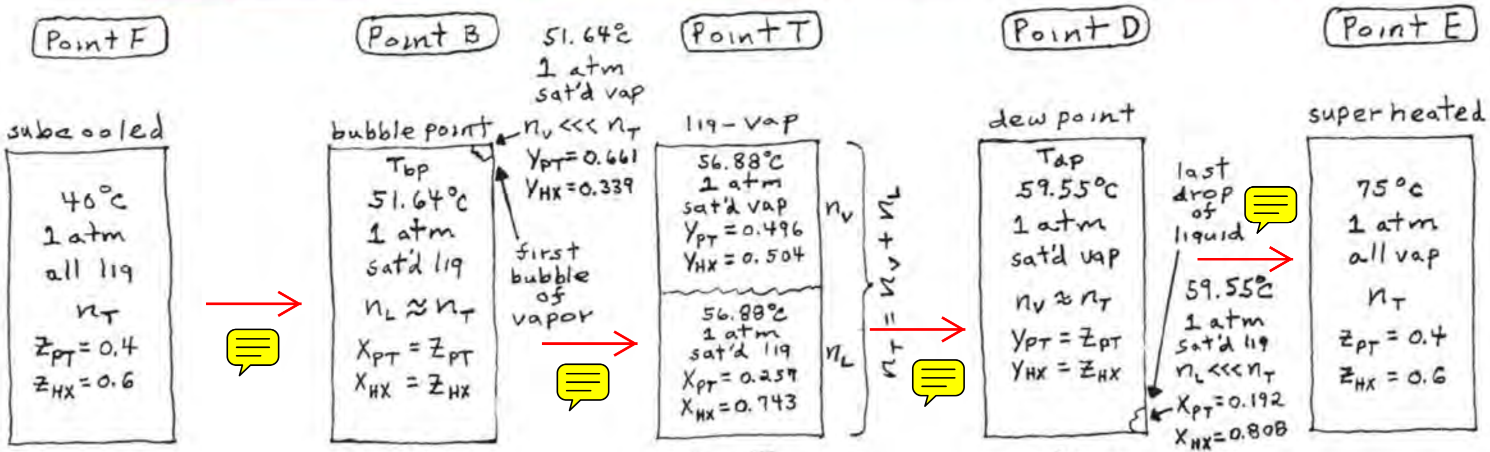


special solutions that do not have iteration

```
$[P_{bp}, \bar{x}, \bar{y}] = vlep[T, V_f = 0, \bar{z}]$
    1. $L_f \leftarrow 1.0$
    2. $P_j^* \leftarrow psat[T, pure\ j]$             for $j = 1, 2, \dots, nc$
    3. $x_j \leftarrow z_j$
    4. $P_{bp} \leftarrow \sum_{j=1}^{nc} P_j^* x_j$   <-- $\sum_{j=1}^{nc} y_j = 1.0$
    5. $K_j \leftarrow P_j^* / P_{bp}$                 for $j = 1, 2, \dots, nc$
    6. $y_j \leftarrow K_j x_j$

$[P_{dp}, \bar{x}, \bar{y}] = vlep[T, V_f = 1, \bar{z}]$
    1. $L_f \leftarrow 0.0$
    2. $P_j^* \leftarrow psat[T, pure\ j]$             for $j = 1, 2, \dots, nc$
    3. $y_j \leftarrow z_j$
    4. $P_{dp} \leftarrow [\sum_{j=1}^{nc} y_j / P_j^*]^{-1}$   <-- $\sum_{j=1}^{nc} x_j = 1.0$
    5. $K_j \leftarrow P_j^* / P_{dp}$                 for $j = 1, 2, \dots, nc$
    6. $x_j \leftarrow y_j / K_j$
```

Raoult's Law Model: Multicomponent VLE

Process of Heating Pentane-Hexane from 40°C to 75°C at 1 atm

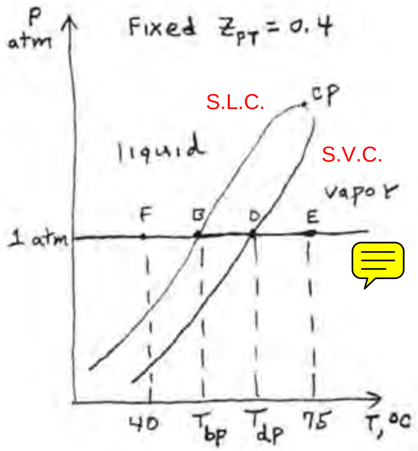


$$V_f = \frac{n_v}{n_T} = 0$$

$$V_f = \frac{n_v}{n_L} = \frac{\overline{LT}}{\overline{LV}} = 0.6$$

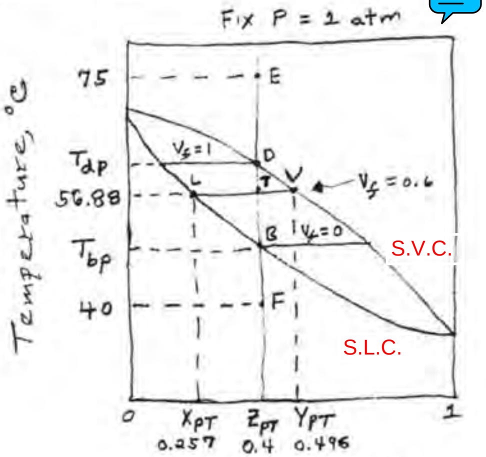
$$V_f = \frac{n_v}{n_T} = 1$$

PT Diagram



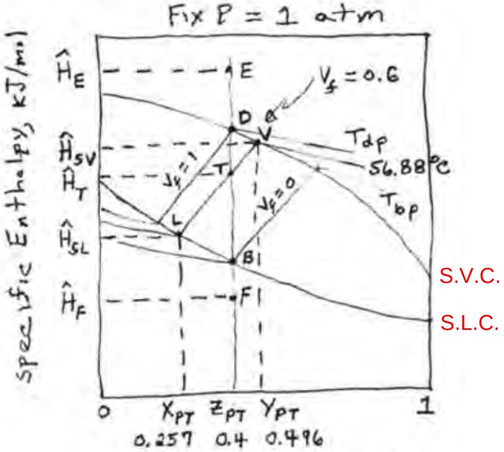
S.L.C. - Saturated Liquid Curve
S.V.C. - Saturated Vapor Curve

TXY Diagram



$$z_{PT} = V_f\, y_{PT} + L_f\, x_{PT}$$

HXY Diagram



$$z_{PT} = V_f\, y_{PT} + L_f\, x_{PT}$$

$$\hat{H}_T = V_f\, \hat{H}_{SV} + L_f\, \hat{H}_{SL}$$

Example Binary System for Vapor-Liquid Equilibrium

Page 5 of 6

Click here to view the Excel "**EZ Setup**"/**Solver** formulation.

```
/*  Raoult's Law applied to n-Pentane and n-Hexane System  */

//  Total and Two Component Material Balances
       1.0  =  Vf  +  Lf

       zPT  =   Vf * yPT  +  Lf * xPT
       zHX  =  Vf * yHX  +  Lf * xHX

//  Vapor-Liquid Equilibrium using Raoult's Law
       yPT  =  kPT * xPT
       yHX  =  kHX * xHX

       kPT  =  PsatPT / P
       kHX  =  PsatHX / P

//   Antoine Equations for the Two Components, F&R, 3rd Ed., Table B.4
       log(PsatPT)  =  6.84471  -  1060.793 / (T +  231.541)          //  range 13.3 to 36.8 C
       log(PsatHX)  =  6.88555  -  1175.817 / (T +  224.867)          //  range 13.0 to 69.5 C

//   Two mixture equations for the liquid and vapor phases
       xPT  +  xHX  -  yPT  -  yHX  =  0

//   Given Information
       Vf     =  0.0
       P      =  760
       zPT  =  0.40
       zHX  =  1.0  -  zPT
```

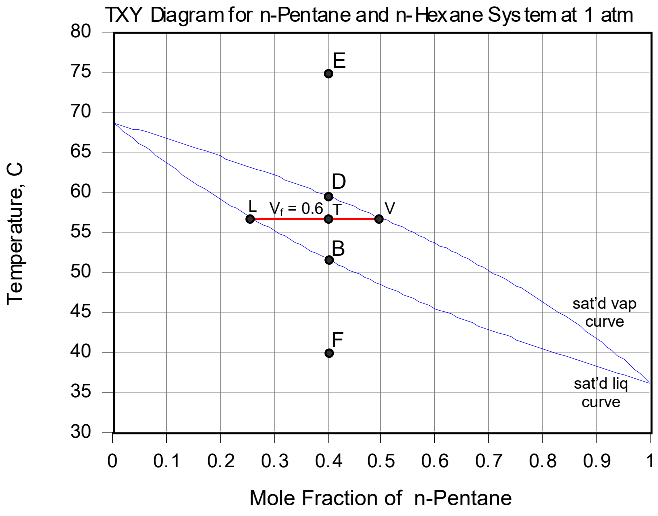
This Excel "**EZ Setup**"/**Solver** formulation is the VLE mathematical model given on "Page 1 of 6" above but written for a binary system.

The Excel **Solver** iterates on all of the equations simultaneously using the optimization technique of minimizing the sum of squares.

The "EZ Setup" formulation sets a value of 1.0 for all the unknowns to get the iteration started.

You solves this mathematical model three times using the Excel **Solver** by changing the value for vapor fraction (V_f). The results for vapor fractions of 1.0, 0.6, and 0.0 are shown below.

Excel SolverTable TXY Diagram



Excel Solver Solutions

[T_{dp}, X_{PT}, X_{HX}] = vlet [P, V_f, Z_{PT}]

P = 1 atm T_{dp} = 59.55ºC
V_f = 1.0 X_{PT} = 0.1916
Z_{PT} = 0.4 X_{HX} = 0.8084

[T_{eq}, X_{PT}, Y_{PT}] = vlet [P, V_f, Z_{PT},]

P = 1 atm T_{eq} = 56.88ºC
V_f = 0.6 X_{PT} = 0.2565
Z_{PT} = 0.4 Y_{PT} = 0.4956

[T_{bp}, Y_{PT}, Y_{HX}] = vlet [P, V_f, Z_{PT}]

P = 1 atm T_{bp} = 51.64ºC
V_f = 0.0 Y_{PT} = 0.6607
Z_{PT} = 0.4 Y_{HX} = 0.3393

What would the equilibrium results for this pentane/hexane example look like if an equation of state was used to model the K-values instead of Raoult's Law? As an enhancement exercise, **click here** and do the equilibrium calculations for this example using the Peng-Robinson equation.

Alternate "EZ Setup" Solution for Example Binary System

Page 6 of 6

Click here to view the Excel "**EZ Setup**"/**Solver** formulation.

```
/*  Raoult's Law applied to n-Pentane and n-Hexane System  */

//  Total and Two Component Material Balances
       1.0  =  Vf  +  Lf

       zPT  =   Vf * yPT  +  Lf * xPT
       zHX  =  Vf * yHX  +  Lf * xHX

//  Vapor-Liquid Equilibrium using Raoult's Law
       yPT  =  kPT * xPT
       yHX  =  kHX * xHX

       kPT  =  PsatPT / P
       kHX  =  PsatHX / P

//   Antoine Equations for the Two Components, F&R, 3rd Ed., Table B.4
       log(PsatPT)  =  6.84471  -  1060.793 / (T +  231.541)          //  range 13.3 to 36.8 C
       log(PsatHX)  =  6.88555  -  1175.817 / (T +  224.867)          //  range 13.0 to 69.5 C

//   Two mixture equations for the liquid and vapor phases
       fT  =  xPT  +  xHX  -  yPT  -  yHX
        T  =  40

//   Given Information
       Vf     =  0.6
       P      =  760
       zPT  =  0.40
       zHX  =  1.0  -  zPT
```

This Excel "**EZ Setup**"/**Solver** formulation simulates the ITERATE loop for the scalar unknown of temperature found in the multicomponent "**vlet**" math algorithm given on "Page 2 of 6" above, but for a binary system.

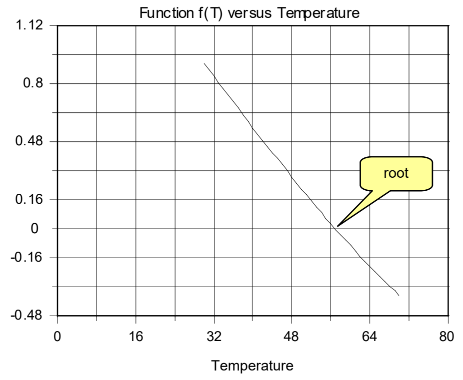
The iteration variable **T** and the iteration function **fT** are written into the "**EZ Setup**" math model as shown by the two aqua-highlighted lines below.

This technique of simulating an ITERATE loop can be used as a fall back whenever the "**EZ Setup**"/ **Solver** has difficulty solving the math model.

The simulation of an ITERATE loop is done by using the Excel **Solver** and **SolverTable** Add-Ins. A case study on temperature from 50 to 70°C was done, and the table of partial results is shown below. In this table, the function fT is close to zero near 57°C. Another case study could be done from 56 to 57°C to get the equilibrium temperature of 56.88°C for a vapor fraction of 0.60.

T	fT	kHX	kPT	xPT	yPT
50	0.218885	0.533297	1.570680	0.297973	0.468018
51	0.186165	0.552683	1.619650	0.291590	0.472274
52	0.153740	0.572625	1.669800	0.285332	0.476446
53	0.121622	0.593136	1.721120	0.279198	0.480534
54	0.089823	0.614227	1.773650	0.273189	0.484541
55	0.058353	0.635908	1.827400	0.267301	0.488466
56	0.027221	0.658192	1.882380	0.261535	0.492310
57	-0.003562	0.681091	1.938620	0.255890	0.496074
58	-0.033989	0.704616	1.996140	0.250363	0.499758
59	-0.064051	0.728779	2.054950	0.244953	0.503365
60	-0.093741	0.753592	2.115070	0.239659	0.506894
61	-0.123052	0.779068	2.176520	0.234479	0.510347
62	-0.151979	0.805218	2.239310	0.229412	0.513725
63	-0.180515	0.832055	2.303480	0.224456	0.517029
64	-0.208656	0.859592	2.369030	0.219609	0.520261
65	-0.236398	0.887840	2.435980	0.214870	0.523420
66	-0.263737	0.916813	2.504360	0.210237	0.526509
67	-0.290671	0.946522	2.574180	0.205708	0.529528
68	-0.317195	0.976982	2.645460	0.201280	0.532480
69	-0.343309	1.008200	2.718220	0.196954	0.535364
70	-0.369011	1.040200	2.792480	0.192726	0.538183

The simulation of an ITERATE loop is depicted below by plotting f(T) versus T. The desired root is where the curve crosses the x-axis



To learn more about doing a manual iteration on a scalar quantity, see the "Development of a Math Algorithm" in the *CinChE* manual, Chapter 4, specifically Pages 4-16 to 4-17.

larger

Problem 6.59
in F&R, 3rd Ed.

1 of 10

Problem Statement **{Problem 6.59 in F&R, 3rd Edition, but modified}**

A vapor feed stream at 120°C, 1.0 atm, 150.0 L/s, 50.0 mole% n-butane, and 50.0 mole% n-hexane is cooled and compressed to partially condense the vapor. The vapor and liquid product streams emerge from this process operation at some equilibrium temperature and 340 mm Hg gauge. The vapor product contains 60.0 mole% n-butane, and the barometric pressure is 1.00 atm. What are the equilibrium temperature in °C, the molar composition of the liquid product, the molar flow rate of the n-hexane in the liquid product, and the mass flow rates (lb_m/s) of the vapor and liquid product streams?

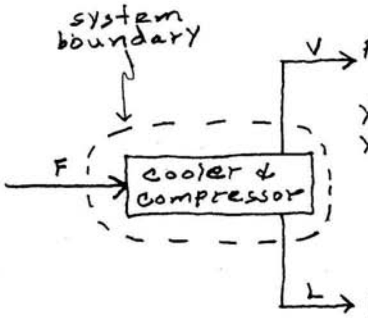
An example vapor-liquid-equilibrium problem for a binary system with the assumption that Raoult's Law applies over the whole range of mole fractions (i.e., from zero to one). As discussed on Page 6-4, chemical components that are sub-critical with respect to temperature have the potential to condense. The critical temperatures for n-butane and n-hexane are 425.17 K and 507.90 K, respectively. At the operating temperature of 120ºC (393.15 K), both chemical components will distribute themselves in the saturated liquid and saturated vapor phases.

Model Assumptions

1. continuous process
2. steady state
3. no reactions
4. ideal gas for Stream F
5. vapor-liquid equilibrium for Streams V & L
6. Raoult's Law Model for VLE; ideal gas for stream V and ideal solution for stream L
7. Antoine Equation for vapor pressure of pure n-butane and n-hexane

Conceptual Model

T_F = 120°C
P_F = 1 atm
Ph_F = vap
$\dot{n}_F$ = ?
$z_{F,Bu}$ = 0.50
$z_{F,HX}$ = 0.50



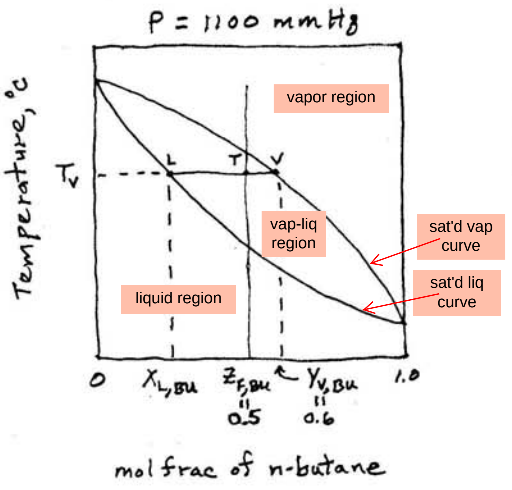
T_V = ?
P_V = (340 + 760) mm Hg
Ph_V = sat'd vap
$\dot{n}_V$ = ?
$y_{V,Bu}$ = 0.60
$y_{V,HX}$ = 0.40

T_L = T_V
P_L = P_V
Ph_L = sat'd liq
$\dot{n}_L$ = ?
$x_{L,Bu}$ = ?
$x_{L,HX}$ = ?

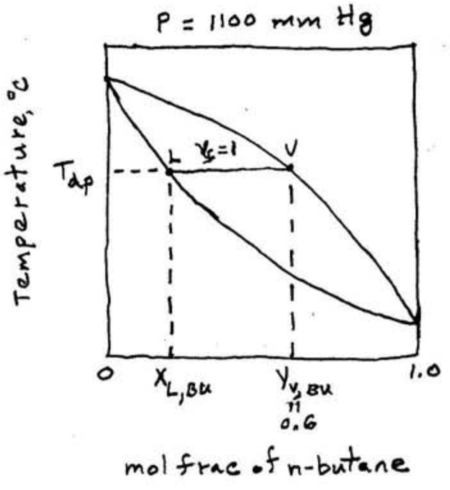
Other Givens:
$\dot{V}_F$ = 150.0 L/s
P_b = 1 atm

Finds:
T_V in °C
$x_{L,Bu}$ in mol frac
$x_{L,HX}$ in mol frac
$\dot{n}_{L,HX}$ in mol/s
$\dot{m}_L$ in lbm/s
$\dot{m}_V$ in lbm/s

TXY Diagram for VLE



TXY Diagram for Stream V



Problem 6.59
in F&R, 3rd Ed.

3 of 10

Mathematical Model

① total: $\dot{n}_F - \dot{n}_V - \dot{n}_L = 0$

② butane: $0.5\,\dot{n}_F - 0.6\,\dot{n}_V - \dot{n}_{L,Bu} = 0$

check hexane: $0.5\,\dot{n}_F - 0.4\,\dot{n}_V - \dot{n}_{L,HX} = 0$

in vlet function Mix L: $\dot{n}_L = \dot{n}_{L,Bu} + \dot{n}_{L,HX}$

③ ideal gas: $P_F \dot{V}_F = \dot{n}_F R T_F$

④ comp L: $\dot{n}_{L,Bu} = \dot{n}_L X_{L,Bu}$

⑤ $\dot{n}_{L,HX} = \dot{n}_L X_{L,HX}$

⑥ $M_V = \dfrac{\dot{m}_V}{\dot{n}_V}$

⑦ $M_V = 0.60\,M_{Bu} + 0.40\,M_{HX}$

⑧ $M_L = \dfrac{\dot{m}_L}{\dot{n}_L}$

⑨ $M_L = X_{L,Bu} M_{Bu} + X_{L,HX} M_{HX}$

⑩ to ⑫ VLE: $[T_V, \bar{X}_L] = \text{vlet}[P_V, V_f = 1, \bar{Y}_V]$

$$
\begin{aligned}
\#\ \text{vars} &= 18 \\
\#\ \text{eqns} &= \underline{12} \\
\text{dof} &= 6
\end{aligned}
$$

knows: $T_F,\ P_F,\ \dot{V}_F,\ \bar{Y}_V\ (Y_{V,Bu} + Y_{V,HX}),\ P_V$

Constants: $R,\ M_{Bu},\ M_{HX}$

Mathematical Algorithm

```
$[T_V, \bar{X}_L, \dot{n}_{L,HX}, \dot{m}_V, \dot{m}_L] = \text{process}[T_F, P_F, \dot{V}_F, \bar{Y}_V, P_V]$
③        1. $\dot{n}_F \leftarrow P_F \dot{V}_F/(RT_F)$
⑦        2. $M_V \leftarrow 0.60\,M_{Bu} + 0.40\,M_{HX}$
⑩ to ⑫  3. $[T_V, \bar{X}_L] \leftarrow \text{vlet}[P_V, V_f = 1, \bar{Y}_V]$
⑨        4. $M_L \leftarrow X_{L,Bu} M_{Bu} + X_{L,HX} M_{HX}$
         5. SOLVE $\dot{n}_V, \dot{n}_L, \dot{n}_{L,Bu}$ IN
①            $\dot{n}_V + \dot{n}_L = \dot{n}_F$
②            $0.6\dot{n}_V + \dot{n}_{L,Bu} = 0.5\dot{n}_F$
④            $X_{L,Bu}\dot{n}_L - \dot{n}_{L,Bu} = 0$
            END
            $\dot{n}_L = \frac{(0.60 - 0.50)}{(0.60 - X_{L,Bu})}\dot{n}_F$
            $\dot{n}_V = \dot{n}_F - \dot{n}_L$
            $\dot{n}_{L,Bu} = 0.5\dot{n}_F - 0.60\dot{n}_V$
⑧        6. $\dot{m}_L \leftarrow M_L \dot{n}_L$
⑥        7. $\dot{m}_V \leftarrow M_V \dot{n}_V$
⑤        8. $\dot{n}_{L,HX} \leftarrow \dot{n}_L X_{L,HX}$
```

Dimensional Consistency

Basis: mol, second, no energy

```
(3)     1. $\frac{mol}{s} \leftarrow atm \cdot \frac{L}{s} \cdot \frac{mol\ K}{0.08206\ L \cdot atm} \cdot \frac{1}{(°C + 273.15)\ K}$
(7)     2. $\frac{g}{mol} \leftarrow \sum\left(\text{unitless} \cdot \frac{g}{g\text{-}mol}\right)$
(10-12) 3. $[°C, \text{mol frac}] \leftarrow \text{vlet}[\text{mm Hg}, \text{unitless}, \text{mol frac}]$
(9)     4. $\frac{g}{mol} \leftarrow$ same as step 2
(8)     6. $\frac{lbm}{s} \leftarrow \frac{mol}{s} \cdot \frac{g}{mol} \left\langle \frac{lbm}{453.592\ g} \right\rangle$
(6)     7. $\frac{lbm}{s} \leftarrow$ Same as Step 6.
```

Manual Solution

Basis: cgs system, $\dot{V}_F = 150.0 \text{ L/s}$

Givens: $T_F = 120°\text{C} = 393.15 \text{ K}$ $P_F = 1 \text{ atm}$
$P_V = 1100 \text{ mm Hg}$ $y_V = 60\%\ \text{Bu},\ 40\%\ \text{HX}$

Constants: $M_{Bu} = 58.12$, $M_{HX} = 86.17$ { F&R, 3rd Ed. Table B.1
$R = 0.08206\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$, F&R, 3rd Ed., back flap

1. $$\dot{n}_F = \frac{(1\text{ atm})(150.0\ \frac{\text{L}}{\text{s}})}{393.15\text{ K}}\cdot\frac{\text{mol}\cdot\text{K}}{0.08206\ \text{L}\cdot\text{atm}} = 4.649449 \text{ mol/s}$$

2. $$M_V = 0.60(58.12) + 0.40(86.17) = 69.34 \text{ g/mol}$$

3. $$\left.\begin{aligned} T_V &= 56.983°\text{C} = \boxed{57°\text{C}} \\ x_{L,Bu} &= 0.149479 = \boxed{0.15} \\ x_{L,HX} &= 0.850521 = \boxed{0.85} \end{aligned}\right\}$$ see Page 6 for **"EZ Setup"** solution of the vlet function

4. $$M_L = 0.149479(58.12) + 0.850521(86.17) = 81.977114 \text{ g/mol}$$

5. $$\dot{n}_L = \frac{(0.60 - 0.50)}{(0.60 - 0.149479)}\left(4.649449\ \frac{\text{mol}}{\text{s}}\right) = 1.032016 \text{ mol/s}$$

$$\dot{n}_V = 4.649449\ \frac{\text{mol}}{\text{s}} - 1.032016\ \frac{\text{mol}}{\text{s}} = 3.617433 \text{ mol/s}$$

$$\dot{n}_{L,Bu} = 0.5\left(4.649449\ \frac{\text{mol}}{\text{s}}\right) - 0.60\left(3.617433\ \frac{\text{mol}}{\text{s}}\right) = 0.154265 \text{ mol/s}$$

6. $$\dot{m}_L = \left(81.977114\ \frac{\text{g}}{\text{mol}}\right)\left(1.032016\ \frac{\text{mol}}{\text{s}}\right)\left\langle\frac{\text{lbm}}{453.592\text{ g}}\right\rangle = 0.186515\ \frac{\text{lbm}}{\text{s}} = \boxed{0.19 \text{ lbm/s}}$$

7. $$\dot{m}_V = \left(69.34\ \frac{\text{g}}{\text{mol}}\right)\left(3.617433\ \frac{\text{mol}}{\text{s}}\right)\left\langle\frac{\text{lbm}}{453.592\text{ g}}\right\rangle = 0.552992\ \frac{\text{lbm}}{\text{s}} = \boxed{0.55 \text{ lbm/s}}$$

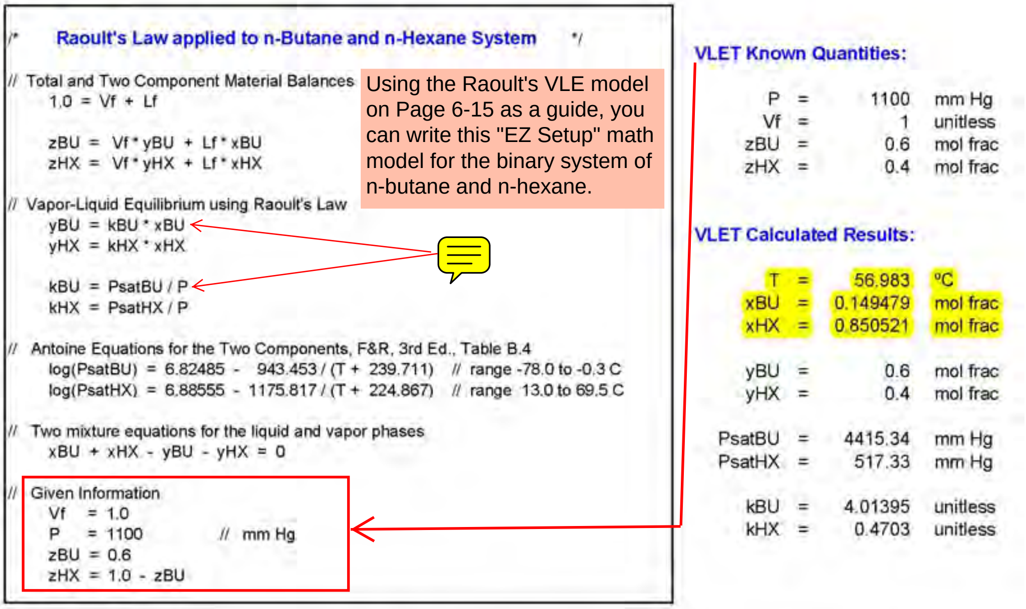
8. $$\dot{n}_{L,HX} = \left(1.032016\ \frac{\text{mol}}{\text{s}}\right)(0.850521) = 0.877751\ \frac{\text{mol}}{\text{s}} = \boxed{0.88 \text{ mol/s}}$$

Problem 6.59
in F&R, 3rd Ed.

6 of 10

"EZ Setup" Model for the vlet[P_V, $V_f = 1$, $Y_{V,BU}$ & $Y_{V,HX}$] Function

Click here to view this Excel "**EZ Setup**"/**Solver** formulation.



```
/*   Raoult's Law applied to n-Butane and n-Hexane System      */

// Total and Two Component Material Balances
    1.0  =  Vf  +  Lf

    zBU  =  Vf * yBU  +  Lf * xBU
    zHX  =  Vf * yHX  +  Lf * xHX

// Vapor-Liquid Equilibrium using Raoult's Law
    yBU  =  kBU * xBU
    yHX  =  kHX * xHX

    kBU  =  PsatBU / P
    kHX  =  PsatHX / P

//  Antoine Equations for the Two Components, F&R, 3rd Ed., Table B.4
    log(PsatBU)  =  6.82485  -   943.453 / (T +  239.711)   //  range -78.0 to -0.3 C
    log(PsatHX)  =  6.88555  -  1175.817 / (T +  224.867)   //  range  13.0 to 69.5 C

//  Two mixture equations for the liquid and vapor phases
    xBU  +  xHX  -  yBU  -  yHX  =  0

//  Given Information
    Vf   =  1.0
    P    =  1100           //  mm Hg
    zBU  =  0.6
    zHX  =  1.0  -  zBU
```

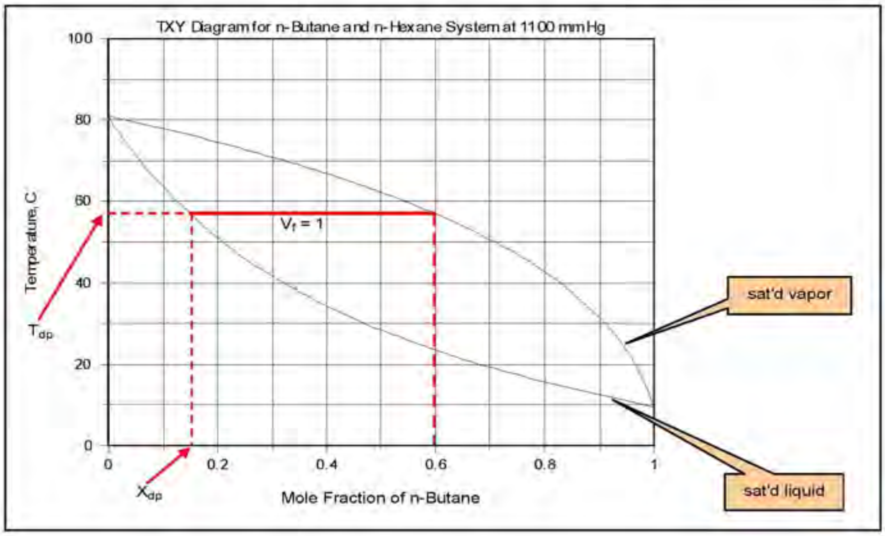
Using the Raoult's VLE model on Page 6-15 as a guide, you can write this "EZ Setup" math model for the binary system of n-butane and n-hexane.

VLET Known Quantities:

```
   P    =      1100    mm Hg
   Vf   =         1    unitless
   zBU  =       0.6    mol frac
   zHX  =       0.4    mol frac
```

VLET Calculated Results:

```
   T    =    56.983    °C
   xBU  =  0.149479    mol frac
   xHX  =  0.850521    mol frac

   yBU  =       0.6    mol frac
   yHX  =       0.4    mol frac

PsatBU  =   4415.34    mm Hg
PsatHX  =    517.33    mm Hg

   kBU  =   4.01395    unitless
   kHX  =    0.4703    unitless
```



Problem 6.59
in F&R, 3rd Ed.

Heuristic Observations

A. Numerical Solution

- check: $0.5\dot{n}_F - 0.4\dot{n}_V - \dot{n}_{L,HX} \overset{?}{=} 0$

$$0.5\left(4.64944\,\tfrac{mol}{s}\right) - 0.4\left(3.617433\,\tfrac{mol}{s}\right) - 0.877751\,\tfrac{mol}{s} = -4.2 \times 10^{-6}$$

OK!

- An alternate solution is to use the Reverse Lever Rule in the TXY Diagram for VLE on Page 2:

$$V_f = \frac{\overline{LT}}{\overline{LV}} = \frac{z_{F,Bu} - x_{L,Bu}}{y_{V,Bu} - x_{L,Bu}} = \frac{0.5 - 0.149479}{0.6 - 0.149479} = 0.778035$$

$$V_f = \frac{\dot{n}_V}{\dot{n}_L} = \frac{3.617433\ mol/s}{4.649449\ mol/s} = 0.778035$$

OK!

B. Mathematical Algorithm

Know T_V instead of composition $\bar{y}_V$. In the math model, the n-butane balance needs to be revised, the composition equations for stream V are needed, and the "vlet" equation must be replaced with $[V_f, \bar{x}_L, \bar{y}_V] = vlevf[T_V, P_V, \bar{z}_F]$.

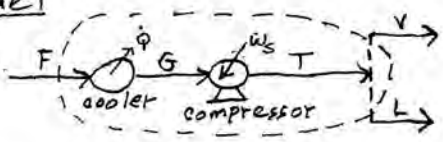
The math algorithm for this new math model would be more complex because the SOLVE will have four unknowns: $\dot{n}_V$, $\dot{n}_L$, $\dot{n}_{V,Bu}$, and $\dot{n}_{L,Bu}$.

C. Mathematical Model

Instead of solving the equations in the math model manually as was done on Page 5, the math model on Page 3 could be programmed directly into **"EZ Setup"** with the aided of an user-defined function for "vlet". See Pages 8 to 10.

D. Conceptual Model

- Note that:



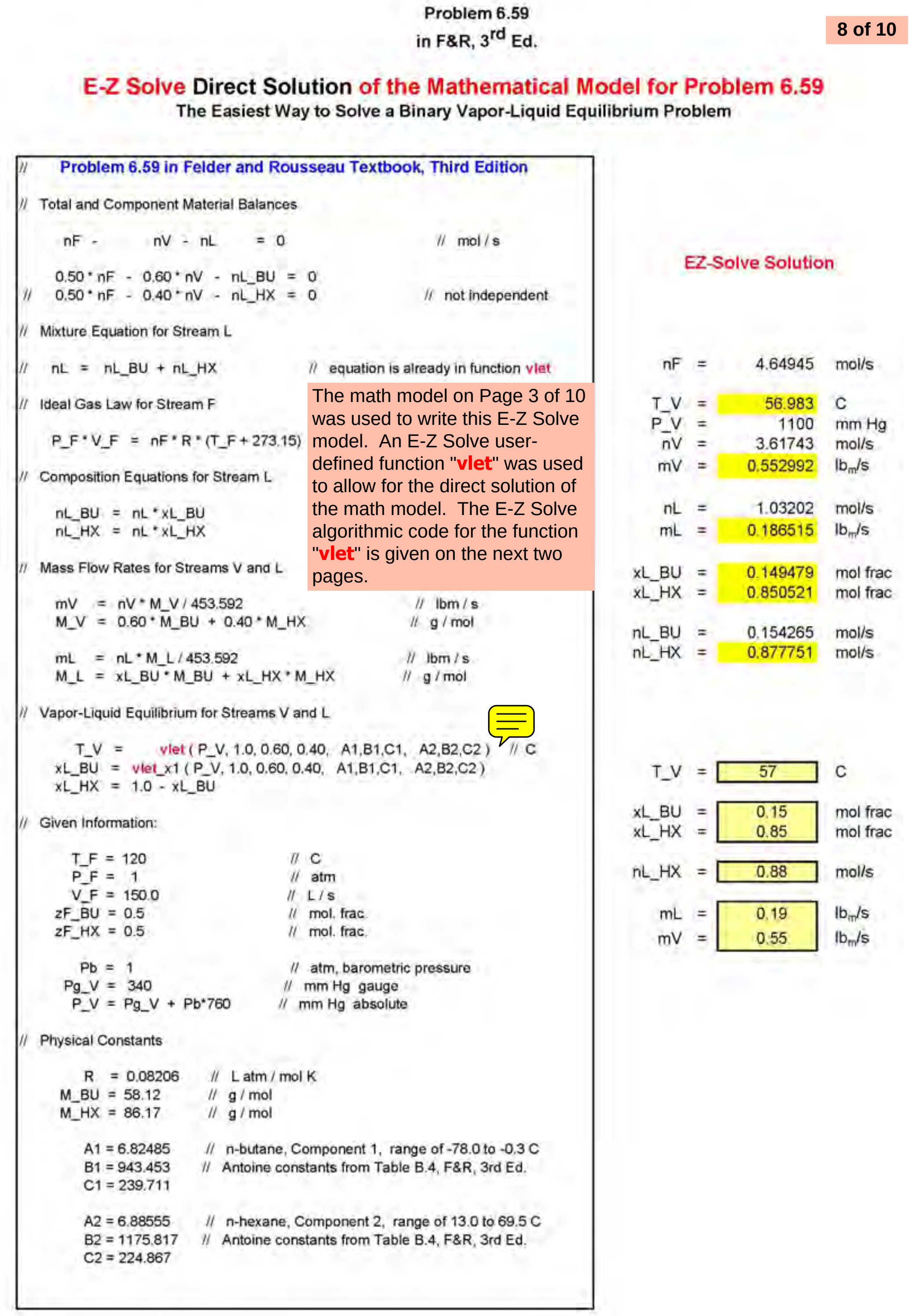
Stream T has vapor & liquid in equilibrium.

Flowrate and composition of streams F&T are the same

- How good are Assumptions 4, 6, and 7?
Using HYSYS with PRSV for rigorous VLE, you get $T_V = 57.43$ °C (−0.78% dev.) and $x_{L,Bu} = 0.171452$ (−14.7% dev.)

Click here to view the Excel "**EZ Setup**"/**Solver** formulation, which replaces the "**E-Z Solve**" solution on this page.

8 of 10



Problem 6.59
in F&R, 3rd Ed.

E-Z Solve Direct Solution of the Mathematical Model for Problem 6.59

The Easiest Way to Solve a Binary Vapor-Liquid Equilibrium Problem

```
//     Problem 6.59 in Felder and Rousseau Textbook, Third Edition

//  Total and Component Material Balances

      nF  -          nV  -  nL        =  0                          //  mol / s

    0.50 * nF  -  0.60 * nV  -  nL_BU  =  0
//  0.50 * nF  -  0.40 * nV  -  nL_HX  =  0                         //  not independent

//  Mixture Equation for Stream L

//    nL  =   nL_BU  +  nL_HX                  //  equation is already in function vlet

//  Ideal Gas Law for Stream F

     P_F * V_F  =  nF * R * (T_F + 273.15)

//  Composition Equations for Stream L

      nL_BU  =  nL * xL_BU
      nL_HX  =  nL * xL_HX

//  Mass Flow Rates for Streams V and L

      mV    =  nV * M_V / 453.592                          //  lbm / s
      M_V  =  0.60 * M_BU  +  0.40 * M_HX                 //  g / mol

      mL    =  nL * M_L / 453.592                          //  lbm / s
      M_L  =  xL_BU * M_BU  +  xL_HX * M_HX               //  g / mol

//  Vapor-Liquid Equilibrium for Streams V and L

         T_V  =        vlet ( P_V, 1.0, 0.60, 0.40,   A1,B1,C1,   A2,B2,C2 )   // C
      xL_BU  =  vlet_x1 ( P_V, 1.0, 0.60, 0.40,   A1,B1,C1,   A2,B2,C2 )
      xL_HX  =  1.0  -  xL_BU

//  Given Information:

         T_F  =  120                            //  C
         P_F  =   1                             //  atm
         V_F  =  150.0                          //  L / s
      zF_BU  =  0.5                             //  mol. frac.
      zF_HX  =  0.5                             //  mol. frac.

          Pb  =   1                             //  atm, barometric pressure
       Pg_V  =   340                           //  mm Hg  gauge
        P_V  =  Pg_V  +  Pb*760              //  mm Hg  absolute

//  Physical Constants

         R    =  0.08206        //  L atm / mol K
      M_BU  =  58.12           //  g / mol
      M_HX  =  86.17           //  g / mol

         A1 = 6.82485        //  n-butane, Component 1,  range of -78.0 to -0.3 C
         B1 = 943.453       //  Antoine constants from Table B.4, F&R, 3rd Ed.
         C1 = 239.711

         A2 = 6.88555        //  n-hexane, Component 2,  range of 13.0 to 69.5 C
         B2 = 1175.817      //  Antoine constants from Table B.4, F&R, 3rd Ed.
         C2 = 224.867
```

The math model on Page 3 of 10 was used to write this E-Z Solve model. An E-Z Solve user-defined function "**vlet**" was used to allow for the direct solution of the math model. The E-Z Solve algorithmic code for the function "**vlet**" is given on the next two pages.

EZ-Solve Solution

nF = 4.64945 mol/s

T_V = 56.983 C
P_V = 1100 mm Hg
nV = 3.61743 mol/s
mV = 0.552992 lb_m/s

nL = 1.03202 mol/s
mL = 0.186515 lb_m/s

xL_BU = 0.149479 mol frac
xL_HX = 0.850521 mol frac

nL_BU = 0.154265 mol/s
nL_HX = 0.877751 mol/s

T_V = 57 C

xL_BU = 0.15 mol frac
xL_HX = 0.85 mol frac

nL_HX = 0.88 mol/s

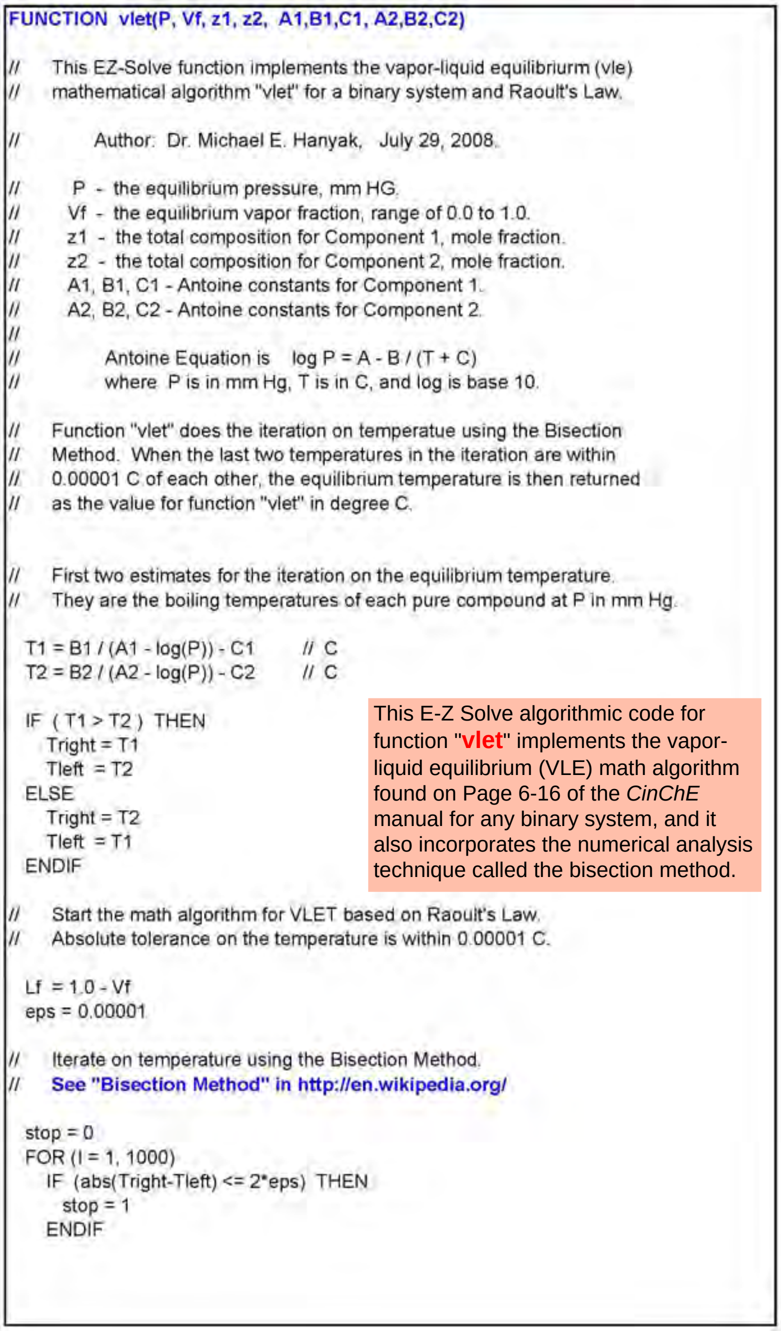
mL = 0.19 lb_m/s
mV = 0.55 lb_m/s

Click here to view the "**EZ Setup**" built-in "**vleT2**" function, which replaces the "**E-Z Solve**" version given below.

Problem 6.59
in F&R, 3rd Ed.

9 of 10

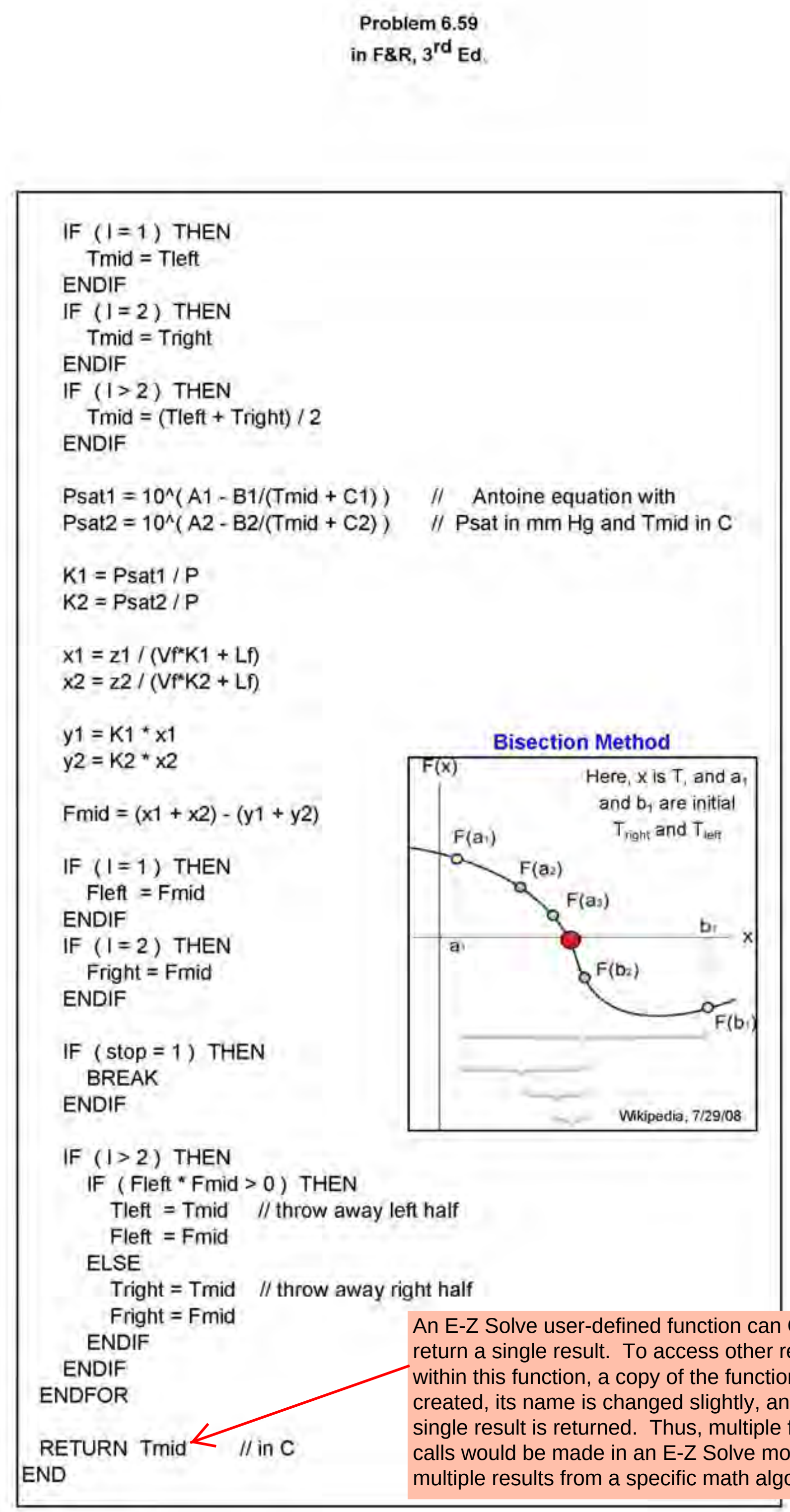
E-Z Solve User-Defined "vlet" Function in File "vle_alg.msp"



```
FUNCTION  vlet(P, Vf, z1, z2,  A1,B1,C1, A2,B2,C2)

//    This EZ-Solve function implements the vapor-liquid equilibrirum (vle)
//    mathematical algorithm "vlet" for a binary system and Raoult's Law.

//          Author:  Dr. Michael E. Hanyak,   July 29, 2008.

//       P  -  the equilibrium pressure, mm HG.
//      Vf  -  the equilibrium vapor fraction, range of 0.0 to 1.0.
//      z1  -  the total composition for Component 1, mole fraction.
//      z2  -  the total composition for Component 2, mole fraction.
//      A1, B1, C1 - Antoine constants for Component 1.
//      A2, B2, C2 - Antoine constants for Component 2.
//
//           Antoine Equation is    log P = A - B / (T + C)
//           where  P is in mm Hg, T is in C, and log is base 10.

//    Function "vlet" does the iteration on temperatue using the Bisection
//    Method.  When the last two temperatures in the iteration are within
//    0.00001 C of each other, the equilibrium temperature is then returned
//    as the value for function "vlet" in degree C.


//    First two estimates for the iteration on the equilibrium temperature.
//    They are the boiling temperatures of each pure compound at P in mm Hg.

  T1 = B1 / (A1 - log(P)) - C1       // C
  T2 = B2 / (A2 - log(P)) - C2       // C

  IF  ( T1 > T2 )  THEN
     Tright = T1
     Tleft  = T2
  ELSE
     Tright = T2
     Tleft  = T1
  ENDIF

//    Start the math algorithm for VLET based on Raoult's Law.
//    Absolute tolerance on the temperature is within 0.00001 C.

  Lf  = 1.0 - Vf
  eps = 0.00001

//    Iterate on temperature using the Bisection Method.
//    See "Bisection Method" in http://en.wikipedia.org/

  stop = 0
  FOR (I = 1, 1000)
     IF  (abs(Tright-Tleft) <= 2*eps)  THEN
       stop = 1
     ENDIF
```

This E-Z Solve algorithmic code for function "**vlet**" implements the vapor-liquid equilibrium (VLE) math algorithm found on Page 6-16 of the *CinChE* manual for any binary system, and it also incorporates the numerical analysis technique called the bisection method.

10 of 10



Problem 6.59
in F&R, 3rd Ed.

```
    IF ( I = 1 ) THEN
      Tmid = Tleft
    ENDIF
    IF ( I = 2 ) THEN
      Tmid = Tright
    ENDIF
    IF ( I > 2 ) THEN
      Tmid = (Tleft + Tright) / 2
    ENDIF

    Psat1 = 10^( A1 - B1/(Tmid + C1) )     //   Antoine equation with
    Psat2 = 10^( A2 - B2/(Tmid + C2) )     // Psat in mm Hg and Tmid in C

    K1 = Psat1 / P
    K2 = Psat2 / P

    x1 = z1 / (Vf*K1 + Lf)
    x2 = z2 / (Vf*K2 + Lf)

    y1 = K1 * x1
    y2 = K2 * x2

    Fmid = (x1 + x2) - (y1 + y2)

    IF ( I = 1 ) THEN
      Fleft  = Fmid
    ENDIF
    IF ( I = 2 ) THEN
      Fright = Fmid
    ENDIF

    IF ( stop = 1 ) THEN
      BREAK
    ENDIF

    IF ( I > 2 ) THEN
      IF ( Fleft * Fmid > 0 ) THEN
        Tleft  = Tmid     // throw away left half
        Fleft  = Fmid
      ELSE
        Tright = Tmid     // throw away right half
        Fright = Fmid
      ENDIF
    ENDIF
  ENDFOR

  RETURN  Tmid       // in C
END
```

Bisection Method

Wikipedia, 7/29/08

An E-Z Solve user-defined function can ONLY return a single result. To access other results within this function, a copy of the function is created, its name is changed slightly, and another single result is returned. Thus, multiple functional calls would be made in an E-Z Solve model to get multiple results from a specific math algorithm.

larger

Example 6.3-2, Part A
in F&R, 3rd Ed.

1 of 9

Problem Statement **{Example 6.3-2, Part 2, in F&R, 3rd Edition, but modified}**

A feed stream of air at 5260 mm Hg and 10 Δ°C of superheat contains 10.0% water by volume and flows at a rate of 123.4 lb_m/h. What are the molar and mass liquid fractions in percentages if the air is cooled to 80°C at constant pressure? What is the final molar composition of the gas phase, and what are the flow rates of the exiting oxygen and nitrogen in mol/s? What is the temperature of the feed stream?

Does all of the water vapor in the moist air condense? If not, what percentage of it does?

An example vapor-liquid-equilibrium problem with the assumption of a one-condensable system; that is, moist air being cooled and partially condensing out some of the water. As discussed on Pages 6-3 to 6-4, some chemical components can be sub-critical and some super-critical with respect to temperature. The critical temperatures for nitrogen, oxygen, and water are 126.20 K, 154.40 K, and 647.40 K, respectively. At the operating temperature of 80°C (353.15 K), water is sub-critical, and oxygen and nitrogen are super-critical. Thus, water has the potential to condense, and we will describe its vapor-liquid equilibrium using Raoult's Law. Since oxygen and nitrogen can not condense, they are called non-condensables. However, they are soluble in water, as discussed on Page 6-3 under Henry's Law.

This problem is solved **two ways**. First, we assume that Raoult's Law applies for water and that the oxygen and nitrogen do not appear in the saturated liquid; that is, the liquid is pure water. Second, we assume that Raoult's Law applies for water and that Henry's Law applies for oxygen and nitrogen; that is, they are soluble in water. We will compare the two solutions and see if the first way is a suitable solution.

Assumptions

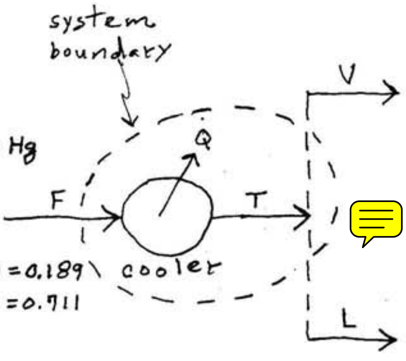
1. Continuous process
2. steady state
3. no reaction
4. mole % is equal to volume %; that is, ideal gas
5. vapor-liquid equilibrium for streams V & L
6. Raoult's Law Model for VLE; ideal gas for stream V and ideal solution for stream L
7. Antoine Equation for vapor pressure of pure water
8. Water vapor in moist air only condenses
9. O_2 and N_2 are insoluble in liquid water
10. dry air is 21 mol % O_2 and 79 mol % N_2

Example 6.3-2, Part A
in F&R, 3rd Ed.

2 of 9

Conceptual Model

T_F = ?
P_F = 5260 mm Hg
Ph_F = gas
$\dot{n}_F$ = ?
$z_{F,WA}$ = 0.100
z_{F,O_2} = 0.90(0.21) = 0.189
z_{F,N_2} = 0.90(0.79) = 0.711



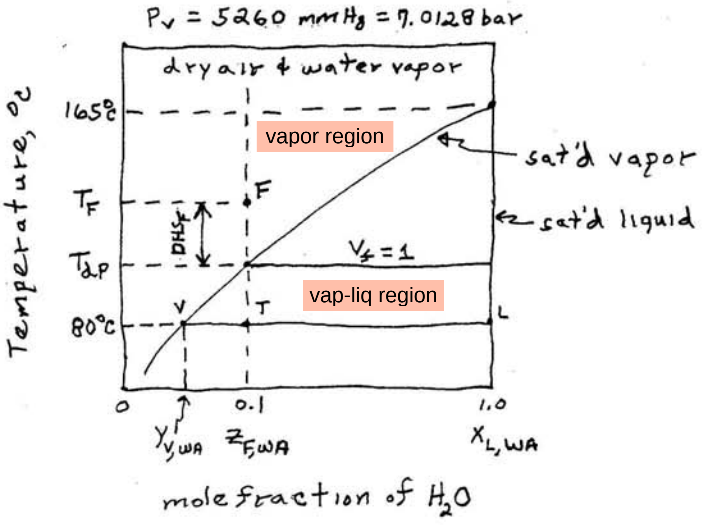
T_V = 80°C
P_V = P_F = 5260 mm Hg
Ph_V = sat'd vap
$\dot{n}_V$ = ?
$y_{V,WA}$ = ?
y_{V,O_2} = ?
y_{V,N_2} = ?

T_L = T_V
P_L = P_F = 5260 mm Hg
Ph_L = sat'd liq
$\dot{n}_L$ = ?
$x_{L,WA}$ = 1.0

other Givens:
$\dot{m}_F$ = 123.4 lbm/h
DSH_F = 10 Δ°C

Finds:
L_f in %, molar basis
L'_f in %, mass basis
$\overline{y}_V$ in mol. frac.
$\dot{n}_{V,O_2}$ in mol/s
$\dot{n}_{V,N_2}$ in mol/s
T_F in °C

TXY Diagram for VLE



Example 6.3-2, Part A
in F&R, 3rd Ed.

3 of 9

Mathematical model

① total: $\dot{n}_F - \dot{n}_V - \dot{n}_L = 0$

② water: $0.100\,\dot{n}_F - \dot{n}_{V,WA} - \dot{n}_L = 0$

check O_2: $0.189\,\dot{n}_F - \dot{n}_{V,O2} = 0$

check N_2: $0.711\,\dot{n}_F - \dot{n}_{V,N2} = 0$

in vlevf function Mix V: $\dot{n}_V = \dot{n}_{V,WA} + \dot{n}_{V,O2} + \dot{n}_{V,N2}$

③ $M_F = \dfrac{\dot{m}_F}{\dot{n}_F}$

④ $M_F = 0.100 M_{WA} + 0.189 M_{O2} + 0.711 M_{N2}$

⑤ Comp V: $\dot{n}_{V,WA} = \dot{n}_V\, Y_{V,WA}$

⑥ $\dot{n}_{V,O2} = \dot{n}_V\, Y_{V,O2}$

⑦ $\dot{n}_{V,N2} = \dot{n}_V\, Y_{V,N2}$

⑧ to ⑪ VLE: $[V_f, \bar{Y}_V] = \text{vlevf}[T_V, P_V, \bar{Z}_F]$

⑫ $V_f + L_f = 1.0$

⑬ $L_f' = \dfrac{\dot{m}_L}{\dot{m}_F}$

⑭ $\dot{m}_L = \dot{n}_L\, M_{WA}$

⑮ $T_F = T_{dp} + DSH_F$

⑯ $T_{dp} = \text{vlet}[P_V, V_f = 1, \bar{Z}_F]$

$\#$ vars = 23
$\#$ eqns = $\underline{16}$
dof 7

knowns: $\dot{m}_F$, DSH_F, $\bar{Z}_F$, T_V, P_V

constants: M_{WA}, M_{O2}, M_{N2}

Mathematical Algorithm

```
$[L_f, L_f', \bar{Y}_V, \dot{n}_{V,j}'s, T_F] = \text{cooler}[\dot{m}_F, DSH_F, \bar{Z}_F, T_V, P_V]$

④        1.  $M_F \leftarrow 0.100 M_{WA} + 0.189 M_{O2} + 0.711 M_{N2}$
③        2.  $\dot{n}_F \leftarrow \dot{m}_F / M_F$
⑧ to ⑪   3.  $[V_f, \bar{Y}_V] \leftarrow \text{vlevf}[T_V, P_V, \bar{Z}_F]$
⑫        4.  $L_f \leftarrow 1.0 - V_f$
⑯        5.  $T_{dp} \leftarrow \text{vlet}[P_V, V_f = 1, \bar{Z}_F]$
⑮        6.  $T_F \leftarrow T_{dp} + DSH_F$
         7.  SOLVE $\dot{n}_V, \dot{n}_L, \dot{n}_{V,WA}$ IN
                 $\dot{n}_V + \dot{n}_L = \dot{n}_F$
                 $\dot{n}_L + \dot{n}_{V,WA} = 0.1 \dot{n}_F$
                 $Y_{V,WA} \dot{n}_V - \dot{n}_{V,WA} = 0$
             END
                 $\dot{n}_V = \frac{(1.0 - 0.1)}{(1.0 - Y_{V,WA})} \cdot \dot{n}_F$
                 $\dot{n}_L = \dot{n}_F - \dot{n}_V$
                 $\dot{n}_{V,WA} = 0.1 \dot{n}_F - \dot{n}_L$
⑭        8.  $\dot{m}_L \leftarrow \dot{n}_L M_{WA}$
⑬        9.  $L_f' \leftarrow \dot{m}_L / \dot{m}_F$
⑦        10. $\dot{n}_{V,N2} \leftarrow \dot{n}_V Y_{V,N2}$
⑥        11. $\dot{n}_{V,O2} \leftarrow \dot{n}_V Y_{V,O2}$
```

Dimensional Consistency

Basis: mol, second, no energy

(4) 1. $\frac{\text{lbm}}{\text{lb-mol}} \leftarrow \sum(\text{unitless})(\text{lbm}/\text{lb-mol})$

(3) 2. $\frac{\text{mol}}{\text{s}} \leftarrow \frac{\text{lbm}}{\text{h}} \cdot \frac{\text{lb-mol}}{\text{lbm}} \cdot \left\langle \frac{453.592 \text{ mol}}{\text{lb-mol}} \cdot \frac{\text{h}}{3600 \text{ s}} \right\rangle$

(8) to (11) 3. [unitless, mol frac] ← vlevf [°C, mm Hg, mol frac]

(16) 5. °C ← vlet [mm Hg, unitless, mol frac]

(15) 6. $°\text{C} \leftarrow °\text{C} + \Delta °\text{C}$

(14) 8. $\frac{\text{g}}{\text{s}} \leftarrow \frac{\text{mol}}{\text{s}} \cdot \frac{\text{g}}{\text{g-mol}}$

(13) 9. $\text{unitless} \leftarrow \frac{\text{g}}{\text{s}} \cdot \frac{\text{h}}{\text{lbm}} \cdot \left\langle \frac{3600 \text{ s}}{\text{h}} \cdot \frac{\text{lbm}}{453.592 \text{ g}} \right\rangle$

Example 6.3-2, Part A
in F&R, 3rd Ed.

5 of 9

Manual Solution

Basis: cgs system, $\dot{m}_F = 123.4$ lbm/h

Givens: $DSH_F = 10\Delta°C$, $\bar{z}_F = 0.100$ WA, 0.189 O_2, 0.711 N_2
$T_V = 80°C$, $P_V = 5260$ mmHg $= 7.0128$ bar

Constants: $M_{WA} = 18.016$, $M_{O2} = 32$, $M_{N2} = 28.02$ $\left\{ \begin{array}{l} \text{F\&R, 3rd Ed.} \\ \text{Table B.1} \end{array} \right.$

1. $M_F = 0.100(18.016) + 0.189(32) + 0.711(28.02) = 27.771820$

2. $\dot{n}_F = \left(\frac{123.4 \text{ lbm}}{h}\right)\left(\frac{\text{lb-mol}}{27.77182 \text{ lbm}}\right)\left\langle\frac{453.592 \text{ mol}}{\text{lb-mol}} \cdot \frac{h}{3600 s}\right\rangle$
$= 0.559853$ mol/s

3. $V_f = 0.965188$
$y_{V,WA} = 0.067540 = \boxed{0.068}$
$y_{V,O2} = 0.195817 = \boxed{0.196}$
$y_{V,N2} = 0.736644 = \boxed{0.737}$
} See Page 6 for the "EZ Setup" solution of the vlevf function

4. $L_f = 1.0 - 0.965188 = 0.034812 = \boxed{3.48\ \%}$

5. $T_{dp} = 90.0072\ °C$ } See Page 6 for "EZ Setup" of the vlet function

6. $T_F = 90.0072 + 10.0 = 100.0072\ °C = \boxed{100.\ °C}$

7. $\dot{n}_V = \frac{(1.0 - 0.1)}{(1.0 - 0.06754)}\left(0.559853 \frac{mol}{s}\right) = 0.540364$ mol/s
$\dot{n}_L = 0.559853 \frac{mol}{s} - 0.540364 \frac{mol}{s} = 0.019489$ mol/s
$\dot{n}_{V,WA} = 0.1\left(0.559853 \frac{mol}{s}\right) - 0.019489 \frac{mol}{s} = 0.036496$ mol/s
$= \boxed{0.0365 \text{ mol/s}}$

8. $\dot{m}_L = \left(0.019489 \frac{mol}{s}\right)\left(18.016 \frac{g}{mol}\right) = 0.351114$ g/s

9. $L'_f = \left(0.351114 \frac{g}{s}\right)\left(\frac{h}{123.4 \text{ lbm}}\right)\left\langle\frac{3600 s}{h} \cdot \frac{\text{lbm}}{453.592 g}\right\rangle$
$= 0.0225824 = \boxed{2.26\ \%}$

10. $\dot{n}_{V,O2} = 0.195817\left(0.540364 \frac{mol}{s}\right) = 0.105812 \frac{mol}{s} = \boxed{0.106 \text{ mol/s}}$

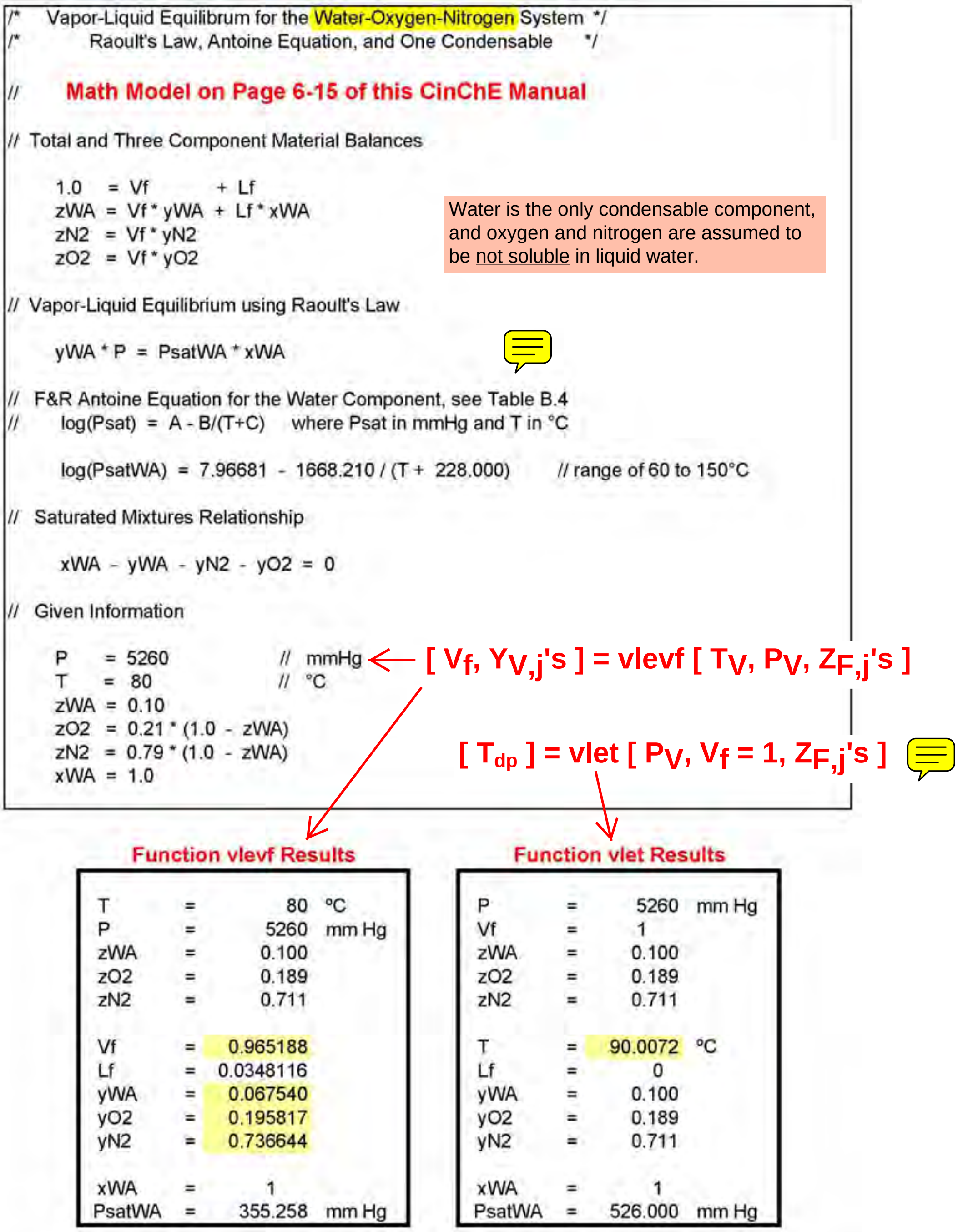
11. $\dot{n}_{V,N2} = 0.736644\left(0.540364 \frac{mol}{s}\right) = 0.398056 \frac{mol}{s} = \boxed{0.398 \text{ mol/s}}$

Click here to complete the Excel **Solver** solutions for this "**EZ Setup**" model.

Example 6.3-2, Part A
in F&R, 3rd Ed.

6 of 9

"EZ Setup" Model for Vapor-Liquid Equilibrium using Raoult's Law



```
/*     Vapor-Liquid Equilibrum for the Water-Oxygen-Nitrogen System  */
/*           Raoult's Law, Antoine Equation, and One Condensable      */

//       Math Model on Page 6-15 of this CinChE Manual

// Total and Three Component Material Balances

       1.0   =  Vf          +  Lf
       zWA   =  Vf * yWA   +  Lf * xWA
       zN2   =  Vf * yN2
       zO2   =  Vf * yO2

// Vapor-Liquid Equilibrium using Raoult's Law

       yWA * P  =  PsatWA * xWA

//  F&R Antoine Equation for the Water Component, see Table B.4
//       log(Psat)  =  A - B/(T+C)     where Psat in mmHg and T in °C

        log(PsatWA)  =  7.96681  -  1668.210 / (T +  228.000)       // range of 60 to 150°C

//  Saturated Mixtures Relationship

        xWA  -  yWA  -  yN2  -  yO2  =  0

//  Given Information

       P      =  5260                //  mmHg
       T      =  80                  //  °C
       zWA  =  0.10
       zO2  =  0.21 * (1.0  -  zWA)
       zN2  =  0.79 * (1.0  -  zWA)
       xWA  =  1.0
```

Water is the only condensable component, and oxygen and nitrogen are assumed to be not soluble in liquid water.

$[\ V_f,\ Y_{V,j}\text{'s}\ ] = \text{vlevf}\ [\ T_V,\ P_V,\ Z_{F,j}\text{'s}\ ]$

$[\ T_{dp}\ ] = \text{vlet}\ [\ P_V,\ V_f = 1,\ Z_{F,j}\text{'s}\ ]$

Function vlevf Results

```
T        =          80   °C
P        =        5260   mm Hg
zWA      =       0.100
zO2      =       0.189
zN2      =       0.711

Vf       =    0.965188
Lf       =   0.0348116
yWA      =    0.067540
yO2      =    0.195817
yN2      =    0.736644

xWA      =           1
PsatWA   =     355.258   mm Hg
```

Function vlet Results

```
P        =        5260   mm Hg
Vf       =           1
zWA      =       0.100
zO2      =       0.189
zN2      =       0.711

T        =     90.0072   °C
Lf       =           0
yWA      =       0.100
yO2      =       0.189
yN2      =       0.711

xWA      =           1
PsatWA   =     526.000   mm Hg
```

Heuristic observations

A. Numerical Solution

- Check:

$$0.189\,\dot{n}_F - \dot{n}_{V,O2} \overset{?}{=} 0 \qquad \text{OK!}$$

$$0.189\,(0.559853 \text{ mol/s}) - 0.105812 \text{ mol/s} = 2.2 \times 10^{-7}$$

$$0.711\,\dot{n}_F - \dot{n}_{V,N2} \overset{?}{=} 0 \qquad \text{OK!}$$

$$0.711\,(0.559853 \text{ mol/s}) - 0.398056 \text{ mol/s} = -5.2 \times 10^{-7}$$

- Not all of the water in the feed stream condenses.

$$\% \text{ condensed} = \frac{0.1\,\dot{n}_F - \dot{n}_{V,WA}}{0.1\,\dot{n}_F} = \frac{0.1\,(0.559853 \frac{mol}{s}) - 0.036496 \frac{mol}{s}}{0.1\,(0.559853 \frac{mol}{s})}$$

$$= 0.348115 = \boxed{34.8\ \%}$$

- An alternate partial solution is to use the Reverse Lever Rule in the TXY diagram for VLE on Page 2:

At T_{dp}: Raoult's Law: $z_{F,WA} P_V = P^*_{WA} X_{L,WA}$

$$0.1\,(5260 \text{ mm Hg}) = P^*_{WA}\,(1.0)$$

$$T_{dp} = tsat[P^*_{WA}] = \boxed{89.99^\circ C} \quad \left\{ \begin{matrix} \text{F\&R steam} \\ \text{calculator} \end{matrix} \right.$$

At 80°C: Raoult's Law: $Y_{V,WA} P_V = P^*_{WA} X_{L,WA}$

$$Y_{V,WA}\,(5260 \text{ mm Hg}) = P^*_{WA}\,(1.0)$$

$$P^*_{WA} = psat[80^\circ C] = 355.5 \text{ mm Hg} \quad \left\{ \begin{matrix} \text{F\&R steam} \\ \text{calculator} \end{matrix} \right.$$

$$Y_{V,WA} = \frac{P^*_{WA}}{P_V} = \frac{355.5 \text{ mm Hg}}{5260 \text{ mm Hg}} = \boxed{0.0675856}$$

$$L_f = \frac{\overline{VT}}{\overline{VL}} = \frac{z_{F,WA} - Y_{V,WA}}{X_{L,WA} - Y_{V,WA}} = \frac{0.1 - 0.0675856}{1.0 - 0.0675856} = \boxed{0.0347639}$$

$$\dot{n}_L = V_f\,\dot{n}_F = (0.0347639)(0.559853 \tfrac{mol}{s}) = \boxed{0.0194627 \tfrac{mol}{s}}$$

B. Mathematical Algorithm

By examining this algorithm, components O_2 and N_2 can be lumped together as one component, called dry air. Thus, step 10 would be changed, and step 11 disappears.

C. Mathematical Model

How good is the last assumption of insoluble O_2 & N_2? By examining the "EZ Setup" model on Page 8, the deviation is less than 0.01 % for L_f and $\bar{Y}_V$ values.

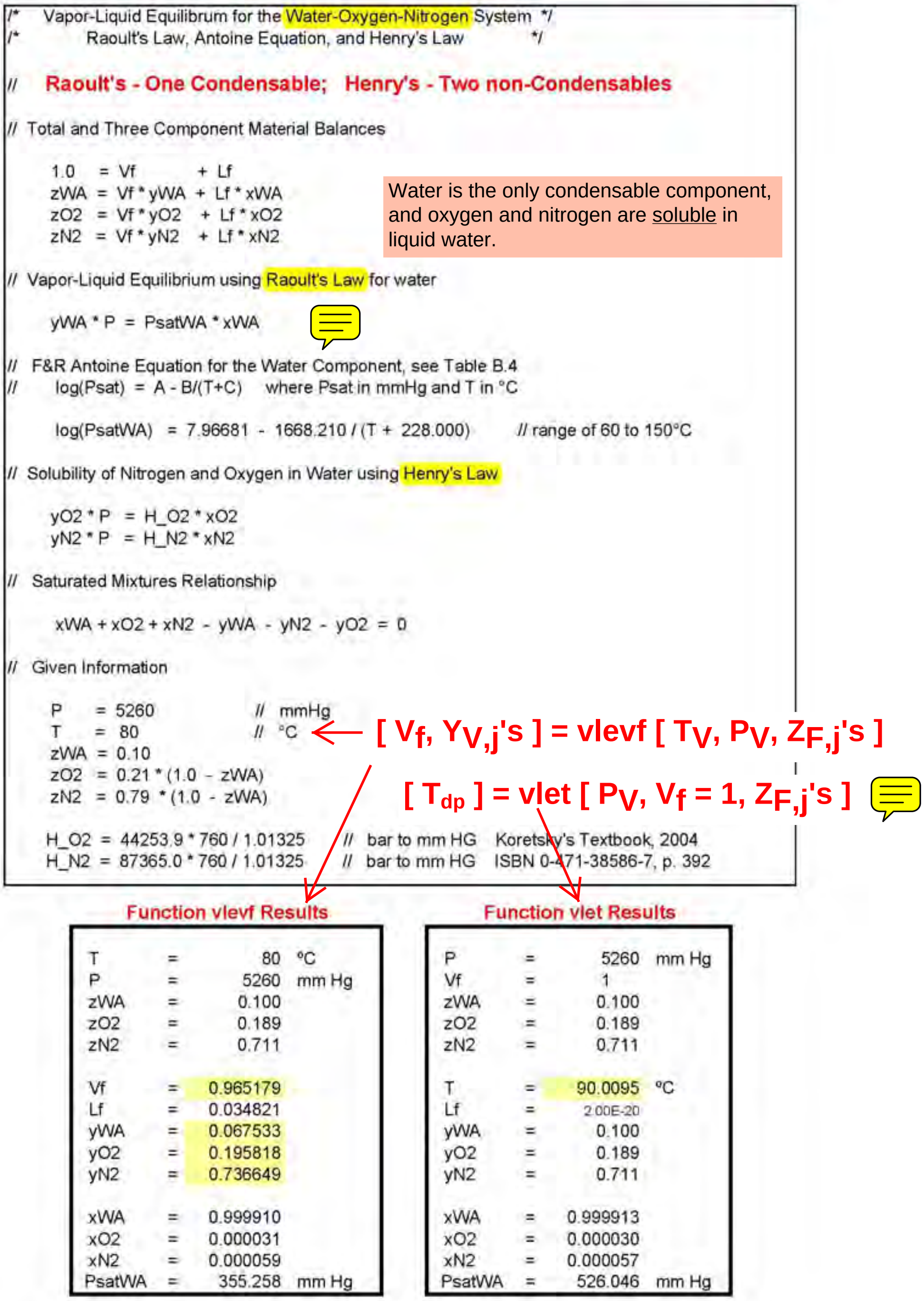
D. Conceptual Model: steam tables instead of Antoine for vapor pressure gives difference of 0.11% for L_f, see Page 9.

Click here to complete the Excel **Solver** solutions for this "**EZ Setup**" model.

Example 6.3-2, Part A
in F&R, 3rd Ed.

8 of 9

"EZ Setup" Model for Vapor-Liquid Equilibrium using Raoult's and Henry's Laws



```
/*   Vapor-Liquid Equilibrum for the Water-Oxygen-Nitrogen System  */
/*          Raoult's Law, Antoine Equation, and Henry's Law         */

//    Raoult's - One Condensable;   Henry's - Two non-Condensables

// Total and Three Component Material Balances

      1.0   = Vf        + Lf
      zWA  = Vf * yWA  + Lf * xWA
      zO2  = Vf * yO2   + Lf * xO2
      zN2  = Vf * yN2   + Lf * xN2

// Vapor-Liquid Equilibrium using Raoult's Law for water

      yWA * P  =  PsatWA * xWA

//  F&R Antoine Equation for the Water Component, see Table B.4
//      log(Psat)  =  A - B/(T+C)    where Psat in mmHg and T in °C

      log(PsatWA)  =  7.96681  -  1668.210 / (T + 228.000)      // range of 60 to 150°C

// Solubility of Nitrogen and Oxygen in Water using Henry's Law

      yO2 * P   =  H_O2 * xO2
      yN2 * P   =  H_N2 * xN2

//  Saturated Mixtures Relationship

      xWA + xO2 + xN2  -  yWA  -  yN2  -  yO2  =  0

//  Given Information

      P     =  5260              //  mmHg
      T     =  80                //  °C
      zWA  =  0.10
      zO2  =  0.21 * (1.0  -  zWA)
      zN2  =  0.79  * (1.0  -  zWA)

      H_O2  =  44253.9 * 760 / 1.01325     //  bar to mm HG    Koretsky's Textbook, 2004
      H_N2  =  87365.0 * 760 / 1.01325     //  bar to mm HG    ISBN 0-471-38586-7, p. 392
```

Water is the only condensable component, and oxygen and nitrogen are soluble in liquid water.

$[\ V_f,\ Y_{V,j}\text{'s}\ ] = \text{vlevf}\ [\ T_V,\ P_V,\ Z_{F,j}\text{'s}\ ]$

$[\ T_{dp}\ ] = \text{vlet}\ [\ P_V,\ V_f = 1,\ Z_{F,j}\text{'s}\ ]$

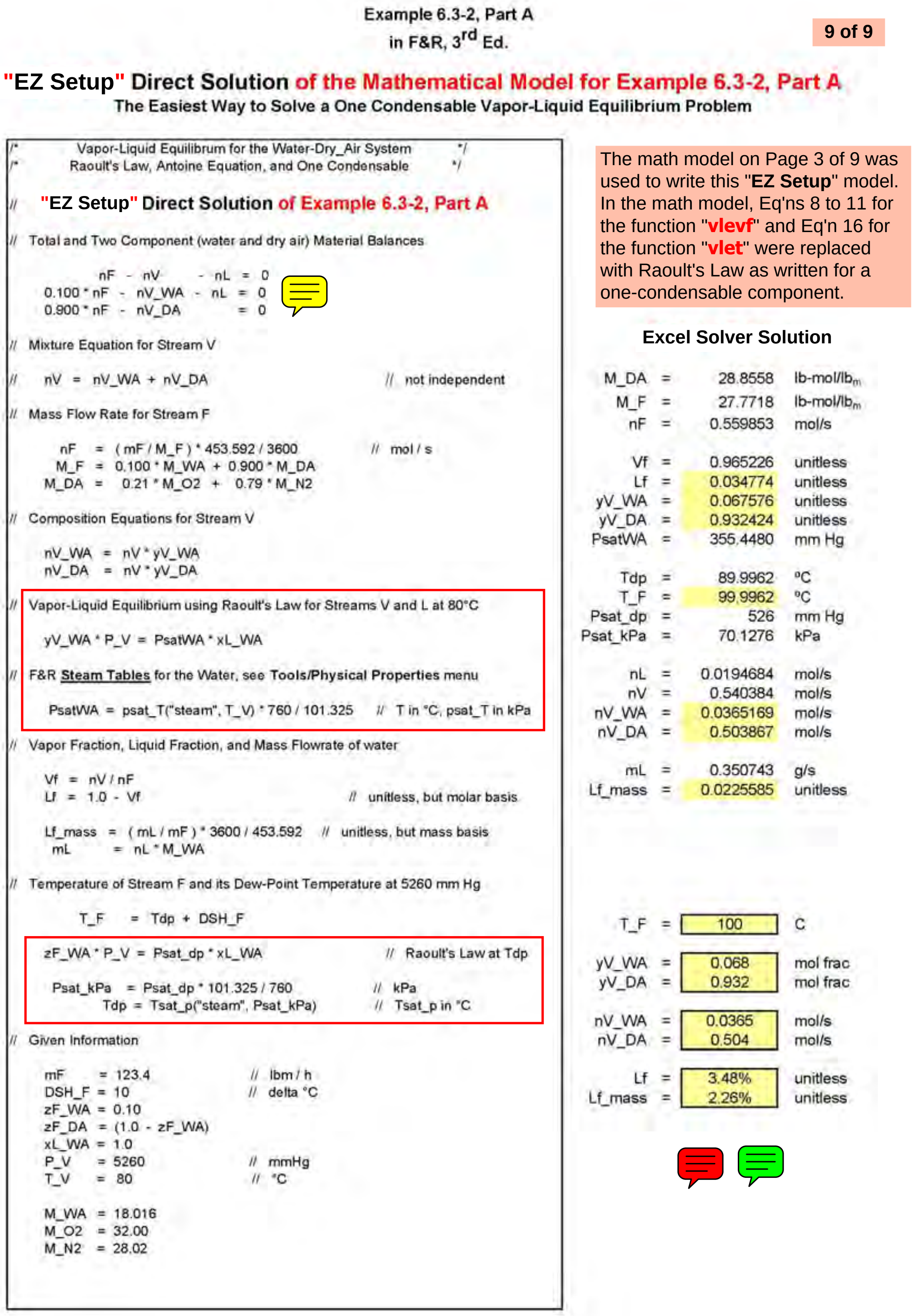
Function vlevf Results

```
T        =          80   °C
P        =        5260   mm Hg
zWA      =       0.100
zO2      =       0.189
zN2      =       0.711

Vf       =    0.965179
Lf       =    0.034821
yWA      =    0.067533
yO2      =    0.195818
yN2      =    0.736649

xWA      =    0.999910
xO2      =    0.000031
xN2      =    0.000059
PsatWA   =     355.258   mm Hg
```

Function vlet Results

```
P        =        5260   mm Hg
Vf       =           1
zWA      =       0.100
zO2      =       0.189
zN2      =       0.711

T        =     90.0095   °C
Lf       =    2.00E-20
yWA      =       0.100
yO2      =       0.189
yN2      =       0.711

xWA      =    0.999913
xO2      =    0.000030
xN2      =    0.000057
PsatWA   =     526.046   mm Hg
```

Click here to complete the Excel **Solver** solution for this "**EZ Setup**" model.



Example 6.3-2, Part A
in F&R, 3rd Ed.

9 of 9

"EZ Setup" Direct Solution of the Mathematical Model for Example 6.3-2, Part A

The Easiest Way to Solve a One Condensable Vapor-Liquid Equilibrium Problem

```
/*        Vapor-Liquid Equilibrum for the Water-Dry_Air System        */
/*        Raoult's Law, Antoine Equation, and One Condensable         */

//   "EZ Setup" Direct Solution of Example 6.3-2, Part A

//  Total and Two Component (water and dry air) Material Balances

           nF  -  nV       -  nL  =  0
   0.100 * nF  -  nV_WA  -  nL  =  0
   0.900 * nF  -  nV_DA        =  0

//  Mixture Equation for Stream V

//     nV  =  nV_WA + nV_DA                         //  not independent

//  Mass Flow Rate for Stream F

       nF    =  ( mF / M_F ) * 453.592 / 3600          //  mol / s
      M_F  =  0.100 * M_WA  +  0.900 * M_DA
    M_DA  =    0.21 * M_O2  +   0.79 * M_N2

//  Composition Equations for Stream V

    nV_WA  =  nV * yV_WA
    nV_DA  =  nV * yV_DA

//  Vapor-Liquid Equilibrium using Raoult's Law for Streams V and L at 80°C

    yV_WA * P_V  =  PsatWA * xL_WA

//  F&R Steam Tables for the Water, see Tools/Physical Properties menu

     PsatWA  =  psat_T("steam", T_V) * 760 / 101.325      //  T in °C, psat_T in kPa

//  Vapor Fraction, Liquid Fraction, and Mass Flowrate of water

    Vf  =  nV / nF
    Lf  =  1.0  -  Vf                                  //  unitless, but molar basis

    Lf_mass  =  ( mL / mF ) * 3600 / 453.592     //  unitless, but mass basis
     mL         =  nL * M_WA

//  Temperature of Stream F and its Dew-Point Temperature at 5260 mm Hg

           T_F      =  Tdp  +  DSH_F

    zF_WA * P_V  =  Psat_dp * xL_WA                     //  Raoult's Law at Tdp

     Psat_kPa    =  Psat_dp * 101.325 / 760             //  kPa
            Tdp  =  Tsat_p("steam", Psat_kPa)           //  Tsat_p in °C

//  Given Information

    mF       =  123.4                //  lbm / h
    DSH_F  =  10                     //  delta °C
    zF_WA  =  0.10
    zF_DA   =  (1.0  -  zF_WA)
    xL_WA  =  1.0
    P_V      =  5260                 //  mmHg
    T_V      =   80                  //  °C

    M_WA   =  18.016
    M_O2    =  32.00
    M_N2    =  28.02
```

The math model on Page 3 of 9 was used to write this "**EZ Setup**" model. In the math model, Eq'ns 8 to 11 for the function "**vlevf**" and Eq'n 16 for the function "**vlet**" were replaced with Raoult's Law as written for a one-condensable component.

Excel Solver Solution

M_DA = 28.8558 lb-mol/lb_m
M_F = 27.7718 lb-mol/lb_m
nF = 0.559853 mol/s

Vf = 0.965226 unitless
Lf = 0.034774 unitless
yV_WA = 0.067576 unitless
yV_DA = 0.932424 unitless
PsatWA = 355.4480 mm Hg

Tdp = 89.9962 ºC
T_F = 99.9962 ºC
Psat_dp = 526 mm Hg
Psat_kPa = 70.1276 kPa

nL = 0.0194684 mol/s
nV = 0.540384 mol/s
nV_WA = 0.0365169 mol/s
nV_DA = 0.503867 mol/s

mL = 0.350743 g/s
Lf_mass = 0.0225585 unitless

T_F = 100 C

yV_WA = 0.068 mol frac
yV_DA = 0.932 mol frac

nV_WA = 0.0365 mol/s
nV_DA = 0.504 mol/s

Lf = 3.48% unitless
Lf_mass = 2.26% unitless

larger

Example 6.3-2, Part B
in F&R, 3rd Ed.

1 of 8

Problem Statement {Example 6.3-2, Part 3, in F&R, 3rd Edition, but modified}

A feed stream of air at 100°C and 5260 mm Hg contains 10.0% water by volume and flows at a rate of 100.0 mol/s. What is the percent condensation of the water vapor if the air is compressed isothermally to 8500 mm Hg? What is the final molar composition of the gas phase? What is the flow rate of the exiting dry air in lb-mol/min? What is the dew-point pressure of the feed stream?

An example vapor-liquid-equilibrium problem with the assumption of a one-condensable system; that is, moist air being compressed isothermally and partially condensing out some of the water. As discussed on Pages 6-3 to 6-4, some chemical components can be sub-critical and some super-critical with respect to temperature. The critical temperatures for nitrogen, oxygen, and water are 126.20 K, 154.40 K, and 647.40 K, respectively. At the operating temperature of 100ºC (373.15 K), water is sub-critical, and oxygen and nitrogen are super-critical. Thus, water has the potential to condense, and we will describe its vapor-liquid equilibrium using Raoult's Law. Since oxygen and nitrogen are non-condensables, we will assume that they do not appear in the saturated liquid; that is, the liquid is pure water.

Assumptions

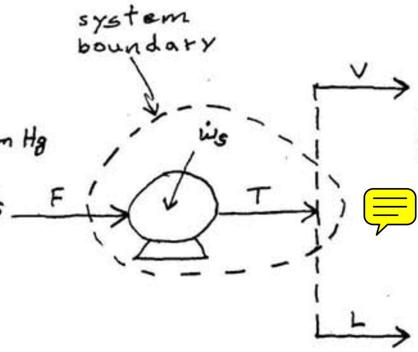
1. Continuous process
2. steady state
3. no reactions
4. mole % is equal to volume %; that is, ideal gas
5. vapor-liquid equilibrium for stream V + L
6. Raoult's Law Model for VLE; ideal gas for stream V and ideal solution for stream L
7. Antoine Equation for vapor pressure of pure water
8. water vapor in moist air only condenses
9. dry air is insoluble in liquid water.
10. dry air is all chemical components in atmospheric air except for water vapor

Example 6.3-2, Part B
in F&R, 3rd Ed.

2 of 8

Conceptual Model

T_F = 100°C
P_F = 5260 mm Hg
Ph_F = gas
$\dot{n}_F$ = 100 mol/s
$z_{F,WA}$ = 0.100
$z_{F,DA}$ = 0.900



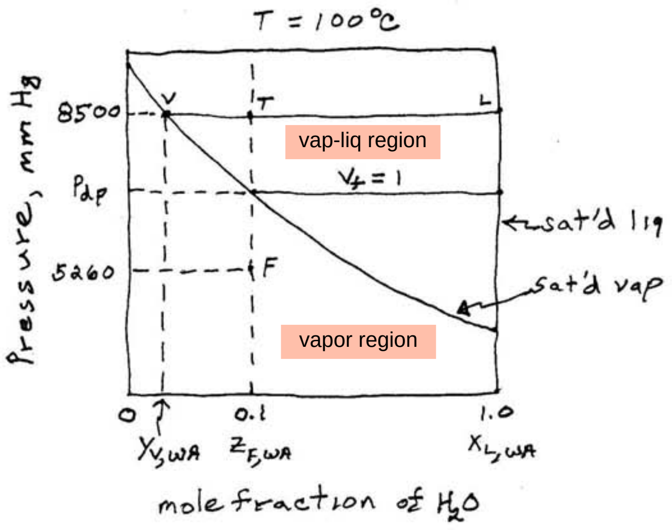
T_V = T_F = 100°C
P_V = 8500 mm Hg
Ph_V = sat'd vap
$\dot{n}_V$ = ?
$y_{V,WA}$ = ?
$y_{V,DA}$ = ?

T_L = T_V
P_L = 8500 mm Hg
Ph_L = sat'd liq
$\dot{n}_L$ = ?
$x_{L,WA}$ = 1.0

other Givens: none

Finds:
% cond = $\dot{n}_L/(0.1\,\dot{n}_F)$
$\bar{Y}_V$ in mol frac
$P_{F,dp}$ in °C
$\dot{n}_{V,DA}$ in lb-mol/min

PXY Diagram for VLE



Example 6.3-2, Part B
in F&R, 3rd Ed.

3 of 8

Mathematical Model

① total: $\dot{n}_F - \dot{n}_V - \dot{n}_L = 0$

② water: $0.1\,\dot{n}_F - \dot{n}_{V,WA} - \dot{n}_L = 0$

check dry air: $0.9\,\dot{n}_F - \dot{n}_{V,DA} = 0$

in vlevf function Mix V: $\dot{n}_V = \dot{n}_{V,WA} + \dot{n}_{V,DA}$

③ Comp V: $\dot{n}_{V,WA} = \dot{n}_V\, y_{V,WA}$

④ $\dot{n}_{V,DA} = \dot{n}_V\, y_{V,DA}$

⑤ to ⑦ VLE: $[V_f, \bar{y}_V] = \text{vlevf}[T_V, P_V, \bar{z}_F]$

⑧ $\%\,\text{cond} = \dfrac{\dot{n}_L}{0.1\,\dot{n}_F}$

⑨ $P_{F,dp} = \text{vlep}[T_V, V_f = 1, \bar{z}_F]$

# vars = 14
# eqns = 9
dof = 5

Knowns: $\dot{n}_F,\ \bar{z}_F,\ T_V,\ P_V$

constants: none

Example 6.3-2, Part B
in F&R, 3rd Ed.

4 of 8

Mathematical Algorithm

$[\,\%\text{cond}, \dot{n}_{V,DA}, \bar{y}_V, P_{F,dp}] = \text{compressor}[\dot{n}_F, \bar{z}_F, T_V, P_V]$

```
(5 to 7)  1.  $[V_f, \bar{y}_V] \leftarrow \text{vlevf}\,[T_V, P_V, \bar{z}_F]$
(9)       2.  $P_{F,dp} \leftarrow \text{vlep}\,[T_V, V_f = 1, \bar{z}_F]$
          3.  SOLVE $\dot{n}_V, \dot{n}_L, \dot{n}_{V,WA}$ IN
(1)               $\dot{n}_V + \dot{n}_L = \dot{n}_F$
(2)               $\dot{n}_L + \dot{n}_{V,WA} = 0.1\dot{n}_F$
(3)               $y_{V,WA}\dot{n}_V - \dot{n}_{V,WA} = 0$
              END
(8)       4.  $\%\text{cond} \leftarrow \dot{n}_L/(0.1\dot{n}_F)$
(4)       5.  $\dot{n}_{V,DA} \leftarrow \dot{n}_V\, y_{V,WA}$
```

$$\left.\begin{aligned} \dot{n}_V &= \frac{(1-0.1)}{(1-y_{V,WA})}\cdot\dot{n}_F \\ \dot{n}_L &= \dot{n}_F - \dot{n}_V \\ \dot{n}_{V,WA} &= 0.1\dot{n}_F - \dot{n}_L \end{aligned}\right\}$$

Dimensional Consistency

Basis: mol, second, no energy

(5 to 7) 1. [unitless, mol frac] ← vlevf [°C, mmHg, mol frac]

(9) 2 [mm Hg] ← vlep [°C , unitless, mol frac]

(4) 5. $\frac{\text{lb-mol}}{\text{min}} \leftarrow \frac{\text{mol V}}{\text{s}}\cdot\frac{\text{mol WA}}{\text{mol V}}\left\langle\frac{\text{lb-mol}}{453.592\text{ g-mol}}\cdot\frac{60\text{ s}}{\text{min}}\right\rangle$

Example 6.3-2, Part B
in F&R, 3rd Ed.

5 of 8

Manual Solution

Basis: cgs system, $\dot{n}_F = 100.0$ mol/s

Givens: $z_F = 10.0$ mol % H_2O, 90.0 mol % dry air
$T_V = 100°C$, $P_V = 8500$ mm Hg

1. $V_f = 0.988370$

$y_{V,WA} = 0.089410 = \boxed{0.089}$
$y_{V,DA} = 0.910590 = \boxed{0.910}$

See Page 6 for the **"EZ Setup"** solution of the vlevf function

2. $P_{F,dp} = 7599.83$ mm Hg $= \boxed{7600 \text{ mmHg}}$

See Page 6 for **"EZ Setup"** solution of vlep function

3. $$\dot{n}_V = \frac{(1-0.100)}{(1-0.089410)}\left(100 \frac{mol}{s}\right) = 98.837018 \text{ mol/s}$$

$$\dot{n}_L = 100 \frac{mol}{s} - 98.837018 \frac{mol}{s} = 1.162982 \text{ mol/s}$$

$$\dot{n}_{V,WA} = 0.1\left(100 \frac{mol}{s}\right) - 1.162982 \frac{mol}{s} = 8.837018 \text{ mol/s}$$

4. $$\% \text{ cond} = \frac{1.162982 \text{ mol/s}}{0.1(100 \text{ mol/s})} * 100 = 11.629820 \% = \boxed{12\%}$$

5. $$\dot{n}_{V,DA} = 0.910590\left(98.837018 \frac{mol}{s}\right)\left\langle \frac{\text{lb-mol}}{453.592 \text{ mol}} \cdot \frac{60 \text{ s}}{\text{min}} \right\rangle$$
$$= 90.0000 \frac{mol}{s} = 11.904972 \frac{\text{lb-mol}}{\text{min}} = \boxed{12 \text{ lb-mol/min}}$$

Click here to complete the Excel **Solver** solutions for this "**EZ Setup**" model.

Example 6.3-2, Part B
in F&R, 3rd Ed.

6 of 8

"EZ Setup" Model for Vapor-Liquid Equilibrium using Raoult's Law

```
/*      Vapor-Liquid Equilibrum for the Water-Dry_Air System          */
/*      Raoult's Law, Antoine Equation, and One Condensable           */

//      Math Model on Page 6-15 of this CinChE Manual

// Total and Two Component Material Balances

      1.0   =  Vf          +  Lf
      zWA   =  Vf * yWA  +  Lf * xWA
      zDA   =  Vf * yDA

// Vapor-Liquid Equilibrium using Raoult's Law

      yWA * P  =  PsatWA * xWA

//  F&R Antoine Equation for the Water Component, see Table B.4
//      log(Psat)  =  A - B/(T+C)     where Psat in mmHg and T in °C

       log(PsatWA)  =  7.96681  -  1668.210 / (T +  228.000)       // range of 60 to 150°C

//  Saturated Mixtures Relationship

       xWA  -  yWA  -  yDA  =  0

//  Given Information

      T     =  100            //  °C
      P     =  8500           //  mm Hg
      zWA   =  0.10
      zDA   =  (1.0  -  zWA)
      xWA   =  1.0
```

Water is the only condensable component, and dry air is not soluble in liquid water.

Dry air contains all chemical components of atmospheric air except for water vapor.

$[\ V_f,\ Y_{V,j}\text{'s}\ ] = \text{vlevf}\ [\ T_V,\ P_V,\ Z_{F,j}\text{'s}\ ]$

$[\ P_{dp}\ ] = \text{vlep}\ [\ T_V,\ V_f = 1,\ Z_{F,j}\text{'s}\ ]$

Function vlevf Results

T	=	100	°C
P	=	8500	mm Hg
zWA	=	0.100	
zDA	=	0.900	
Vf	=	0.988370	
Lf	=	0.011630	
yWA	=	0.089410	
yDA	=	0.910590	
xWA	=	1	
PsatWA	=	759.983	mm Hg

Function vlep Results

T	=	100	°C
Vf	=	1	
zWA	=	0.100	
zDA	=	0.900	
P	=	7599.83	mm Hg
Lf	=	0	
yWA	=	0.100	
yDA	=	0.900	
xWA	=	1	
PsatWA	=	759.983	mm Hg

Example 6.3-2, Part B
in F&R, 3rd Ed.

7 of 8

Heuristic Observations

A. Numerical Solution

Check: $0.9\,\dot{n}_F - \dot{n}_{V,DA} \overset{?}{=} 0$

$$0.9\left(100\ \frac{mol}{s}\right) - 90.00\ \frac{mol}{s} = \overset{ok!}{0.0}$$

B. Mathematical Algorithm & Model

An alternate partial solution is to use the Reverse Lever Rule in the PXY diagram for VLE on Page 2:

At P_{dp}: Raoult's Law: $z_{F,WA}\,P_{dp} = P^*_{WA}\,X_{L,WA}$

$$0.1\,P_{dp} = P^*_{WA}\,(1.0)$$

$$P^*_{WA} = psat[100°c] = 760\ mm\,Hg\ \{F{+}R,\ Table\ B.3\}$$

$$P_{dp} = \frac{760\ mm\,Hg}{0.1} = \boxed{7600\ mm\,Hg}$$

At 8500 mm Hg: Raoult's Law: $Y_{V,WA}\,P_V = P^*_{WA}\,X_{L,WA}$

$$Y_{V,WA}(8500\ mm\,Hg) = P^*_{WA}\,(1.0)$$

$$P^*_{WA} = psat[100°c] = 760\ mm\,Hg\ \{F{+}R,\ Table\ B.3\}$$

$$Y_{V,WA} = \frac{760\ mm\,Hg}{8500\ mm\,Hg} = \boxed{0.0894118}$$

$$V_f = \frac{\overline{TL}}{\overline{VL}} = \frac{X_{L,WA} - z_{F,WA}}{X_{L,WA} - Y_{V,WA}} = \frac{(1-0.9)}{(1-0.0894118)} = \boxed{0.9883721}$$

$$\dot{n}_V = V_f\,\dot{n}_F = 0.9883721\left(100\ \frac{mol}{s}\right) = \boxed{98.83721\ \frac{mol}{s}}$$

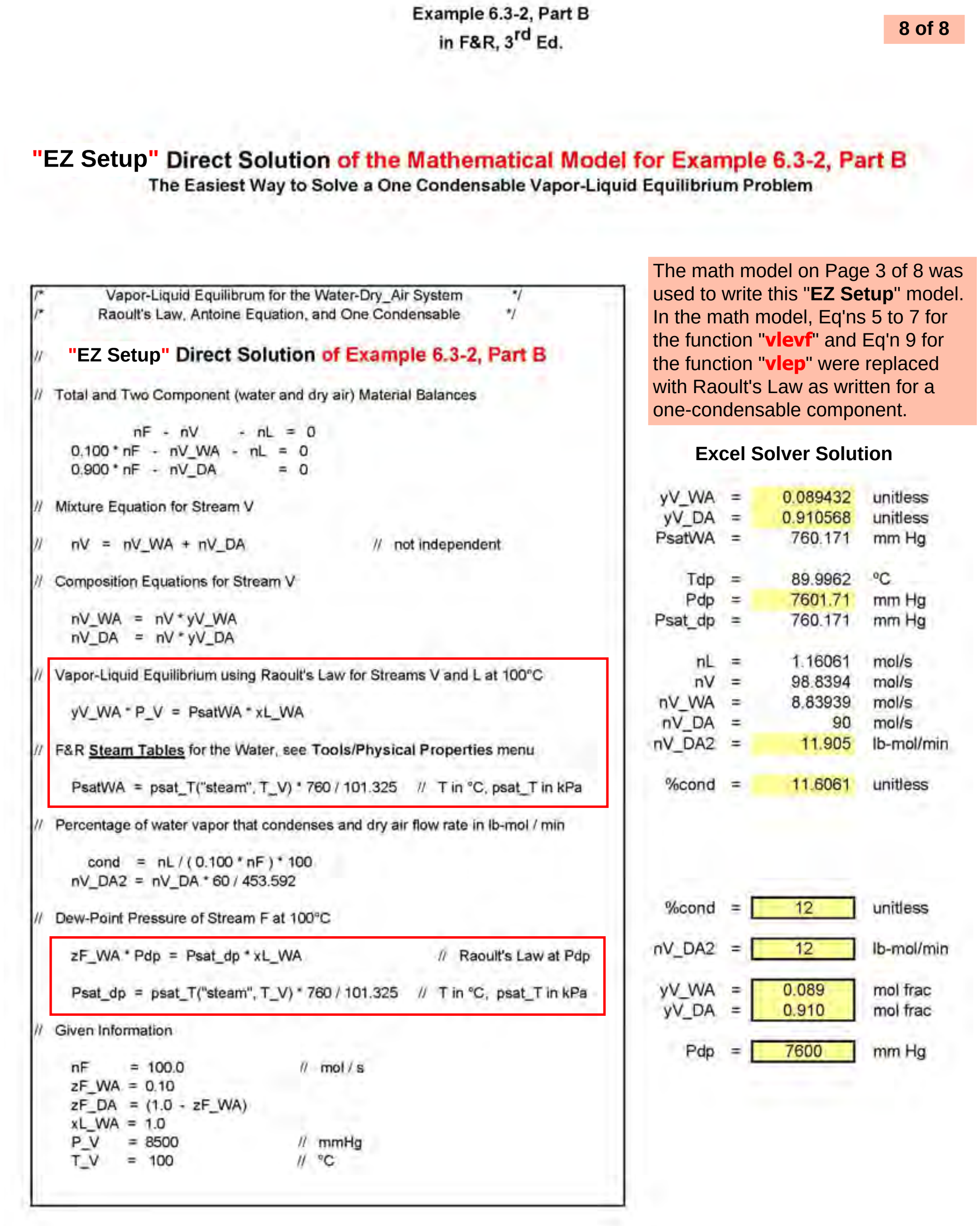
C. Conceptual Model

- See Page 8 for an **"EZ Setup"** direct solution of math model on Page 3.
- How good is the assumption mol% = vol%, since P > 3 atm?

		Stream F	Stream V
	T, °C	100	100
	P, mm Hg	5260	8500
ideal gas:	$\hat{V}$, L/mol	4.424	2.738
HYSYS, PRSV:	$\hat{V}$, L/mol	4.409	2.725
	% dev	0.34%	0.47%

On Page 3-12, ideal gas behavior: $\hat{V}_{ideal} = \frac{RT}{P} > 5$ L/mol. Since the ideal gas values compared to those for PRSV in HYSYS differ by < 0.5%, the assumption is not bad.

Click here to complete the Excel **Solver** solution for this "**EZ Setup**" model.



Example 6.3-2, Part B
in F&R, 3rd Ed.

8 of 8

"EZ Setup" Direct Solution of the Mathematical Model for Example 6.3-2, Part B

The Easiest Way to Solve a One Condensable Vapor-Liquid Equilibrium Problem

```
/*        Vapor-Liquid Equilibrum for the Water-Dry_Air System        */
/*        Raoult's Law, Antoine Equation, and One Condensable         */

//   "EZ Setup" Direct Solution of Example 6.3-2, Part B

//  Total and Two Component (water and dry air) Material Balances

              nF  -  nV       -  nL  =  0
    0.100 * nF  -  nV_WA  -  nL  =  0
    0.900 * nF  -  nV_DA          =  0

//  Mixture Equation for Stream V

//    nV  =  nV_WA  +  nV_DA                       //  not independent

//  Composition Equations for Stream V

    nV_WA  =  nV * yV_WA
    nV_DA  =  nV * yV_DA

//  Vapor-Liquid Equilibrium using Raoult's Law for Streams V and L at 100°C

    yV_WA * P_V  =  PsatWA * xL_WA

//  F&R Steam Tables for the Water, see Tools/Physical Properties menu

    PsatWA  =  psat_T("steam", T_V) * 760 / 101.325    //  T in °C, psat_T in kPa

//  Percentage of water vapor that condenses and dry air flow rate in lb-mol / min

      cond    =  nL / ( 0.100 * nF ) * 100
    nV_DA2  =  nV_DA * 60 / 453.592

//  Dew-Point Pressure of Stream F at 100°C

    zF_WA * Pdp  =  Psat_dp * xL_WA                      //  Raoult's Law at Pdp

    Psat_dp  =  psat_T("steam", T_V) * 760 / 101.325    //  T in °C,  psat_T in kPa

//  Given Information

    nF        =  100.0                    //  mol / s
    zF_WA  =  0.10
    zF_DA   =  (1.0  -  zF_WA)
    xL_WA  =  1.0
    P_V      =  8500                      //  mmHg
    T_V      =   100                      //  °C
```

The math model on Page 3 of 8 was used to write this "**EZ Setup**" model. In the math model, Eq'ns 5 to 7 for the function "**vlevf**" and Eq'n 9 for the function "**vlep**" were replaced with Raoult's Law as written for a one-condensable component.

Excel Solver Solution

```
  yV_WA  =   0.089432   unitless
  yV_DA  =   0.910568   unitless
 PsatWA  =    760.171   mm Hg

    Tdp  =    89.9962   °C
    Pdp  =    7601.71   mm Hg
Psat_dp  =    760.171   mm Hg

     nL  =    1.16061   mol/s
     nV  =    98.8394   mol/s
  nV_WA  =    8.83939   mol/s
  nV_DA  =         90   mol/s
 nV_DA2  =     11.905   lb-mol/min

  %cond  =    11.6061   unitless



  %cond  =      12      unitless

 nV_DA2  =      12      lb-mol/min

  yV_WA  =     0.089    mol frac
  yV_DA  =     0.910    mol frac

    Pdp  =     7600     mm Hg
```

larger

eLEAPS How To

Distillation

An eLEAPS Session

eLEAPS script

1 of 10

Problem Statement { Problem 6.46 in Felder & Rousseau, 2nd Edition }

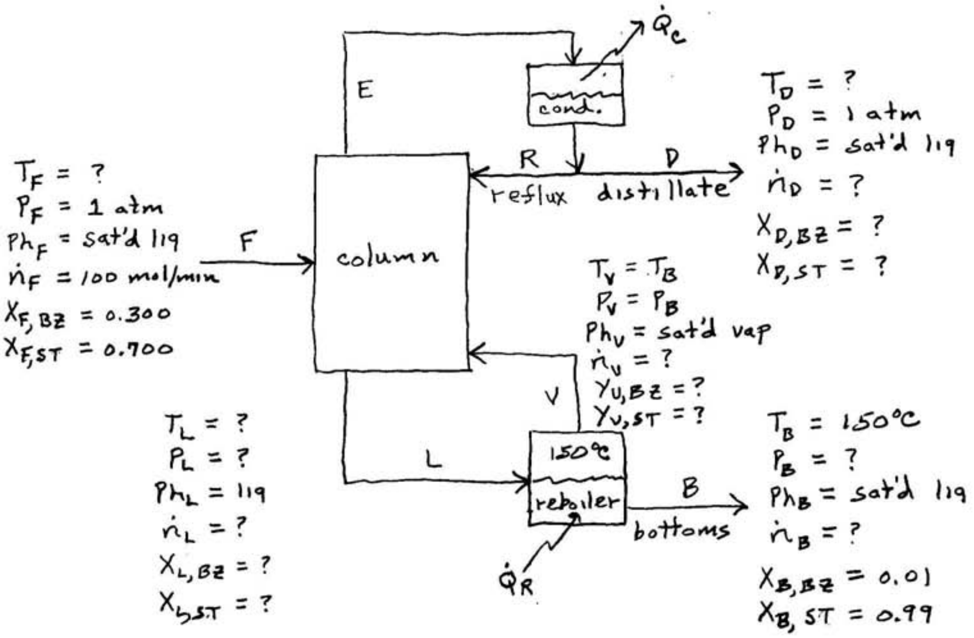
Similar to Problem 6.60 in F&R, 3rd Ed.

A saturated-liquid feed mixture containing 30.0 mole% benzene and 70.0 mole% styrene is to be separated in a distillation column. The column produces an overhead product (a saturated-liquid distillate) and a bottoms product. The bottoms product is 99 mole% styrene and contains 2.0% of the benzene fed to the column.

The liquid stream leaving the bottom of the column (not the bottoms product) goes to a partial reboiler, in which a portion of it is vaporized at 150°C and returned to the bottom of the column. The residual liquid from the reboiler is the bottoms product. The vapor and liquid streams exiting the rebolier are in equilibrium. The boilup ratio, or mole ratio of the vapor and liquid streams leaving the reboiler, is 2.5:1.

Calculate the compositions (component mole fractions) of the distillate product, the vapor returned to the column from the reboiler, and the liquid feed to the reboiler, and estimate the required operating pressure of the reboiler. Also, estimate the temperatures of the feed and distillate streams at a pressure of 1 atm.

Conceptual Model



Other Givens: $\dot{n}_V / \dot{n}_B = 2.5$ boilup ratio

$0.01 \dot{n}_B = 0.02(0.30 \dot{n}_F)$

Finds:

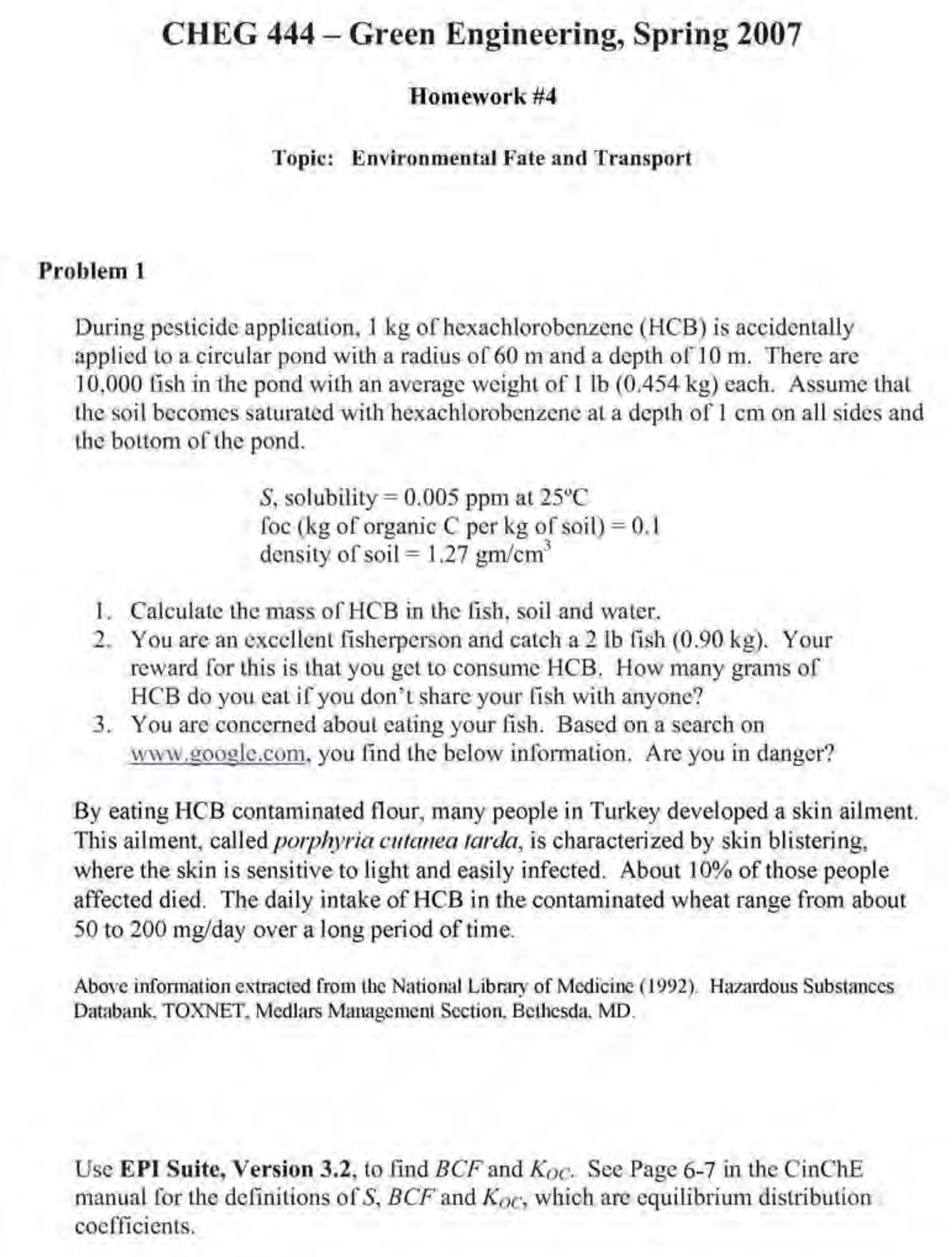
$x_{D,Bz}$ and $x_{D,ST}$ P_B in atm

$y_{V,Bz}$ and $y_{V,ST}$ T_F in °C

$x_{L,Bz}$ and $x_{L,ST}$ T_D in °C

Popup notes and/or web links on Pages 6-50 to 6-55 can be accessed through the above web link for the **eLEAPS script**.

larger



CHEG 444 – Green Engineering, Spring 2007

Homework #4

Topic: Environmental Fate and Transport

Problem 1

During pesticide application, 1 kg of hexachlorobenzene (HCB) is accidentally applied to a circular pond with a radius of 60 m and a depth of 10 m. There are 10,000 fish in the pond with an average weight of 1 lb (0.454 kg) each. Assume that the soil becomes saturated with hexachlorobenzene at a depth of 1 cm on all sides and the bottom of the pond.

S, solubility = 0.005 ppm at 25°C
foc (kg of organic C per kg of soil) = 0.1
density of soil = 1.27 gm/cm^3

1. Calculate the mass of HCB in the fish, soil and water.
2. You are an excellent fisherperson and catch a 2 lb fish (0.90 kg). Your reward for this is that you get to consume HCB. How many grams of HCB do you eat if you don't share your fish with anyone?
3. You are concerned about eating your fish. Based on a search on www.google.com, you find the below information. Are you in danger?

By eating HCB contaminated flour, many people in Turkey developed a skin ailment. This ailment, called *porphyria cutanea tarda*, is characterized by skin blistering, where the skin is sensitive to light and easily infected. About 10% of those people affected died. The daily intake of HCB in the contaminated wheat range from about 50 to 200 mg/day over a long period of time.

Above information extracted from the National Library of Medicine (1992). Hazardous Substances Databank, TOXNET, Medlars Management Section, Bethesda, MD.

Use **EPI Suite, Version 3.2**, to find BCF and K_{OC}. See Page 6-7 in the CinChE manual for the definitions of S, BCF and K_{OC}, which are equilibrium distribution coefficients.

What follows on the next five pages is an "ad hoc" or informal solution to this environmental problem. **Click here** to view a formal solution for the first part of this environmental problem based on the methodology found in Chapter 4 of this *CinChE* manual.

CHEG 472 Homework # 4 ④

Problem 1

Solve HCB mass balance

$$m_{HCB} = C_{wA} V_{wA} + BCF \cdot C_{wA} \cdot m_{fish} + K_{oc} \cdot C_{wA} \cdot m_{carbon}$$

$$1\ kg = C_{wA}(113.09734 \times 10^{6}\ L) + 5153 \cdot C_{wA} \cdot (4540\ kg)$$
$$+ 3380 \cdot C_{wA}\ (19{,}156.3\ kg)$$

$$1 = [113.09734 \times 10^{6} + 5153(4540) + 3380(19{,}156.3)]\ C_{wA}$$

$$C_{wA} = \frac{1}{201.2403 \times 10^{6}} = 4.9692 \times 10^{-9}\ \frac{kg\ HCD}{L\ sol'n}$$

Since $C_{wA} < S = 5 \times 10^{-9}\ \frac{kg\ HCP}{L\ sol'n}$, then calculations are OK.

Mass Ratios

$$m_{wA} = C_{wA} V_{wA} = 4.9692 \times 10^{-9}\ \frac{kg\ HCD}{L\ sol'n} \cdot 113.09734 \times 10^{6}\ L$$
$$= 0.5620\ kg\ HCB$$

$$\dot{m}_{FS} = BCF \cdot C_{wA} \cdot \dot{m}_{fish} = 5153\left(4.9692 \times 10^{-9}\ \frac{kg\ HCP}{L\ soln}\right)(4540\ kg)$$
$$= 0.1163\ kg\ HCB$$

$$\dot{m}_{SL} = K_{oc} \cdot C_{wA} \cdot \dot{m}_{carb} = 3380\left(4.9692 \times 10^{-9}\ \frac{kg\ HCP}{L\ soln}\right)(19{,}156.3\ kg)$$
$$= 0.3217\ kg\ HCB$$

$$\boxed{\dot{m}_{wA} : \dot{m}_{FS} : \dot{m}_{SL} = 56 : 12 : 32}$$

larger

Isenthalpic Flash Vaporization with Refrigerant 22

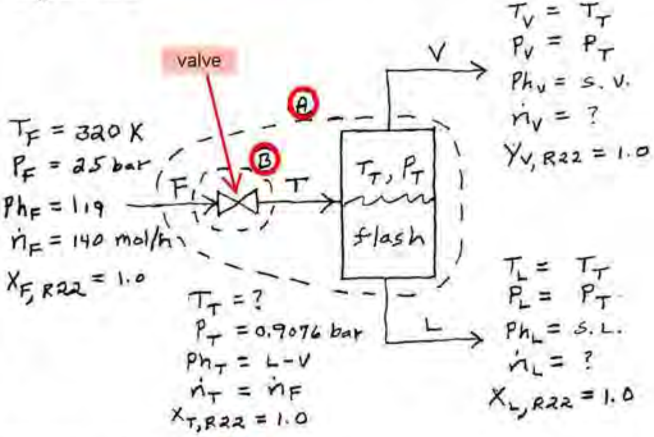
Page 1 of 2

Problem Statement

Requiring material balances, vapor-liquid equilibrium, and the energy balance.

An **isenthalpic** process is one that proceeds without any change in specific enthalpy. It is also known as a throttling process. Refrigerators, air conditioners, and industrial flash separation units use a throttling operation across a valve to produce a liquid and vapor that are assumed to be in equilibrium. This operation is accomplished by expanding a liquid across a valve from a high pressure to a lower pressure, which results in a flash into the two-phase region at a lower temperature. What are the vapor fraction and the flow rate of the vapor in the problem below? Also, what is the flash temperature?

Diagram



Assumptions

1. continuous process
2. steady state
3. no rxn
4. neglect ΔKE + ΔPE
5. adiabatic
6. no shaft work
7. vapor-liquid equil. in stream T
8. T + P the same in streams T, V, L

Math Model Ⓐ

formal method

① Total: $\dot{n}_F - \dot{n}_V - \dot{n}_L = 0$

② Energy: $\dot{n}_F \hat{H}_F - \dot{n}_V \hat{H}_V - \dot{n}_L \hat{H}_L = 0$

③ $\hat{H}_F = \text{r22}[T_F, P_F, \text{liq}]$

④ $\hat{H}_V = \text{r22}[T_V, P_V, \text{sat'd vap}]$

⑤ $\hat{H}_L = \text{r22}[T_L, P_L, \text{sat'd liq}]$

⑥ $T_T = \text{tsat}[P_T, \text{pure R22}]$

⑦+⑧ $T_L = T_V = T_T$

⑨+⑩ $P_L = P_V = P_T$

⑪ $\dot{n}_V = V_f \dot{n}_F$

# vars = 15
# eqns = 11
dof = 4

know: T_F, P_F, $\dot{n}_F$, P_T

Math Model Ⓑ

① $\dot{n}_F - \dot{n}_T = 0$

② $\dot{n}_F \hat{H}_F - \dot{n}_T \hat{H}_T = 0$

③ $\hat{H}_F = \text{r22}[T_F, P_F, \text{liq}]$

④ $T_T = \text{r22}[\hat{H}_T, P_T, \text{L-V}]$

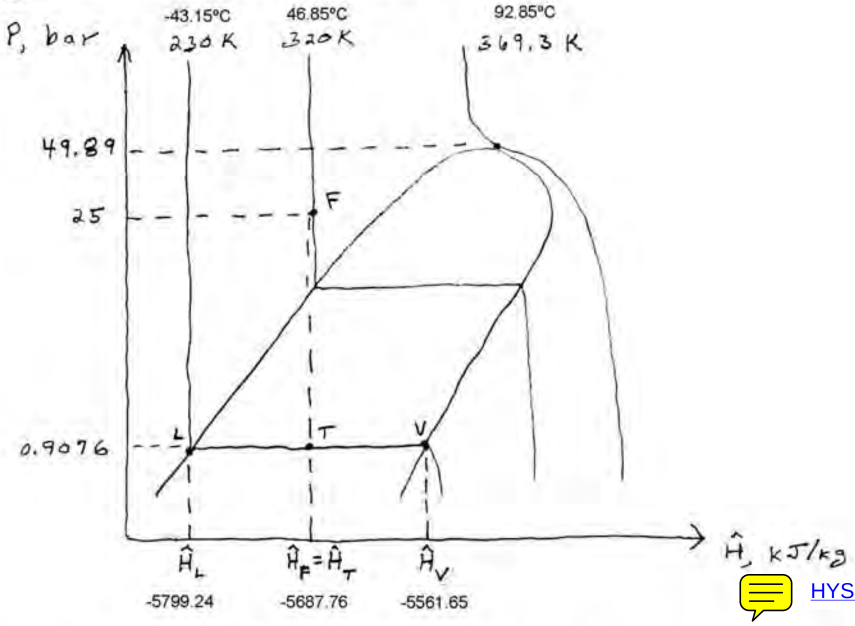
What is unique about the valve operation? It is isenthalpic; that is, constant enthalpy.

# vars = 8
# eqns = 4
dof = 4

know: T_F, P_F, $\dot{n}_F$, P_T

Isenthalpic Flash Vaporization with Refrigerant 22

PH Diagram for Refrigerant 22



HYSYS file

Math Model C

ad hoc method: **based on PH diagram, reverse lever rule, and definitions**

① $V_f = \dfrac{\hat{H}_T - \hat{H}_L}{\hat{H}_V - \hat{H}_L}$ i.e., $V_f = \dfrac{\overline{LT}}{\overline{LV}}$

② $\dot{n}_V = V_f\, \dot{n}_F$

③ $T_T = tsat[P_T, \text{pure R22}]$

\# vars = 8
\# eqns = 3
dof = 5

know: $n_F, \hat{H}_T, \hat{H}_L, \hat{H}_V, P_T$

Solution for Model C

$$V_f = \frac{-5687.76 - (-5799.24)}{-5561.65 - (-5799.24)} = 0.46921167 = \boxed{0.47}$$

$$\dot{n}_V = 0.46921167\,(140\ \text{mol/h}) = 65.6896380\ \frac{\text{mol}}{\text{h}} = \boxed{66\ \frac{\text{mol}}{\text{h}}}$$

$$T_T = tsat\left[0.9076\ \text{bar}, \begin{matrix}\text{pure}\\ \text{R-22}\end{matrix}\right] = 230\ \text{K}$$

$$= -43.15°\text{C} = \boxed{-43°\text{C}}$$

Introduction

This chapter on energy balances has four major objectives. First, a general form of the energy balance discussed in Chapter 2 is used to develop the first principle equations for energy balances. You should review this material in Chapter 2 before continuing to read here. Second, chemical process classifications with respect to energy are summarized for continuous, batch, semi-batch, and semi-continuous system, as well as for steady-state and unsteady-state operations. Third, several key examples that show how to use the first principle equations and to determine specific enthalpies (energy per mole or per mass) are given in the form of graphic organizers. Fourth, example energy balance problems are provided, whose solutions were generated using the problem solving strategy described in Chapter 4. Most of these examples are worked-out problems found in various editions of the Felder and Rousseau textbook [2005] entitled "*Elementary Principles of Chemical Processes*." Once you understand the solution to an example in this *CinChE* chapter, you should compare it to its counterpart in the appropriate edition of the Felder and Rousseau textbook and analyze the differences. The information on energy balances and process classifications, as well as the graphic organizers, will help you to understand the example problems.

Energy Balance

As presented in Chapter 2, the energy balance accounts for the amount of energy associated with a system; that is, a process unit or set of process units. Its general form is:

$$\begin{matrix}\text{energy rates}\\ \text{flowing in}\end{matrix} - \begin{matrix}\text{energy rates}\\ \text{flowing out}\end{matrix} \pm \begin{matrix}\text{heat}\\ \text{rates}\end{matrix} \pm \begin{matrix}\text{work}\\ \text{rates}\end{matrix} = \frac{d(energy)_{sys}}{dt}$$

where the "energy rates", "heat rates", and "work rates" each have units of energy per time like kJ/h, cal/s, or BTU/min. The "$(energy)_{sys}$" has units of just energy like kJ, cal, or BTU.

Index and Limit Conventions

A.	Index i	denotes a process stream;	Limit nt	is the total number of streams.
B.	Index j	denotes a chemical component;	Limit nc	is the total number of components.
C.	Index k	denotes a chemical element;	Limit ne	is the total number of elements.
D.	Index l	denotes a chemical reaction;	Limit nr	is the total number of reactions.

Chemical Reactions

A. **Stoichiometric Equations:** example, $1\ CH_4 + 2\ O_2 \rightarrow 1\ CO_2 + 2\ H_2O$

$$\sum_{reactants} \upsilon_{l,j}\, C_{j,l} \rightarrow \sum_{products} \upsilon_{l,j}\, C_{j,l} \qquad for \quad l = 1, 2, \cdots, nr$$

B. **Stoichiometric Balances:** { conservation of total mass for a chemical reaction }

$$\sum_{j=1}^{nc} \upsilon_{l,j}\, M_j = 0 \qquad for \quad l = 1, 2, \cdots, nr$$

where $\upsilon_{l,j}$ is the stoichiometric coefficient for the *j-th* component in the *l-th* reaction. In any balance equation, it is positive (+) for a product and negative (−) for a reactant. It has units of (mass-mole of *j-th*)/(mass-reaction of *l-th*). Example units are (g-mol *j-th*)/(g-rxn *l-th*), (kg-mol *j-th*)/(kg-rxn *l-th*), and (lb-mol *j-th*)/(lb-rxn *l-th*).

$C_{j,l}$ is the chemical formula for *j-th* component in the *l-th* reaction.

M_j is molecular weight of the *j-th* component in units of mass/mass-mole.

The stoichiometric balance equation is written "*nr*" times, once for each chemical reaction.

D. Practical Energy Balance:

The specific energy of the material in the process streams or within the system boundary only at the initial and final times is composed of the following forms of energy:

$$\hat{E} = \hat{U} + \hat{E}_K + \hat{E}_P + other \qquad \text{units of energy/mass-mole}$$

where	$\hat{E}$	is	the specific energy of the material mixture, which contains "*nc*" chemical components or compounds, in units of energy/mass-mole.
	$\hat{U}$	is	the specific internal energy of the material mixture.
	$\hat{E}_K$	is	the specific kinetic energy of the material mixture.
	$\hat{E}_P$	is	the specific potential energy of the material mixture.
	other	is	other forms of energy like electrical and nuclear.

The total amount of work performed between the surroundings and the system is as follows:

$$\dot{W} = \underset{\substack{\text{shaft}\\ \text{work}}}{\dot{W}_S} + \underset{\dot{W}_f \text{ is flow work or } PV \text{ work}}{\underbrace{\sum_{i=1}^{ni} \dot{n}_i \left(P\hat{V}\right)_i - \sum_{i=ni+1}^{nt} \dot{n}_i \left(P\hat{V}\right)_i}} \qquad \text{units of energy/time}$$

Substituting for $\hat{E}$ and $\dot{W}$ in the general energy balance and neglecting other energy forms particularly nuclear, the differential form reduces to

$$\sum_{i=1}^{ni} \dot{n}_i \left(\hat{H}_i + \hat{E}_{K,i} + \hat{E}_{P,i}\right) - \sum_{i=ni+1}^{nt} \dot{n}_i \left(\hat{H}_i + \hat{E}_{K,i} + \hat{E}_{P,i}\right) \pm \dot{Q} \pm \dot{W}_S = \frac{d\left(n\left\{\hat{U} + \hat{E}_K + \hat{E}_P\right\}\right)_{sys}}{dt}$$

where $\hat{H}_i$ is by definition $\hat{U}_i + \left(P\hat{V}\right)_i$, and it is called the specific enthalpy of a mixture of chemical components in units (energy/mass-mole).

When the changes in kinetic and potential energies are negligible, the **differential form** of the energy balance becomes:

$$\sum_{i=1}^{ni} \dot{n}_i \hat{H}_i - \sum_{i=ni+1}^{nt} \dot{n}_i \hat{H}_i \pm \dot{Q} \pm \dot{W}_S = \frac{d\left(n\hat{U}\right)_{sys}}{dt}$$

The assumption to "neglect ΔKE and ΔPE" is a good one for most problems in this introductory course. Since most process units are stationary, their system does not possess kinetic and potential energy changes. When the process stream pipes, going into and out of the system boundary, are relatively close in distance to one another and when their diameters are roughly the same, the potential and kinetic energy changes, respectively, are negligible compared to the enthalpy changes for those process streams. The $\hat{E}_K$ and $\hat{E}_P$ terms for process streams will become significant terms when you learn to analyze fluid flow systems in a later course of the chemical engineering curriculum.

click here

The differential from of the energy balance above is our starting point to describe the energy balances for continuous, batch, semi-batch, and semi-continuous processes.

F. Variable Definitions for the Energy Balance Equations:

where	ni	is	the number of process streams flowing into the system boundary.
	nt	is	the total number of process streams around the system boundary.
	$\dot{n}_i$	is	the total molar flow rate of the *i-th* stream in units of (mass-mole of *i*)/time.
	$\hat{H}_i$		is the specific enthalpy of the *i-th* stream in units of (energy of *i*) /(mass-mole of *i*). Stream *i-th* is a mixture of non-reacting chemical compounds call components of which a total of "*nc*" of them exists.
	$\dot{Q}$	is	the heat flow between the system and the surroundings in units of (energy/time). The sign in front of $\dot{Q}$ is positive (+) when heat is transferred into the system, and it is negative (−) when heat is lost to the surroundings. Note that the value of $\dot{Q}$ will always be positive.
	$\dot{W}_S$	is	the shaft work occurring between the system and the surroundings in units of (energy/time). The sign in front of $\dot{W}$ is positive (+) when work is done on the system, and it is negative (−) when work is done by the system. Note that the value of $\dot{W}$ will always be positive.
	$\frac{d\left(n\hat{U}\right)_{sys}}{dt}$	is	the accumulation (or depletion) rate of the internal energy within the system boundary in units of (energy of *sys*)/time. It equals zero for the assumption of steady-state operation. For unsteady-state operation, this term must be accounted for in the energy balance.
	n_i	is	the total moles of the *i-th* process stream over the time period ($t_f - t_i$) in units of (mass-mole of *i*). If the molar flow rate of the *i-th* process stream ($\dot{n}_i$) is <u>constant</u> with time over the period ($t_f - t_i$), then variable n_i can be replaced with $\dot{n}_i \Delta t$, or $\dot{n}_i (t_f - t_i)$.
	Q	is	the heat transferred between the system and the surroundings in units of energy. If $\dot{Q}$ is constant with time, $Q = \dot{Q}\Delta t = \dot{Q}\left(t_f - t_i\right)$.
	W_S	is	the shaft work occurring between the system and the surroundings in units of energy. If $\dot{W}_S$ is constant with time, $W = \dot{W}_S \Delta t$.
	$(n)_{sys,i}$ or $(n)_{sys,f}$	is	the total moles in the system initially (t_i) or finally (t_f) in units of (mass-mole of *sys*). $(n)_{sys,i} = (n_1)_{sys,i} + (n_2)_{sys,i} + \cdots + (n_{nc})_{sys,i}$ $(n)_{sys,f} = (n_1)_{sys,f} + (n_2)_{sys,f} + \cdots + (n_{nc})_{sys,f}$
	$(\hat{U})_{sys,i}$ or $(\hat{U})_{sys,f}$	is	the specific internal energy within the system initially (t_i) or finally (t_f) in units of (energy of *sys*)/(mass-mole of *sys*).
	$(\hat{H})_{sys,i}$ or $(\hat{H})_{sys,f}$	is	the specific enthalpy within the system initially (t_i) or finally (t_f) in units of (energy of *sys*)/(mass-mole of *sys*). Note $\hat{H} \equiv \hat{U} + P\hat{V}$.
	$(P)_{sys,i}$ or $(P)_{sys,f}$	is	pressure within system initially (t_i) or finally (t_f) in units force/area.
	$(\hat{V})_{sys,i}$ or $(\hat{V})_{sys,f}$	is	the specific volume within the system initially (t_i) or finally (t_f) in units of (volume of *sys*)/(mass-mole of *sys*).

For simplicity, the energy balances above have only <u>one</u> heat term and <u>one</u> work term. In general, the system boundary could have multiple heat streams and/or multiple shaft work streams crossing it. For multiple heat and/or shaft work streams, you would write additional terms in the energy balance.

The **specific internal energy** is the energy possessed by the molecules in a mixture of substances. It is associated with the translational, rotational, and vibrational motion of the molecules, as well as the chemical bonding between atoms of the molecules. **PV work** is the energy required to push the flowing material into or out of an open system. Conversion factors for PV work are available on Page 3-6 of this *CinChE* manual.

Example Problems

When you complete the development of the mathematical model for any energy balance problem, you will write the differential energy balance given in Eq. 7.1d or 7.5d for continuous processes, or write the integral energy balance given in Eq. 7.1i or 7.6i for batch, semi-batch, and semi-continuous processes.

The list below summarizes the graphic organizers (**go**) and example problems (**ep**) that appear in the remainder of this chapter. The example problems require the application of material balance principles, possibly phase equilibrium principles, and energy balance principles, and they were solved using the problem solving strategy outlined in Chapter 4. The example problems start with non-reactor process units where no phase changes occur. These examples are then followed by non-reactor process units with phase changes. For both types of non-reactor examples, the heat-of-reaction method with no chemical reactions is used to write the energy balances. Finally, examples are presented for reactor process units that use either the heat-of-formation or heat-of-reaction method to write the energy balances. In all of the example problems, the procedures to calculate the specific enthalpy for mixtures of chemical compounds will be illustrated. When a mixture contains only one chemical component (i.e., *nc* = 1), the calculation for a mixture specific enthalpy will be that for a pure chemical compound.

Non-Reaction Examples Using the Heat-of-Reaction Method

blue crib

Reaction Examples Using the Heat-of-Formation Method

pink crib

If you have any questions about the graphic organizers or example problem solutions, please consult with one of your teammates or contact the instructor. The instructor is very willing to help you, if you ask.

larger

CHEG 200 | Mixture Enthalpy by Equations | 1 of 2

Energy Balance

{neglect KE and PE changes}

Equation 7.5d-a with no heat-of-reaction terms

$$\sum_{in} \dot{n}_i \hat{H}_i - \sum_{out} \dot{n}_i \hat{H}_i \pm \dot{Q} \pm \dot{W}_s = \frac{d(n\hat{U})_{sys}}{dt}$$

↑ molar enthalpy of mixture i

$\hat{H}_i \equiv \hat{U}_i + P_i \hat{V}_i$

{in is +}
{out is −}

$\hat{U}$ is specific internal energy

$\hat{H}_i$ = hmix $[T_i, P_i, \bar{X}_i]$ for each mixture i

Mixture $\hat{H}_i$

Eq. 7.7 $$\hat{H}_i = \sum_{j=1}^{nc} X_{i,j} \hat{H}_j + \Delta \hat{H}_{mix}$$

↑ for pure j @ T_i, P_i, Ph_i

↑ heat of mixing @ $T_i, P_i, \bar{X}_i$ } is zero for ideal solution

e.g.: $H_F = 0.4\, \hat{H}_{F,PT} + 0.6\, \hat{H}_{F,HX}$ {liquid feed of pentane and hexane at 30°C and 2 atm}

Pure $\hat{H}_j$

Eq. 7.8 $$\hat{H}_j = \hat{H}_j^o [T_j^o, P_j^o, Ph_j^o] + \Delta \hat{H}_j [T_i, P_i, Ph_i \leftarrow T_j^o, P_j^o, Ph_j^o]$$

arbitrarily set to 0.

stable phase of pure j @ a reference temp. & pressure

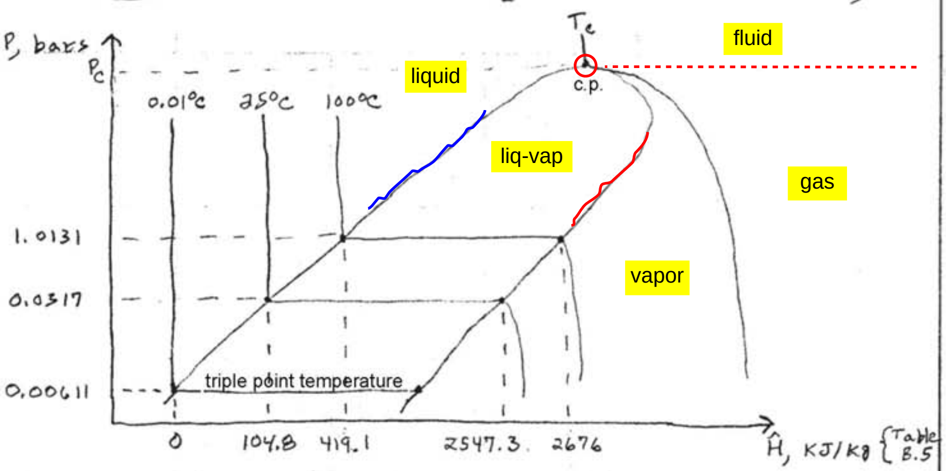
graph, table, equations, or program. Enthalpy change from reference state to state of mixture i.

click here for a tutorial on sketching property diagrams.

Graph of Pure $\Delta \hat{H}_j$

for example H_2O. (see Table B.5 in F&R, 3rd)

click here



click here

$$\hat{H}_{WA} = \hat{H}^o_{WA} + \Delta \hat{H}_{WA}[100°c, 1atm, \text{sat'd vap} \leftarrow 0.01°c, 0.00611 \text{ bar}, \text{sat'd liq}]$$
$$= 0 + 2676 \text{ kJ/kg}$$

CHEG 200 | mixture Enthalpy by Equations | 2 of 2

Pure $\Delta\hat{H}_j$ Equation

where $Ph_i = Ph_j^o$ = liquid, gas, vapor, or solid

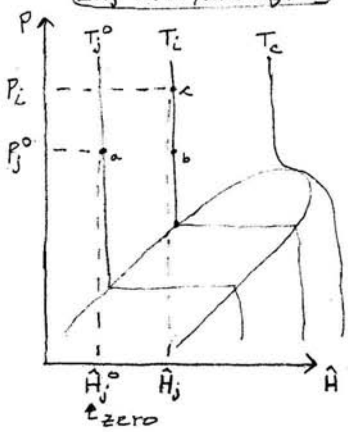
$$d\hat{H} = \left(\frac{\partial\hat{H}}{\partial T}\right)_P dT + \left(\frac{\partial\hat{H}}{\partial P}\right)_T dP$$

$$d\hat{H} = C_p\, dT + \left[\hat{V} - T\left(\frac{\partial\hat{V}}{\partial T}\right)_P\right] dP$$

$$\underbrace{\int_{\hat{H}_j^o}^{\hat{H}_j} d\hat{H}}_{\hat{H}_j - \hat{H}_j^o} = \underbrace{\int_{T_j^o}^{T_i} C_{p,j}\, dT}_{\text{Path } a\to b} + \underbrace{\int_{P_j^o}^{P_i} \left[\hat{V} - T\left(\frac{\partial\hat{V}}{\partial T}\right)_P\right] dP}_{\text{Path } b\to c}$$

Cp or Cv without or with a hat (^) over it will always mean per unit amount.

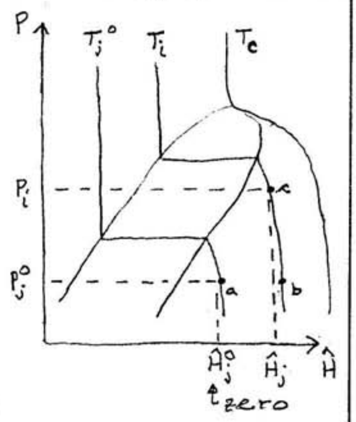
$\Delta\hat{H}_j$ in Liquid Region



Differential Changes

change	solid	liquid	ideal gas $P \le 3$ atm	real gas
$\left(\frac{\partial\hat{H}}{\partial T}\right)_P$	C_p^S	C_p^L	C_p^G	need eos
$\left(\frac{\partial\hat{H}}{\partial P}\right)_T$	$\hat{V}$	$\hat{V}$	zero	need eos
$\left(\frac{\partial\hat{V}}{\partial T}\right)_P$	≈ 0	≈ 0	$\frac{R}{P}$	need eos
$\left(\frac{\partial\hat{U}}{\partial T}\right)_{\hat{V}}$	$C_v^S \approx C_p^S$	$C_v^L \approx C_p^L$	$C_v^G = C_p^G - R$	need eos
$\left(\frac{\partial\hat{U}}{\partial\hat{V}}\right)_T$	≈ 0	≈ 0	zero	need eos

$\Delta\hat{H}_j$ in gas/vapor region



eos - equation of state

$$d\hat{U} = \left(\frac{\partial\hat{U}}{\partial T}\right)_{\hat{V}} dT + \left(\frac{\partial\hat{U}}{\partial\hat{V}}\right)_T d\hat{V}$$

$$d\hat{U} = C_v\, dT \quad \text{for solid, liquid, and ideal gas}$$

C_p Heat Capacity

{Table B.2 + B.10, F&R, 3rd Ed.}

$$C_p = a + bT + cT^2 + dT^3 \qquad \text{i.e. } C_p \text{ is function of } T$$

$$\hat{H}_2 - \hat{H}_1 = \int_{T_1}^{T_2} (a + bT + cT^2 + dT^3)\, dT$$

$$\Delta\hat{H} = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) + \frac{d}{4}(T_2^4 - T_1^4)$$

Enthalpy Tables:

Water or steam - Table B.5, B.6, or B.7
Some Common Gases - Table B.8 or B.9

larger

CHEG 200

Energy Balance Introduction

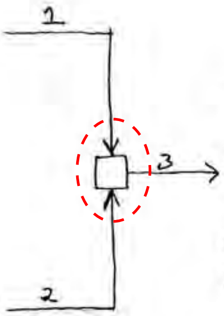
1 of 5

Diagram

Problem Statement: Two process streams containing n-pentane and n-hexane are mixed adiabatically to form a third stream. What is the temperature of the third stream?

$T_1 = 20°C$
$P_1 = 1$ atm
$Ph_1 =$ liquid
$\dot{n}_1 = 45$ gmol/h
$x_{1,PT} = 0.40$
$x_{1,HX} = 0.60$

$T_2 = 40°C$
$P_2 = 1$ atm
$Ph_2 =$ liquid
$\dot{n}_2 = 55$ gmol/h
$x_{2,PT} = 0.60$
$x_{2,HX} = 0.40$



$T_3 = ?$
$P_3 = 1$ atm
$Ph_3 =$ liquid
$\dot{n}_3 = ?$
$x_{3,PT} = ?$
$x_{3,HX} = ?$

Assumptions

1. steady state
2. no rxn
3. neglect ΔKE + ΔPE
4. adiabatic
5. no shaft work
6. continuous process

Find:

T_3 in °C

Click here to view a strategy for phase determination.

Math Model

① Total: $\dot{n}_1 + \dot{n}_2 - \dot{n}_3 = 0$

② PT: $0.40\dot{n}_1 + 0.60\dot{n}_2 - \dot{n}_{3,PT} = 0$

③ HX: $0.60\dot{n}_1 + 0.40\dot{n}_2 - \dot{n}_{3,HX} = 0$

✓ Mix 3: $\dot{n}_3 = \dot{n}_{3,PT} + \dot{n}_{3,HX}$

Equation 7.5d-a with no heat-of-reaction, heat, and shaft work terms:

④ energy: $\dot{n}_1\hat{H}_1 + \dot{n}_2\hat{H}_2 - \dot{n}_3\hat{H}_3 = 0$

⑤ $\hat{H}_1 = \text{hmix}[T_1, P_1, \bar{x}_1]$

⑥ $\hat{H}_2 = \text{hmix}[T_2, P_2, \bar{x}_2]$

⑦ $\hat{H}_3 = \text{hmix}[T_3, P_3, \bar{x}_3]$

⑧ $\dot{n}_{3,PT} = \dot{n}_3 x_{3,PT}$

⑨ $\dot{n}_{3,HX} = \dot{n}_3 x_{3,HX}$

\# vars = 20
\# eqns = 9
DOF = 11

$\bar{x}_i \equiv x_{i,PT} + x_{i,HX}$

$\psi_i \equiv T_i, P_i, \dot{n}_i, \bar{x}_i$

Math Algorithm

$[T_2] = \text{mixer}[\psi_1, \psi_2, P_3]$

① 1. $\dot{n}_3 \leftarrow \dot{n}_1 + \dot{n}_2$

② 2. $\dot{n}_{3,PT} \leftarrow 0.40\dot{n}_1 + 0.60\dot{n}_2$

③ 3. $\dot{n}_{3,HX} \leftarrow 0.60\dot{n}_1 + 0.40\dot{n}_2$

⑧ 4. $x_{3,PT} \leftarrow \dot{n}_{3,PT} / \dot{n}_3$

⑨ 5. $x_{3,HX} \leftarrow \dot{n}_{3,HX} / \dot{n}_3$

⑤ 6. $\hat{H}_1 \leftarrow \text{hmix}[T_1, P_1, \bar{x}_1]$

⑥ 7. $\hat{H}_2 \leftarrow \text{hmix}[T_2, P_2, \bar{x}_2]$

④ 8. $\hat{H}_3 \leftarrow (\dot{n}_1\hat{H}_1 + \dot{n}_2\hat{H}_2)/\dot{n}_3$

9. Iterate T_3 in

⑦ $f(T_3) \leftarrow \hat{H}_3 - \text{hmix}[T_3, P_3, \bar{x}_3]$

Until $f(T_3) = 0$

Energy Balance Introduction

2 of 5

Functional form: **How to evaluate** $hmix[T_2, P_2, \overline{X}_2]$**?**

$$\hat{H}_2 = 0.60 * \hat{H}_{PT} + 0.40 * \hat{H}_{HX} + \Delta\hat{H}_{mix} \qquad (1)$$

Eq. 7.7

where $\hat{H}_2$ is molar enthalpy (kJ/gmol) of mixture at 40ºC and 1 atm.

$\hat{H}_{PT}$ is molar enthalpy (kJ/gmol) of pure n-pentane at 40ºC and 1 atm.

$\hat{H}_{HX}$ is molar enthalpy (kJ/gmol) of pure n-hexane at 40ºC and 1 atm.

$\Delta\hat{H}_{mix}$ is molar enthalpy of mixing that is assumed zero for ideal solution.

$$\hat{H}_{PT} = \underset{\text{zero}}{\hat{H}^o_{PT}} + \Delta\hat{H}_{PT}[40^\circ C, 1\,atm,\, liq \Leftarrow \underbrace{T^o_{PT}, P^o_{PT}, Ph^o_{PT}}_{\text{n-PT reference state}}] \qquad (2)$$

Eq. 7.8

$$\hat{H}_{HX} = \underset{\text{zero}}{\hat{H}^o_{HX}} + \Delta\hat{H}_{HX}[40^\circ C, 1\,atm,\, liq \Leftarrow \underbrace{T^o_{HX}, P^o_{HX}, Ph^o_{HX}}_{\text{n-HX reference state}}] \qquad (3)$$

Eq. 7.8

where $\hat{H}^o_{PT}$ is molar enthalpy of pure n-pentane at arbitrarily-selected reference state.

$\hat{H}^o_{HX}$ is molar enthalpy of pure n-hexane at arbitrarily-selected reference state.

$\Delta\hat{H}_{PT}$ is molar enthalpy change to go from n-PT reference state to 40ºC and 1 atm.

$\Delta\hat{H}_{HX}$ is molar enthalpy change to go from n-HX reference state to 40ºC and 1 atm.

Enthalpy Change of a Pure Substance is represented by an exact differential:

see p. 7-17

$$\int_{\hat{H}^o_j}^{\hat{H}_j} d\hat{H} = \int_{T^o_j}^{T_j} \hat{c}^{Ph}_{P,j}\, dT + \int_{P^o_j}^{P_j} \left[\hat{V} - T\left(\frac{\partial \hat{V}}{\partial T}\right)_P \right] dP \qquad (4)$$

sensible enthalpy change; that is, no phase change.

where $\hat{c}^{Ph}_{P,j}$ is molar heat capacity of comp. j for a liquid, gas, or solid in Table B.2 of F&R, 3rd Ed.

Thus the molar liquid enthalpy changes for pure n-pentane and pure n-hexane are:

Units of kJ/gmol	Excel APEx Add-In Function
$\Delta\hat{H}_{PT} = \int_{T^o_{PT}}^{40^\circ C} \left(155.4\times10^{-3} + 43.68\times10^{-5}T\right)\, dT$	enthalpy("n-pentane",Tpt,T2,"C","l")
$\Delta\hat{H}_{HX} = \int_{T^o_{HX}}^{40^\circ C} \left(216.3\times10^{-3}\right)\, dT$	enthalpy("n-hexane",Tpt,T2,"C","l")
	T2 = 40ºC, Tpt = T^o_{PT}, Thx = T^o_{HX} Ppt = 1 atm, Phx = 1 atm

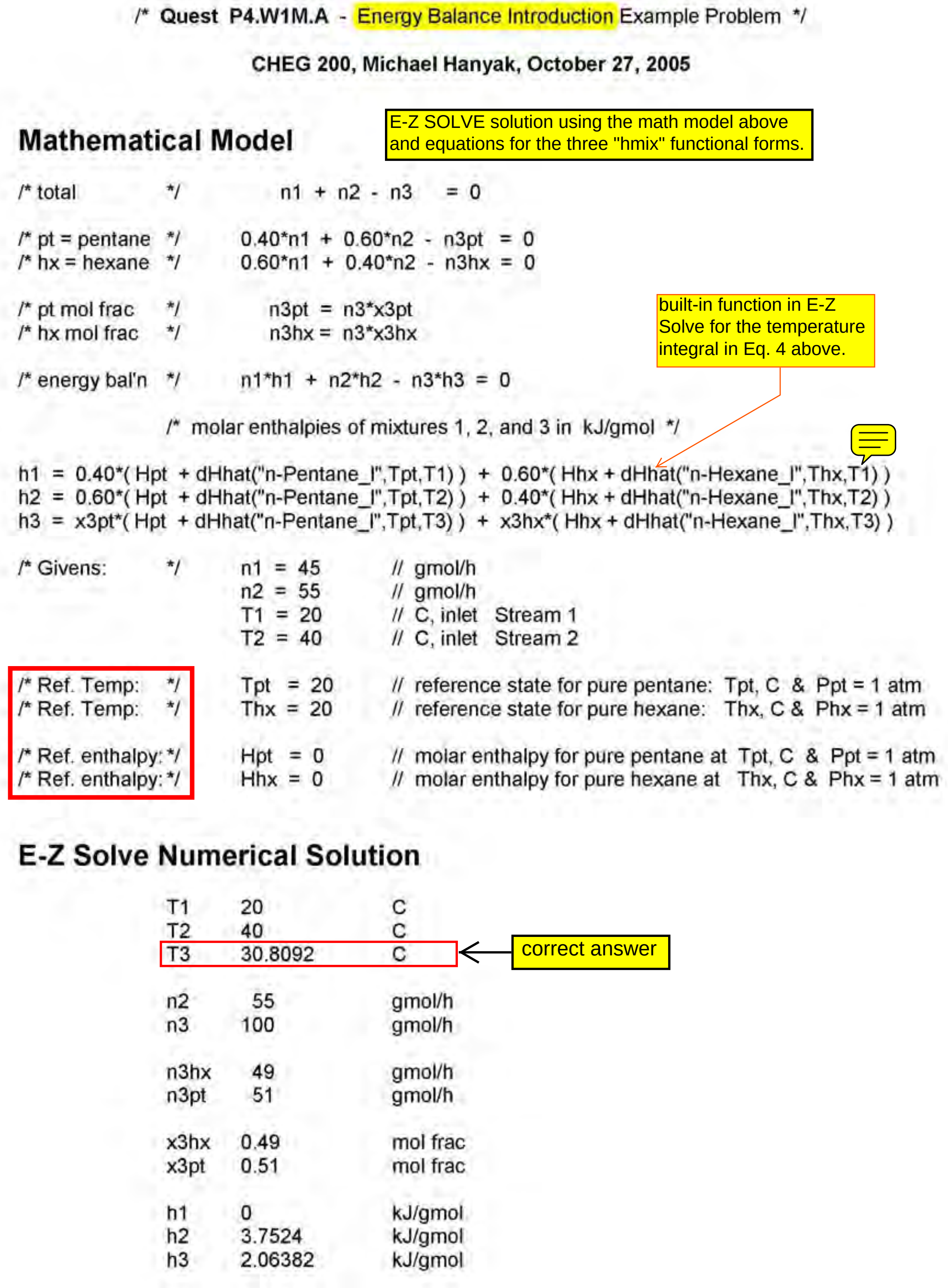
reference states for n-PT & n-HX

where the pressure or second integral in Eq. 4 is zero since its limits of integration are both the same value of 1 atm.

Energy Balance Introduction

3 of 5

Select the "click here" web link at the bottom of this page to view an Excel "EZ Setup" math model that replaces the "E-Z Solve" model given below.



/* **Quest P4.W1M.A** - Energy Balance Introduction Example Problem */

CHEG 200, Michael Hanyak, October 27, 2005

Mathematical Model

E-Z SOLVE solution using the math model above and equations for the three "hmix" functional forms.

```
/* total         */            n1  +  n2  -  n3     =  0

/* pt = pentane  */       0.40*n1  +  0.60*n2  -  n3pt  =  0
/* hx = hexane   */       0.60*n1  +  0.40*n2  -  n3hx  =  0

/* pt mol frac   */           n3pt  =  n3*x3pt
/* hx mol frac   */           n3hx =  n3*x3hx

/* energy bal'n  */       n1*h1  +  n2*h2  -  n3*h3  =  0

                 /*  molar enthalpies of mixtures 1, 2, and 3 in  kJ/gmol  */

h1  =  0.40*( Hpt  + dHhat("n-Pentane_l",Tpt,T1) )  +  0.60*( Hhx + dHhat("n-Hexane_l",Thx,T1) )
h2  =  0.60*( Hpt  + dHhat("n-Pentane_l",Tpt,T2) )  +  0.40*( Hhx + dHhat("n-Hexane_l",Thx,T2) )
h3  =  x3pt*( Hpt  + dHhat("n-Pentane_l",Tpt,T3) )  +  x3hx*( Hhx + dHhat("n-Hexane_l",Thx,T3) )

/* Givens:       */       n1  =  45       //  gmol/h
                          n2  =  55       //  gmol/h
                          T1  =  20       //  C, inlet   Stream 1
                          T2  =  40       //  C, inlet   Stream 2

/* Ref. Temp:    */       Tpt   =  20     //  reference state for pure pentane:  Tpt, C  &  Ppt = 1 atm
/* Ref. Temp:    */       Thx  =  20      //  reference state for pure hexane:   Thx, C &  Phx = 1 atm

/* Ref. enthalpy: */      Hpt   =  0      //  molar enthalpy for pure pentane at  Tpt, C  &  Ppt = 1 atm
/* Ref. enthalpy: */      Hhx  =  0       //  molar enthalpy for pure hexane at   Thx, C &  Phx = 1 atm
```

built-in function in E-Z Solve for the temperature integral in Eq. 4 above.

E-Z Solve Numerical Solution

```
T1      20          C
T2      40          C
T3      30.8092     C

n2       55         gmol/h
n3      100         gmol/h

n3hx     49         gmol/h
n3pt     51         gmol/h

x3hx    0.49        mol frac
x3pt    0.51        mol frac

h1      0           kJ/gmol
h2      3.7524      kJ/gmol
h3      2.06382     kJ/gmol
```

correct answer

Before examining the derivation on the next two pages, **click here** to conduct an exercise to show the arbitrariness of the pure-component reference states using the mathematical model above as implemented in "**EZ Setup**". Note that this arbitrariness **only** applies to the heat-of-reaction method for the energy balance with **no** chemical reactions.

Energy Balance Introduction

4 of 5

Why Arbitrary Component Reference States? (no reactions)

Begin with the energy balance to mix two process streams to form a third one. These three streams labeled 1, 2, and 3 are mixtures of two chemical components—n-pentane (PT) and n-hexane (HX).

When we determine the molar enthalpy of a mixture ($\hat{H}_i$, *kJ/kgmol*), we can arbitrarily pick a reference state for each component (T_j° & P_j°) and assign zero to the molar enthalpy of the pure component at that reference state ($\hat{H}_j^\circ = 0$). Why can we do this? Let's look at the following derivation for the answer.

Eqn #	Derivation	Comments
1	$\dot{n}_1\hat{H}_1 + \dot{n}_2\hat{H}_2 - \dot{n}_3\hat{H}_3 = 0$	start with the energy balance
2	$\hat{H}_1 = x_{1,PT}\hat{H}_{PT} + x_{1,HX}\hat{H}_{HX} + \Delta\hat{H}_{mix}$	$\hat{H}_1 = hmix\left[T_1, P_1, \overline{X}_1\right]$
	Multiplying Eq. 2 with $\dot{n}_1$, gives:	
3	$\dot{n}_1\hat{H}_1 = \dot{n}_{1,PT}\hat{H}_{PT} + \dot{n}_{1,HX}\hat{H}_{HX}$ ideal solution	$\dot{n}_1\hat{H}_1 = hmix\left[T_1, P_1, \dot{n}_{1,j}'s\right]$
	Molar enthalpy of pure n-pentane in Eq. 3 is calculated by:	
4	$\hat{H}_{PT} = \underbrace{\hat{H}_{PT}^\circ\left[T_{PT}^\circ, P_{PT}^\circ, Ph_{PT}^\circ\right]}_{\text{term is set arbitrarily to zero for pure n-PT}} + \underbrace{\Delta\hat{H}_{PT}\left[T_1, P_1, Ph_1 \Leftarrow T_{PT}^\circ, P_{PT}^\circ, Ph_{PT}^\circ\right]}_{\text{term is the enthalpy change to go from pure n-PT reference state to mixture state}}$	units of kJ/kgmol
	Simplifying the notation in Eq. 4 gives:	
5	$\hat{H}_{PT} = \hat{H}_{PT}^\circ + \Delta\hat{H}_{PT}\left[T_1, P_1\right]$	molar enthalpy for pure n-PT
	Similarly, we can find the molar enthalpy of pure n-hexane by:	
6	$\hat{H}_{HX} = \hat{H}_{HX}^\circ + \Delta\hat{H}_{HX}\left[T_1, P_1\right]$	molar enthalpy for pure n-HX
	Substituting Eqs. 5 and 6 into Eq. 3 gives:	
7	$\dot{n}_1\hat{H}_1 = \dot{n}_{1,PT}\left\{\hat{H}_{PT}^\circ + \Delta\hat{H}_{PT}\left[T_1, P_1\right]\right\} + \dot{n}_{1,HX}\left\{\hat{H}_{HX}^\circ + \Delta\hat{H}_{HX}\left[T_1, P_1\right]\right\}$	$\dot{n}_1\hat{H}_1 = hmix\left[T_1, P_1, \dot{n}_{1,j}'s\right]$ *kJ / h*
	Applying the same procedure used in Eqs. 2 thru 7, the energy contents of Streams 2 and 3 are:	
8	$\dot{n}_2\hat{H}_2 = \dot{n}_{2,PT}\left\{\hat{H}_{PT}^\circ + \Delta\hat{H}_{PT}\left[T_2, P_2\right]\right\} + \dot{n}_{2,HX}\left\{\hat{H}_{HX}^\circ + \Delta\hat{H}_{HX}\left[T_2, P_2\right]\right\}$	$\dot{n}_2\hat{H}_2 = hmix\left[T_2, P_2, \dot{n}_{2,j}'s\right]$ *kJ / h*
9	$\dot{n}_3\hat{H}_3 = \dot{n}_{3,PT}\left\{\hat{H}_{PT}^\circ + \Delta\hat{H}_{PT}\left[T_3, P_3\right]\right\} + \dot{n}_{3,HX}\left\{\hat{H}_{HX}^\circ + \Delta\hat{H}_{HX}\left[T_3, P_3\right]\right\}$	$\dot{n}_3\hat{H}_3 = hmix\left[T_3, P_3, \dot{n}_{3,j}'s\right]$ *kJ / h*
	where $\hat{H}_{PT}^\circ$ in Eqs. 7, 8, and 9 is at the reference state of T_{PT}° and P_{PT}° for n-pentane.	
	where $\hat{H}_{HX}^\circ$ in Eqs. 7, 8, and 9 is at the reference state of T_{HX}° and P_{HX}° for n-hexane.	
	Substituting Eqs. 7, 8, and 9 into the energy balance of Eq. 1 and factoring the reference enthalpy terms gives:	
10	$\boxed{\left\{\dot{n}_{1,PT} + \dot{n}_{2,PT} - \dot{n}_{3,PT}\right\}} \cdot \hat{H}_{PT}^\circ + \boxed{\left\{\dot{n}_{1,HX} + \dot{n}_{2,HX} - \dot{n}_{3,HX}\right\}} \cdot \hat{H}_{HX}^\circ +$	component reference states
	$\dot{n}_{1,PT} \cdot \Delta\hat{H}_{PT}\left[T_1, P_1\right] + \dot{n}_{1,HX} \cdot \Delta\hat{H}_{HX}\left[T_1, P_1\right] +$	
	$\dot{n}_{2,PT} \cdot \Delta\hat{H}_{PT}\left[T_2, P_2\right] + \dot{n}_{2,HX} \cdot \Delta\hat{H}_{HX}\left[T_2, P_2\right] -$	
	$\dot{n}_{3,PT} \cdot \Delta\hat{H}_{PT}\left[T_3, P_3\right] - \dot{n}_{3,HX} \cdot \Delta\hat{H}_{HX}\left[T_3, P_3\right] = 0$	energy balance equation

Energy Balance Introduction

5 of 5

Arbitrary Component Reference States, Cont'd (no reactions)

Eqn #	Derivation	Comments
	Remember that the two component material balances are:	
11	$\dot{n}_{1,PT} + \dot{n}_{2,PT} - \dot{n}_{3,PT} = 0$	for n-pentane
12	$\dot{n}_{1,HX} + \dot{n}_{2,HX} - \dot{n}_{3,HX} = 0$	for n-hexane
	Substituting Eqs. 11 and 12 into the energy balance of Eq. 10 gives:	
13	$\{\ zero\ \}\cdot\hat{H}^\circ_{PT} + \{\ zero\ \}\cdot\hat{H}^\circ_{HX} +$	Each $\hat{H}^\circ_j$ is multiplied by 0
	$\dot{n}_{1,PT}\cdot\Delta\hat{H}_{PT}[T_1,P_1] + \dot{n}_{1,HX}\cdot\Delta\hat{H}_{HX}[T_1,P_1] +$	
	$\dot{n}_{2,PT}\cdot\Delta\hat{H}_{PT}[T_2,P_2] + \dot{n}_{2,HX}\cdot\Delta\hat{H}_{HX}[T_2,P_2] -$	
	$\dot{n}_{3,PT}\cdot\Delta\hat{H}_{PT}[T_3,P_3] - \dot{n}_{3,HX}\cdot\Delta\hat{H}_{HX}[T_3,P_3] = 0$	energy balance equation

Conclusions

In the energy balance of Eq. 13, each component reference enthalpy of $\hat{H}^\circ_j$ is multiplied by its component balance. Thus an $\hat{H}^\circ_j$ is always multiplied by zero. Because of this fact, we can arbitrarily pick a reference temperature (T°_j) and pressure (P°_j) for a component and assign any value to its reference enthalpy ($\hat{H}^\circ_j$). For convenience, we usually assign zero to a component reference enthalpy, $\hat{H}^\circ_j = 0$.

The reference temperature (T°_j) and pressure (P°_j) for each component does not have to be the same; they all could be different. However, once you pick a reference state for a component, you must use that component reference state in any enthalpy mixture (*hmix*) calculations.

In the energy balance, the enthalpy changes ($\Delta\hat{H}_j{}'s$) are calculated from the reference state of the components to the state of the mixtures. In Eq. 13, they are expressed fully as follows:

Form		
1.PT	$\Delta\hat{H}_{PT}\left\|T_1,P_1,Ph_1 \Leftarrow T^\circ_{PT},P^\circ_{PT},Ph^\circ_{PT}\right\|$	units of kJ/kgmol
1.HX	$\Delta\hat{H}_{HX}\left\|T_1,P_1,Ph_1 \Leftarrow T^\circ_{HX},P^\circ_{HX},Ph^\circ_{HX}\right\|$	units of kJ/kgmol
2.PT	$\Delta\hat{H}_{PT}\left\|T_2,P_2,Ph_2 \Leftarrow T^\circ_{PT},P^\circ_{PT},Ph^\circ_{PT}\right\|$	units of kJ/kgmol
2.HX	$\Delta\hat{H}_{HX}\left\|T_2,P_2,Ph_2 \Leftarrow T^\circ_{HX},P^\circ_{HX},Ph^\circ_{HX}\right\|$	units of kJ/kgmol
3.PT	$\Delta\hat{H}_{PT}\left\|T_3,P_3,Ph_3 \Leftarrow T^\circ_{PT},P^\circ_{PT},Ph^\circ_{PT}\right\|$	units of kJ/kgmol
3.HX	$\Delta\hat{H}_{HX}\left\|T_3,P_3,Ph_3 \Leftarrow T^\circ_{HX},P^\circ_{HX},Ph^\circ_{HX}\right\|$	units of kJ/kgmol

Each of these functional forms for a pure component can be represented by a graph, a table, a set of equations, or a computer program.

A misconception is perpetuated about the reference molar enthalpy of a compound in some textbooks. They claim that it is arbitrary because the reference enthalpies of a compound cancel each other out when substituted into the energy balance. Why does this misconception exists? Click here to learn the probable cause of this misconception.

larger

Simultaneous Material and Energy Balance Example

1 of 5

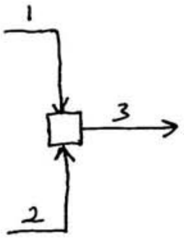
Problem Statement

Similar to the "Continuous Mixing Example" on Page 7-18, except in this problem you are solving for n_2 and n_3 given T_3, instead of solving for T_3 and n_3 given n_2.

A process stream of n-pentane and n-hexane at 20°C and 1 atm is mixed isobarically with a second process stream of n-pentane and n-hexane at 40°C to form a third process stream at 31°C. The first stream flows at 45 gmol/h and contains 40 mole percent of n-pentane. The second stream contains 40 mole percent of n-hexane. What are the flow rates of the second and third streams? Draw and label your diagram, list your assumptions and develop your math model and algorithm. Complete the numerical solution using E-Z Solve.

Diagram

$T_1 = 20°C$
$P_1 = 1$ atm
$Ph_1 = 1.19$
$\dot{n}_1 = 45$ gmol/h
$x_{1,PT} = 0.40$
$x_{1,HX} = 0.60$



$T_3 = 31°C$
$P_3 = 1$ atm
$Ph_3 = 1.19$
$\boxed{\dot{n}_3 = ?}$
$x_{3,PT} = ?$
$x_{3,HX} = ?$

$T_2 = 40°C$
$P_2 = 1$ atm
$Ph_2 = 1.19$
$\boxed{\dot{n}_2 = ?}$
$x_{2,PT} = 0.60$
$x_{2,HX} = 0.40$

Assumptions

1. continuous process
2. steady state
3. no reactions
4. neglect ΔKE + ΔPE
5. adiabatic
6. no shaft work

Math Model

see next page

Math Algorithm

see next page

Simultaneous Mat'l and Energy Balance Example

Math Model

Exact same math model used in the "Continuous Mixing Example" on Page 7-18.

① Total: $\underline{\dot{n}}_1 + \dot{n}_2 - \dot{n}_3 = 0$

② pentane: $0.40\underline{\dot{n}}_1 + 0.60\dot{n}_2 - \dot{n}_{3,PT} = 0$

③ hexane: $0.60\underline{\dot{n}}_1 + 0.40\dot{n}_2 - \dot{n}_{3,HX} = 0$

④ $\dot{n}_{3,PT} = \dot{n}_3 x_{3,PT}$

⑤ $\dot{n}_{3,HX} = \dot{n}_3 x_{3,HX}$

⑥ $\dot{n}_1\hat{H}_1 + \dot{n}_2\hat{H}_2 - \dot{n}_3\hat{H}_3 = 0$

Equation 7.5d-a with no heat-of-reaction, heat, and shaft work terms

⑦ $\hat{H}_1 = hmix[\underline{T}_1, \underline{P}_1, \underline{\bar{X}}_1]$

⑧ $\hat{H}_2 = hmix[\underline{T}_2, \underline{P}_2, \underline{\bar{X}}_2]$

⑨ $\hat{H}_3 = hmix[T_3, P_3, \bar{X}_3]$

#vars = 20
#eqns = −9
dof = 11

Math Algorithm

$[\dot{n}_2, \dot{n}_3] \leftarrow f[\Psi_1, T_2, P_2, \bar{X}_2, T_3, P_3]$

$\boxed{\Psi_1 \equiv T_1, P_1, \dot{n}_1, \bar{X}_1}$

⑦ 1. $\hat{H}_1 \leftarrow hmix[T_1, P_1, \bar{X}_1]$

⑧ 2. $\hat{H}_2 \leftarrow hmix[T_2, P_2, \bar{X}_2]$

3. NSolve $\dot{n}_2, \dot{n}_3, \dot{n}_{3,PT}, \dot{n}_{3,HX}, x_{3,PT}, x_{3,HX}, \hat{H}_3$ in

① $\dot{n}_1 + \dot{n}_2 - \dot{n}_3 = 0$

② $0.40\dot{n}_1 + 0.60\dot{n}_2 - \dot{n}_{3,PT} = 0$

③ $0.60\dot{n}_1 + 0.40\dot{n}_2 - \dot{n}_{3,HX} = 0$

④ $\dot{n}_{3,PT} = \dot{n}_3 x_{3,PT}$

⑤ $\dot{n}_{3,HX} = \dot{n}_3 x_{3,HX}$

⑥ $\dot{n}_1\hat{H}_1 + \dot{n}_2\hat{H}_2 - \dot{n}_3\hat{H}_3 = 0$

⑨ $\hat{H}_3 = hmix[T_3, P_3, \bar{X}_3]$

END

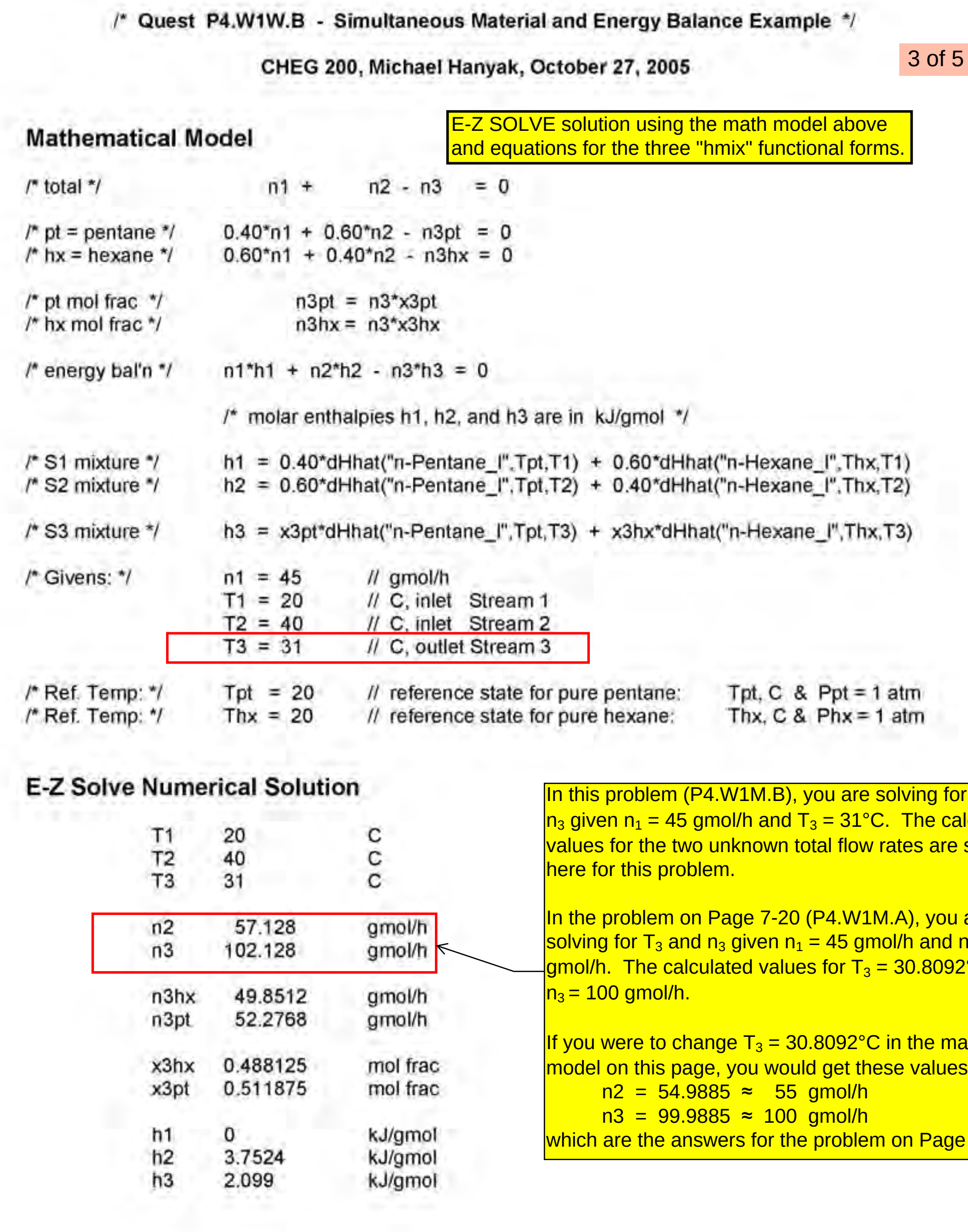
Equations 1, 2, and 3 are linear; each term in each equation has one unknown variable raised to the 1 power.

Equations 4, 5, and 6 are nonlinear; at least one term in each equation has an unknown variable times an unknown variable.

Equation 9 is nonlinear because of the functional form "hmix[...]".

In a NSOLVE construct, at least one equation must be nonlinear. If all equations were linear, than a linear SOLVE construct would be used.

Select the "click here" web link at the bottom of this page to view an Excel "EZ Setup" math model that replaces the "E-Z Solve" model given below.



/* Quest P4.W1W.B - Simultaneous Material and Energy Balance Example */

CHEG 200, Michael Hanyak, October 27, 2005

3 of 5

Mathematical Model

E-Z SOLVE solution using the math model above and equations for the three "hmix" functional forms.

```
/* total */              n1 +      n2 - n3    = 0

/* pt = pentane */   0.40*n1 + 0.60*n2 - n3pt  = 0
/* hx = hexane */    0.60*n1 + 0.40*n2 - n3hx  = 0

/* pt mol frac  */          n3pt  = n3*x3pt
/* hx mol frac */           n3hx =  n3*x3hx

/* energy bal'n */   n1*h1  + n2*h2 - n3*h3 = 0

                     /*  molar enthalpies h1, h2, and h3 are in  kJ/gmol  */

/* S1 mixture */     h1  = 0.40*dHhat("n-Pentane_l",Tpt,T1)  + 0.60*dHhat("n-Hexane_l",Thx,T1)
/* S2 mixture */     h2  = 0.60*dHhat("n-Pentane_l",Tpt,T2)  + 0.40*dHhat("n-Hexane_l",Thx,T2)

/* S3 mixture */     h3  = x3pt*dHhat("n-Pentane_l",Tpt,T3)  + x3hx*dHhat("n-Hexane_l",Thx,T3)

/* Givens: */        n1  = 45        // gmol/h
                     T1  = 20        // C, inlet   Stream 1
                     T2  = 40        // C, inlet   Stream 2
                     T3  = 31        // C, outlet Stream 3

/* Ref. Temp: */     Tpt  = 20       // reference state for pure pentane:     Tpt, C  &  Ppt = 1 atm
/* Ref. Temp: */     Thx  = 20       // reference state for pure hexane:      Thx, C &  Phx = 1 atm
```

E-Z Solve Numerical Solution

```
T1      20          C
T2      40          C
T3      31          C

n2       57.128     gmol/h
n3      102.128     gmol/h

n3hx     49.8512    gmol/h
n3pt     52.2768    gmol/h

x3hx    0.488125    mol frac
x3pt    0.511875    mol frac

h1      0           kJ/gmol
h2      3.7524      kJ/gmol
h3      2.099       kJ/gmol
```

In this problem (P4.W1M.B), you are solving for n_2 and n_3 given n_1 = 45 gmol/h and T_3 = 31°C. The calculated values for the two unknown total flow rates are shown here for this problem.

In the problem on Page 7-20 (P4.W1M.A), you are solving for T_3 and n_3 given n_1 = 45 gmol/h and n_2 = 55 gmol/h. The calculated values for T_3 = 30.8092°C and n_3 = 100 gmol/h.

If you were to change T_3 = 30.8092°C in the math model on this page, you would get these values:

n2 = 54.9885 ≈ 55 gmol/h
n3 = 99.9885 ≈ 100 gmol/h

which are the answers for the problem on Page 7-20.

Click here to view the Excel "EZ Setup" mathematical model in Worksheet "P4.W1M.B".

Simultaneous Material and Energy Balance Example

4 of 5

Modify original problem on Page 7-23 by adding the sentence: "The third stream contains 51 mole percent of n-pentane."

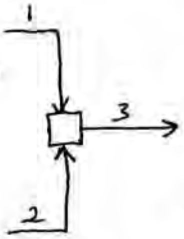
Problem Statement

A process stream of n-pentane and n-hexane at 20°C and 1 atm is mixed isobarically with a second process stream of n-pentane and n-hexane at 40°C to form a third process stream at 31°C. The first stream flows at 45 gmol/h and contains 40 mole percent of n-pentane. The second stream contains 40 mole percent of n-hexane. What are the flow rates of the second and third streams? Draw and label your diagram, list your assumptions and develop your math model and algorithm. Complete the numerical solution using E-Z Solve.

Diagram

$T_1 = 20°C$
$P_1 = 1$ atm
$Ph_1 =$ liq
$\dot{n}_1 = 45$ kgmol/h
$X_{1,PT} = 0.40$
$X_{1,HX} = 0.60$

$T_2 = 40°C$
$P_2 = 1$ atm
$Ph_2 =$ liq
$\dot{n}_2 = ?$
$X_{2,PT} = 0.60$
$X_{2,HX} = 0.40$



$T_3 = 31°C$
$P_3 = 1$ atm
$Ph_3 =$ liq
$\dot{n}_3 = ?$
$X_{3,PT} = 0.51$
$X_{3,HX} = 0.49$

Assumptions

1. continuous process
2. steady state
3. no reactions
4. neglect ΔKE + ΔPE
5. adiabatic
6. no shaft work

Math Model

see next page for two possible math models.

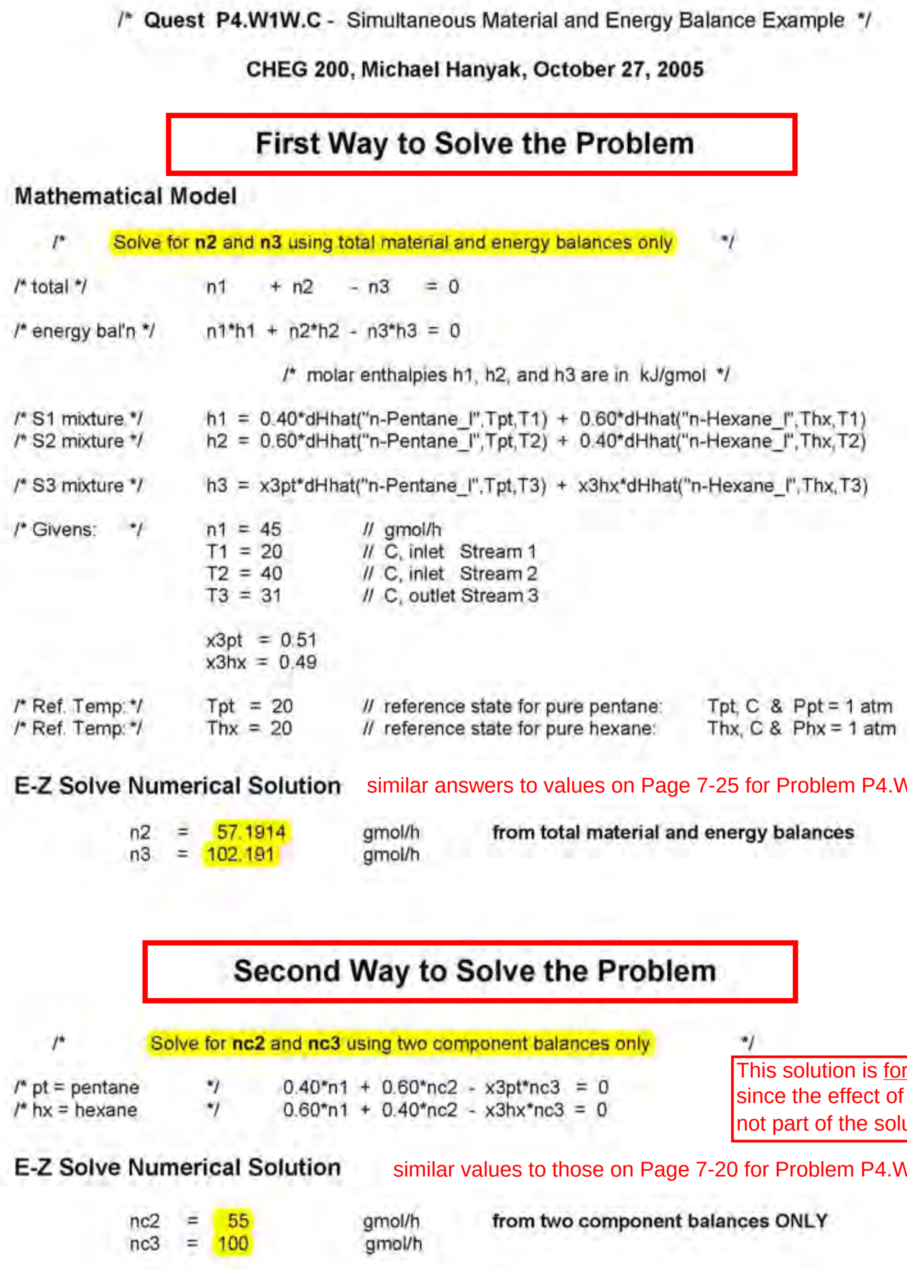
An example of a problem being over specified; that is, too much information is given. In this case, the composition of Stream 3.

With this over specification, you could solve for the unknown flows in Streams 2 and 3, one of two ways:

1. using the total material and energy balances, or
2. using the two component material balances.

The E-Z Solve model on the next page presents these two solutions.

Select the "click here" web link at the bottom of this page to view an Excel "EZ Setup" math model that replaces the "E-Z Solve" model given below.



/* **Quest P4.W1W.C** - Simultaneous Material and Energy Balance Example */

CHEG 200, Michael Hanyak, October 27, 2005

5 of 5

First Way to Solve the Problem

Mathematical Model

```
/*      Solve for n2 and n3 using total material and energy balances only      */

/* total */             n1    + n2    - n3    = 0

/* energy bal'n */      n1*h1  +  n2*h2  -  n3*h3  =  0

                            /* molar enthalpies h1, h2, and h3 are in  kJ/gmol */

/* S1 mixture */        h1  =  0.40*dHhat("n-Pentane_l",Tpt,T1)  +  0.60*dHhat("n-Hexane_l",Thx,T1)
/* S2 mixture */        h2  =  0.60*dHhat("n-Pentane_l",Tpt,T2)  +  0.40*dHhat("n-Hexane_l",Thx,T2)

/* S3 mixture */        h3  =  x3pt*dHhat("n-Pentane_l",Tpt,T3)  +  x3hx*dHhat("n-Hexane_l",Thx,T3)

/* Givens:    */        n1  =  45          // gmol/h
                        T1  =  20          // C, inlet   Stream 1
                        T2  =  40          // C, inlet   Stream 2
                        T3  =  31          // C, outlet Stream 3

                        x3pt  =  0.51
                        x3hx  =  0.49

/* Ref. Temp: */        Tpt  =  20         // reference state for pure pentane:      Tpt, C  &  Ppt = 1 atm
/* Ref. Temp: */        Thx  =  20         // reference state for pure hexane:       Thx, C &  Phx = 1 atm
```

E-Z Solve Numerical Solution similar answers to values on Page 7-25 for Problem P4.W1W.B

n2	=	57.1914	gmol/h	**from total material and energy balances**
n3	=	102.191	gmol/h	

Second Way to Solve the Problem

```
/*          Solve for nc2 and nc3 using two component balances only          */

/* pt = pentane     */      0.40*n1  +  0.60*nc2  -  x3pt*nc3   =  0
/* hx = hexane      */      0.60*n1  +  0.40*nc2  -  x3hx*nc3   =  0
```

This solution is fortuitous since the effect of T_3 is not part of the solution.

E-Z Solve Numerical Solution similar values to those on Page 7-20 for Problem P4.W1W.A

nc2	=	55	gmol/h	**from two component balances ONLY**
nc3	=	100	gmol/h	

Click here to view the Excel "EZ Setup" mathematical model in Worksheet "P4.W1M.C".

larger

CM 200
Hanyak

Energy Balance
Continuous Process

10/30/90
①

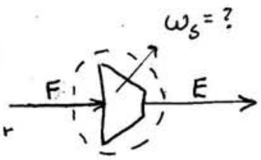
Similar to Example 7.5-3 in F&R, 3rd Ed.

Example 7.5-2 : {in F&R, 2nd Ed.}

Steam enters a turbine at 10 bars, 190°C of superheat, and 2000 kg/h. It exits the turbine, which operates adiabatically, as a saturated vapor at 1 bar. Determine the amount of shaft work produced by the turbine in kW. Also, what is the exit temperature of the steam in °C?

Diagram

T_F = ?
P_F = 10 bars
Ph_F = steam
$\dot{m}_F$ = 2000 kg/hr
$w_{F,WA}$ = 1.0



T_E = ?
P_E = 1 bar
Ph_E = sat'd vap
$\dot{m}_E$ = ?
$w_{E,WA}$ = 1.0

Given: DSH_F = 190°C   Find: $\dot{W}_s$ in kW

Assumptions

1. steady state
2. no rxn
3. neglect ΔE_K + ΔE_P
4. adiabatic
5. continuous process

Model

follow Blue Crib for the heat-of-reaction method

① $\dot{m}_F - \dot{m}_E = 0$ {total balance}

{not indep} $\dot{m}_F - \dot{m}_E = 0$ {component balance}

② $\dot{m}_F \hat{H}_F - \dot{m}_E \hat{H}_E - \dot{W}_s = 0$ {energy balance}

Equation 7.5d-a with no heat-of-reaction and no heat terms

③ $\hat{H}_F = \hat{H}[T_F, P_F, \text{pure } H_2O]$

④ $\hat{H}_E = \hat{H}[T_E, P_E, \text{sat'd steam}]$

⑤ $T_F = T_{dp} + DSH_F$

⑥ $T_{dp} = TSAT[P_F, \text{sat'd vapor}, \text{pure water}]$

⑦ $T_E = TSAT[P_E, \text{sat'd vapor}, \text{pure water}]$

# vars = 11
# eqns = 7
D.O.F. = 4

em 200
Hanyak

Energy Balance
Continuous Process

10/30/90
②

Algorithm

$$[\dot{W}_s, T_E] = f[P_F, \dot{m}_F, DSH_F; P_E]$$

1. $\dot{m}_E \leftarrow \dot{m}_F$ = 2000 kg/hr

2. $T_{dp} \leftarrow$ TSAT [10 bars, sat'd vap, pure water] = 180 °C (Table B.6)

3. $T_F \leftarrow T_{dp} + DSH_F$ = 180 + 190 = 370 °C

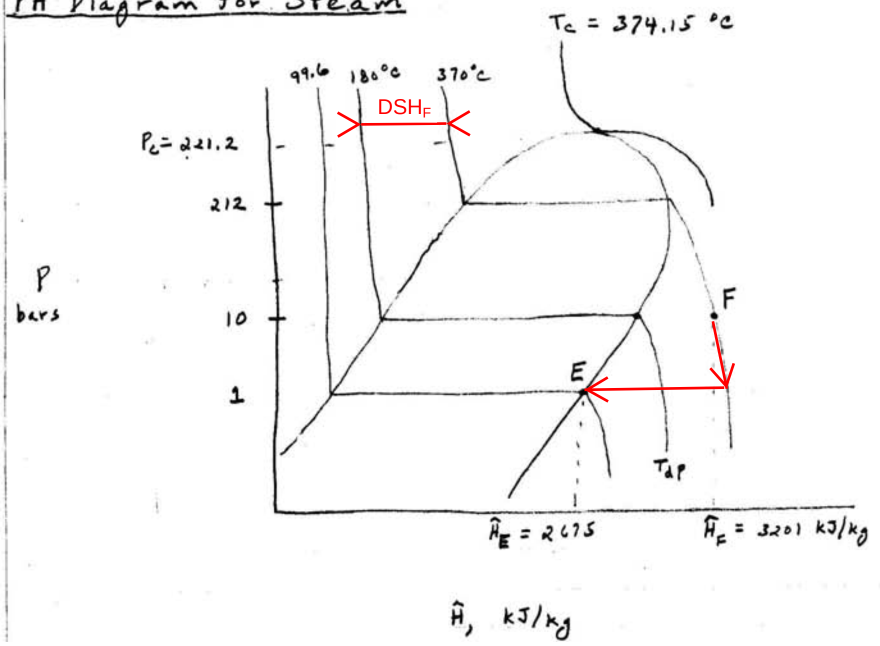
4. $T_E \leftarrow$ TSAT [1 bar, sat'd vapor, pure water] = 99.6 °C (Table B.6)

5. $\hat{H}_F \leftarrow \hat{H}$ [370 °C, 10 bars, pure H_2O] = 3201 kJ/kg (Table B.7, interpolate)

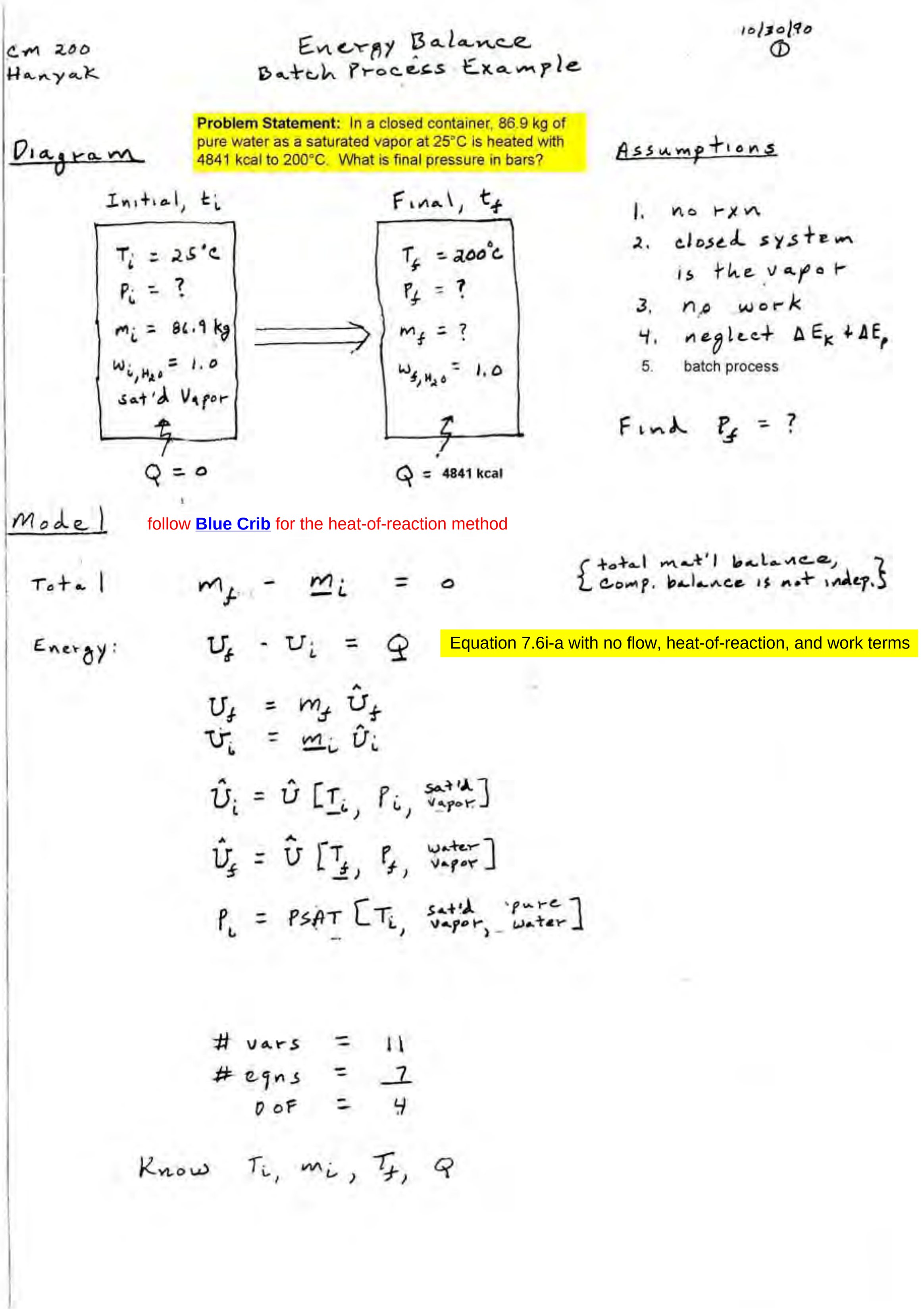
6. $\hat{H}_E \leftarrow \hat{H}$ [99.6 °C, 1 bar, sat'd steam] = 2675 kJ/kg (Table B.6)

7. $\dot{\omega}_s \leftarrow m_F(\hat{H}_F - \hat{H}_E)$ = 2000(3201 - 2675) < 1 h / 3600 s > = 292 kJ/s = $\boxed{292 \text{ kW}}$

PH Diagram for Steam



larger



CM 200
Hanyak

Energy Balance
Batch Process Example

10/30/90
①

Problem Statement: In a closed container, 86.9 kg of pure water as a saturated vapor at 25°C is heated with 4841 kcal to 200°C. What is final pressure in bars?

Diagram

Initial, t_i

$T_i = 25°C$
$P_i = ?$
$m_i = 86.9$ kg
$w_{i,H_2O} = 1.0$
sat'd Vapor

$Q = 0$

Final, t_f

$T_f = 200°C$
$P_f = ?$
$m_f = ?$
$w_{f,H_2O} = 1.0$

Q = 4841 kcal

Assumptions

1. no rxn
2. closed system is the vapor
3. no work
4. neglect $\Delta E_K + \Delta E_p$
5. batch process

Find $P_f = ?$

Model

follow **Blue Crib** for the heat-of-reaction method

Total $m_f - \underline{m_i} = 0$ {total mat'l balance, comp. balance is not indep.}

Energy: $U_f - U_i = Q$ Equation 7.6i-a with no flow, heat-of-reaction, and work terms

$U_f = m_f \hat{U}_f$
$U_i = \underline{m_i} \hat{U}_i$

$\hat{U}_i = \hat{U}[\underline{T_i}, P_i, \text{sat'd vapor}]$

$\hat{U}_f = \hat{U}[\underline{T_f}, P_f, \text{water vapor}]$

$P_i = PSAT[\underline{T_i}, \text{sat'd vapor}, \text{pure water}]$

\# vars = 11
\# eqns = 7
DOF = 4

Know T_i, m_i, T_f, Q

CM 200
Hanyak

Energy Balance
Batch Process Example

10/30/90
②

Algorithm

```
$[P_f] = f[T_i, m_i, T_f, Q]$

1.  $m_f \leftarrow m_i$                                                    $= 86.9$ kg
2.  $P_i \leftarrow$ PSAT[25°C, sat'd vapor, pure water]                    $= 0.317$ bars {Table B.5}
3.  $\hat{U}_i \leftarrow \hat{U}$[25°C, 0.317 bars, sat'd vap]             $= 2409.9$ kJ/kg {Table B.5}
4.  $U_i \leftarrow m_i \hat{U}_i = 86.9\,kg(2409.9\,kJ/kg)$                 $= 209,420$ kJ
5.  $U_f \leftarrow Q + U_i = (4841\,kcal)\langle \frac{kJ}{0.23901\,kcal} \rangle + 209,420$ kJ
                                                                            $= 229,674$ kJ
6.  $\hat{U}_f \leftarrow U_f / m_f = 229,674\,kJ/86.9\,kg$                  $= 2643.$ kJ/kg
7.  ITERATE ON $P_f$ IN
        $f(P_f) := \hat{U}_f - \hat{U}$[200°C, $P_f$, water vapor]
    UNTIL $f(P_f)$ IS 0.0
```

If function $\hat{U}$ is table or graph, iteration is not necessary

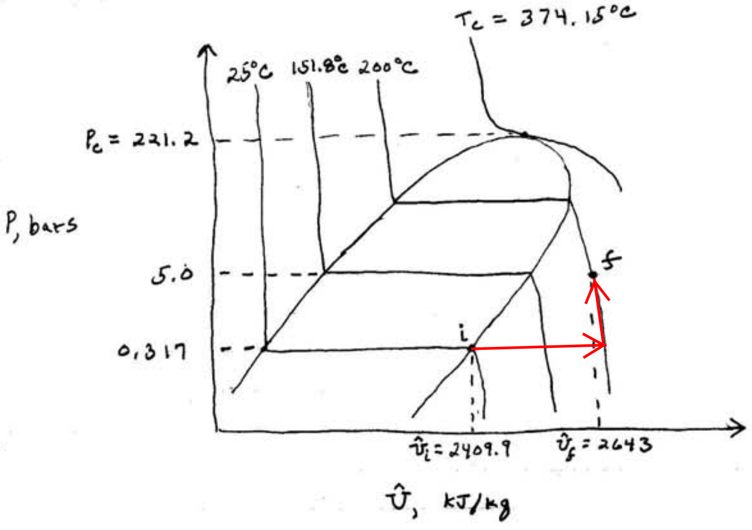
$P_f = 5$ bars from Table B.7

When a table or graph is used for the internal energy function, the ITERATE-UNTIL construct could be replaced with:

P_f = press[200°C, U_f=2643 kJ/kg, water vapor]

where U_f has a cap over it.

PU Diagram for Steam



larger

cm 200
Hanyak

Simultaneous Mat'l & Energy
Example 7.6-3

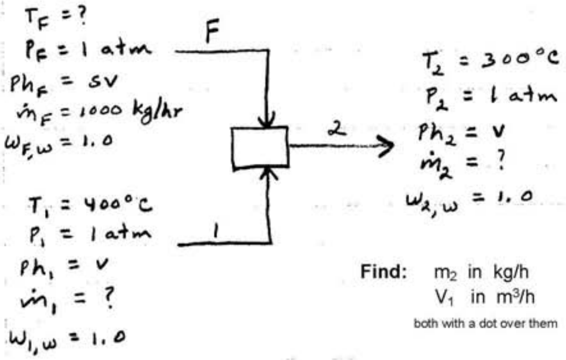
11/5/90
1 of 1

Similar to Example 7.6-3 in F&R, 3rd Ed.

Problem Statement

A process feed stream of saturated steam at 1 atm and 1000 kg/h is mixed with a second process stream of superheated steam at 400°C and 1 atm to form a third process stream of superheated steam at 300°C and 1 atm. Develop the mathematical model and mathematical algorithm to determine the flow rate of the third stream and the required volumetric flow rate of the second stream.

Diagram



Find: $\dot{m}_2$ in kg/h
$\dot{V}_1$ in m³/h

both with a dot over them

Assumptions

1. steady state
2. no rxn
3. no W_s, $Q = 0$
4. neglect ΔE_K & ΔE_P
5. continuous process

Model

follow **Blue Crib** for the heat-of-reaction method

$$\underline{\dot{m}_F} + \dot{m}_1 - \dot{m}_2 = 0$$

$$\dot{m}_F \hat{H}_F + \dot{m}_1 \hat{H}_1 - \dot{m}_2 \hat{H}_2 = 0$$

Equation 7.5d-a with no heat-of-reaction terms

$$\hat{H}_F = \hat{H}\,[\underline{P_F}, \underline{Ph_F}, \underline{\vec{\omega}_F}]$$

$$\hat{H}_1 = \hat{H}\,[\underline{T_1}, \underline{P_1}, \underline{\vec{\omega}_1}]$$

$$\hat{H}_2 = \hat{H}\,[\underline{T_2}, \underline{P_2}, \underline{\vec{\omega}_2}]$$

$$\dot{V}_1 = \dot{m}_1 \hat{V}_1$$

$$\hat{V}_1 = \hat{V}\,[\underline{T_1}, \underline{P_1}, \underline{\vec{\omega}_1}]$$

\# vars = 17
\# eqns = 7
DOF = 10

Algorithm

$$[\dot{m}_2, \dot{V}_1] = f\,[P_F, Ph_F, \dot{m}_F, \vec{\omega}_F, T_1, P_1, \vec{\omega}_1, T_2, P_2, \vec{\omega}_2]$$

1. $\hat{H}_F \leftarrow \hat{H}\,[P_F, Ph_F, \vec{\omega}_F]$
2. $\hat{H}_1 \leftarrow \hat{H}\,[T_1, P_1, \vec{\omega}_1]$
3. $\hat{H}_2 \leftarrow \hat{H}\,[T_2, P_2, \vec{\omega}_2]$
4. $\hat{V}_1 \leftarrow \hat{V}\,[T_1, P_1, \vec{\omega}_1]$
5. SOLVE $\dot{m}_1$, $\dot{m}_2$ IN

$$\dot{m}_1 - \dot{m}_2 = -\dot{m}_F$$
$$\hat{H}_1 \dot{m}_1 - \hat{H}_2 \dot{m}_2 = -\dot{m}_F \hat{H}_F$$

END

6. $\dot{V}_1 \leftarrow \dot{m}_1 \hat{V}_1$

Click here to view an Excel "**EZ Setup**"/**Solve** solution.

larger

ChE 200
Hanyak

Example 8.3-5
F&R, 3rd Ed.

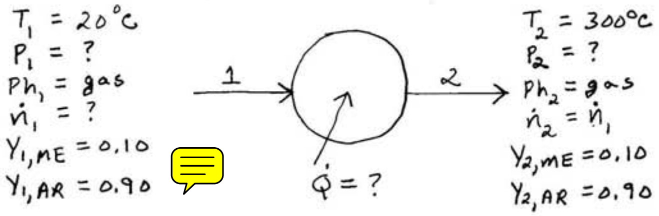
11/11/91
1 of 4

Problem

Similar to Example 8.3-5 in F&R, 3rd Ed.

A process stream contains 10 vol% methane and 90 vol% air is flowing at a rate of 2.00 x 10^3 liters (STP)/min. How many kilowatts of energy are required to increase the temperature of this process stream from 20 to 300°C?

Diagram



Assumptions

1. continuous process
2. steady state
3. no rxn
4. neglect ΔKE & ΔPE
5. no shaft work
6. $P_1 = P_2 = 1$ atm
7. $T_S = 273$ K and $P_S = 1$ atm

Given: $\dot{V}_{1,STP} = 2.00 \times 10^3$ L/min

Find: $\dot{Q}$ in kW

Phase Determination

CH_4 and air are gases at 20°C & 1 atm

see sketched PH diagrams on second page

Math Model

follow **Blue Crib** for the heat-of-reaction method

① $P_S \dot{V}_{1,STP} = \dot{n}_1 R T_S$ F&R, 3rd Ed., p. 194

② $\dot{n}_1 \hat{H}_1 - \dot{n}_1 \hat{H}_2 + \dot{Q} = 0$ Eq. 7.5d-a with no heat-of-reaction

③ $\hat{H}_1 = HMIX[T_1, P_1, \bar{X}_1]$

④ $\hat{H}_2 = HMIX[T_2, P_2, \bar{X}_2]$

Degrees of Freedom

\# vars = 13
\# eqns = 4
DOF = 9

Know: $T_1, P_1, \bar{X}_1, \dot{V}_{1,STP}$
$T_2, P_2, \bar{X}_2, T_S, P_S$

Math Algorithm

$[Q] = f[9 \text{ known variables}]$

1. $\dot{n}_1 \leftarrow \dfrac{P_S \dot{V}_{1,STP}}{R T_S}$
2. $\hat{H}_1 \leftarrow HMIX[T_1, P_1, \bar{X}_1]$
3. $\hat{H}_2 \leftarrow HMIX[T_2, P_2, \bar{X}_2]$
4. $\dot{Q} \leftarrow \dot{n}_1 (\hat{H}_2 - \hat{H}_1)$

Solution

Basis: $\dot{V}_{1,STP} = 2.00 \times 10^3$ L/min

1. $= \left(\dfrac{1 \text{ atm}}{273 K}\right)\left(\dfrac{2.00 \times 10^3 L}{min}\right)\left(\dfrac{g\text{-}mol \; K}{0.08206 \; L \cdot atm}\right)$
$= 89.2762$ mol/min

2. $= -129.6$ J/mol {see page 2}

3. $= 8560$ J/mol {see page 3}

4. $= 89.3 \dfrac{mol}{min} (8560 + 129.6) \dfrac{J}{mol} \left\langle \dfrac{1 kW}{1000 J/s} \right\rangle \left\langle \dfrac{min}{60 s} \right\rangle$
$= 12.9333$ kW $= \boxed{12.9 \text{ kW}}$

CM 200 | Example 8.3-5 | 11/11/91
Hanyak | F&R, 3rd Ed. | 2 of 4

HMIX[T_1, P_1, $\bar{X}_1$] follow **Blue Crib** for the heat-of-reaction method

$\hat{H}_1$ Assumptions

1. ideal solution
2. Ref. state for CH_4 is 20°C and 1 atm, conditions of Stream 1.
3. Ref state for air is 25°C and 1 atm, that of Table B.8.

Eq. 7.7
$$\hat{H}_1 = 0.10\,\hat{H}_{ME} + 0.90\,\hat{H}_{AR} + \cancelto{0}{\Delta\hat{H}_{MIX}}$$
$$= 0.10\,(0.0\ \text{J/mol}) + 0.90\,(-144.0\ \text{J/mol})$$
$$= \boxed{-129.6\ \text{J/mol}}\ \text{for Mixture 1.}$$

Eq. 7.8
$$\hat{H}_{ME} = \cancelto{0}{\hat{H}^{o}_{ME}} + \Delta\hat{H}_{ME}[20^\circ C,\ P_1,\ gas \leftarrow 20^\circ C,\ 1\ atm,\ gas]$$
$$= \int_{20^\circ C}^{20^\circ C} \cancelto{0}{C^{G}_{P,ME}}\,dT + \int_{1\ atm}^{1\ atm} [\hat{V} \cancelto{0}{-T\left(\frac{\partial \hat{V}}{\partial T}\right)_P}]\,dP$$

{Sensible heat change of CH_4 gas, PH Diag., p. 2}

$$= \boxed{0.0\ \text{J/mol}}\ \text{for pure } CH_4.$$

Eq. 7.8
$$\hat{H}_{AR} = \cancelto{0}{\hat{H}^{o}_{AR}} + \Delta\hat{H}_{AR}[20^\circ C,\ P_1,\ gas \leftarrow 25^\circ C,\ 1\ atm,\ gas]$$
$$= \int_{25^\circ C}^{20^\circ C} C^{G}_{P,Air}\,dT + \int_{1\ atm}^{1\ atm} [\hat{V} \cancelto{0}{-T\left(\frac{\partial \hat{V}}{\partial T}\right)_P}]\,dP$$

{Sensible heat change of air gas, PH Diag., p. 2}

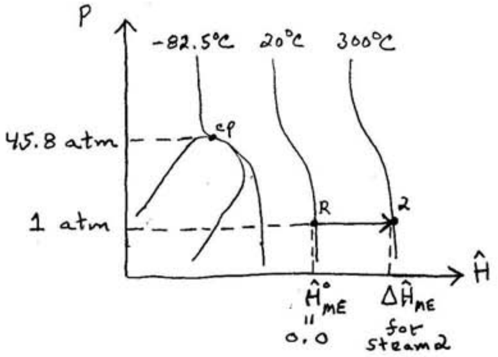
where $\int_{25^\circ C}^{20^\circ C} C^{G}_{P,Air}\,dT = \Delta\hat{H}_{air}[20^\circ C]$ in kJ/mol

← given by Table B.8 in F&R, 3rd Ed.

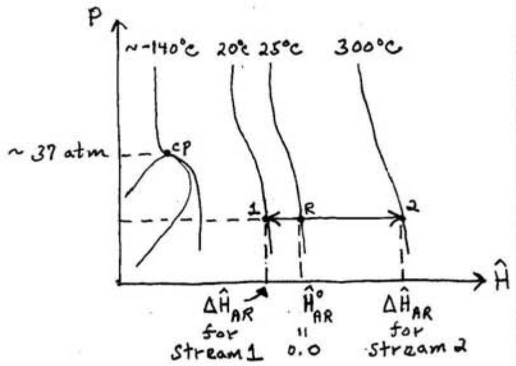
Interpolate for $\Delta\hat{H}_{air}[20^\circ C] = (-0.72) + \frac{(20^\circ C - 0^\circ C)}{(25^\circ C - 0^\circ C)}[0 - (-0.72)]$
$= -0.144$ kJ/mol

$$= -0.144\ \text{kJ/mol}\left\langle \frac{1000\ \text{J}}{\text{kJ}} \right\rangle = \boxed{-144.0\ \text{J/mol}}\ \text{for pure Air.}$$

PH Diagram for CH_4



PH Diagram for Air



CM 200 Hanyak	Example 8.3-5 F&R, 3rd Ed.	11/11/91 3 of 4

HMIX $[T_2, P_2, \bar{X}_2]$

follow **Blue Crib** for the heat-of-reaction method

$\hat{H}_2$ Assumptions

1. Ideal solution
2. Same ref. states as used for $\hat{H}_1$.

Eq. 7.7

$$\hat{H}_2 = 0.10\,\hat{H}_{ME} + 0.90\,\hat{H}_{AR} + \cancelto{0}{\Delta\hat{H}_{MIX}}$$

$$= 0.10(12{,}068\ \text{J/mol}) + 0.90(8170\ \text{J/mol})$$

$$= \boxed{8560\ \text{J/mol}}\ \text{for Mixture 2.}$$

Eq. 7.8

$$\hat{H}_{ME} = \cancelto{0}{\hat{H}^{o}_{ME}} + \Delta\hat{H}_{ME}[300^\circ\text{C}, P_2, \text{gas} \leftarrow 20^\circ\text{C}, 1\,\text{atm}, \text{gas}]$$

$$= \int_{20^\circ\text{C}}^{300^\circ\text{C}} C^{G}_{P,ME}\,dT + \int_{1\,\text{atm}}^{1\,\text{atm}} \left[\hat{V} \cancelto{0}{-\,T\left(\frac{\partial\hat{V}}{\partial T}\right)_P}\right] dP \quad \left\{\begin{array}{l}\text{Sensible heat} \\ \text{change of CH}_4 \\ \text{gas, PH Diag., p. 2}\end{array}\right\}$$

where $C^{G}_{P,ME} = 34.31 + 5.469\times10^{-2}T + 0.3661\times10^{-5}T^2 - 11.00\times10^{-9}T^3$

with C_p in J/mol·°C and T in °C, Table B.2 in F&R.

Note Table B.2 is in kJ/mol°C. Multipled by 1000 to get coefficients in J/mol°C

$$= \int_{20^\circ\text{C}}^{300^\circ\text{C}} (34.31 + 5.469\times10^{-2}\,T + 0.3661\times10^{-5}\,T^2 - 11.00\times10^{-9}\,T^3)\,dT$$

$$= 34.31(300-20) + \frac{0.05469}{2}(300^2-20^2) + \frac{0.3661\times10^{-5}}{3}(300^3-20^3) - \frac{11\times10^{-9}}{4}(300^4-20^4)$$

$$= 9607 + 2450 + 33 - 22 = \boxed{12{,}068\ \text{J/mol}}\ \text{for pure CH}_4.$$

Eq. 7.8

$$\hat{H}_{AR} = \cancelto{0}{\hat{H}^{o}_{AR}} + \Delta\hat{H}_{AR}[300^\circ\text{C}, P_2, \text{gas} \leftarrow 25^\circ\text{C}, 1\,\text{atm}, \text{gas}]$$

$$= \int_{25^\circ\text{C}}^{300^\circ\text{C}} C^{G}_{P,AR}\,dT + \int_{1\,\text{atm}}^{1\,\text{atm}} \left[\hat{V} \cancelto{0}{-\,T\left(\frac{\partial\hat{V}}{\partial T}\right)_P}\right] dP \quad \left\{\begin{array}{l}\text{Sensible heat} \\ \text{change of air} \\ \text{gas, PH diag., p. 2}\end{array}\right\}$$

$$= \Delta\hat{H}_{AR}[300^\circ\text{C}] \quad \left\{\begin{array}{l}\Delta\hat{H}\ \text{of air in kJ/mol} \\ \text{Table B.8, F\&R, 3rd Ed.}\end{array}\right\}$$

$$= 8.17\ \text{kJ/mol} \left\langle \frac{1000\ \text{J}}{\text{kJ}} \right\rangle = \boxed{8170\ \text{J/mol}}\ \text{for air.}$$

larger

CM 200 Example 8.4-4 11/15/90
Hanyak F&R, 2nd Ed. 1 of 5

Example 8.4-4

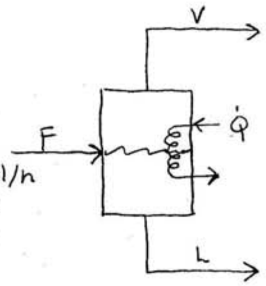
Similar to Example 8.4-4 in F&R, 3rd Ed.

energy balancing with phase changes

A liquid process stream at 10°C contains 50.0 mol% benzene and 50.0 mol% toluene. This liquid mixture enters a process vessel where it is heated to 50°C and 164 mm Hg to form a vapor phase and liquid phase. The liquid product stream leaving the vessel contains 40 mol% benzene, while the vapor product stream leaving the vessel contains 66.3 mol% benzene. How much heat must be transferred to the mixture per mole of feed?

Diagram

$T_F = 10°C$
$P_F = ?$
$Ph_F = liq$
$\dot{n}_F = 1.0$ mol/h
$X_{F,BZ} = 0.5$
$X_{F,TL} = 0.5$



$T_V = 50°C$
$P_V = 164$ mm Hg
$Ph_V =$ sat. vap
$\dot{n}_V = ?$
$X_{V,BZ} = 0.663$
$X_{V,TL} = 0.337$

$T_L = 50°C$
$P_L = 164$ mm Hg
$Ph_L =$ sat. liq
$\dot{n}_L = ?$
$X_{L,BZ} = 0.4$
$X_{L,TL} = 0.6$

Assumptions

1. steady state
2. no rxn
3. neglect ΔKE & ΔPE
4. no shaft work
5. Vap-Liq equilibrium
6. $P_F = 1$ atm
7. continuous process

click here

Math Model

follow **Blue Crib** for the heat-of-reaction method

① Total: $\dot{n}_F - \dot{n}_V - \dot{n}_L = 0$

② BZ: $0.5\,\dot{n}_F - 0.663\,\dot{n}_V - 0.4\,\dot{n}_L = 0$

Check TL: $0.5\,\dot{n}_F - 0.337\,\dot{n}_V - 0.6\,\dot{n}_L = 0$

③ Energy: $\dot{n}_F \hat{H}_F - \dot{n}_V \hat{H}_V - \dot{n}_L \hat{H}_L + \dot{Q} = 0$

Eq. 7.5d-a with no heat-of-reaction terms

④ $\hat{H}_F = \text{HMIX}[T_F, P_F, \bar{X}_F]$

⑤ $\hat{H}_V = \text{HMIX}[T_V, P_V, \bar{X}_V]$

⑥ $\hat{H}_L = \text{HMIX}[T_L, P_L, \bar{X}_L]$

Degrees of Freedom

\# vars = 19
\# eqns = 6
DOF = 13

Know: T_F, P_F, $\dot{n}_F$, $\bar{X}_F$
T_V, P_V, $\bar{X}_V$
T_L, P_L, $\bar{X}_L$

CM 200 Example 8.4-4 11/15/90
Hanyak F&R, 2nd Ed 2 of 5

Math Algorithm

$[Q] = f\,[13 \text{ known variables}]$

1. $\hat{H}_F \leftarrow \text{HMIX}\,[T_F, P_F, \bar{X}_F]$ $= 0$ J/mol {see below}
2. $\hat{H}_L \leftarrow \text{HMIX}\,[T_L, P_L, \bar{X}_L]$ $= 5{,}940$ J/mol {see page 3}
3. $\hat{H}_V \leftarrow \text{HMIX}\,[T_V, P_V, \bar{X}_V]$ $= 39{,}244$ J/mol {see page 4}
4. SOLVE for $\dot{n}_V$ & $\dot{n}_L$ in

$$\left.\begin{aligned} \dot{n}_V + \dot{n}_L &= \dot{n}_F \\ 0.663\,\dot{n}_V + 0.4\,\dot{n}_L &= 0.5\,\dot{n}_F \end{aligned}\right\} \quad \begin{aligned} n_V &= 0.3802 \text{ mol/h} \\ n_L &= 0.6198 \text{ mol/h} \end{aligned}$$

END

5. $\dot{Q} \leftarrow \dot{n}_V\hat{H}_V + \dot{n}_L\hat{H}_L - \dot{n}_F\hat{H}_F$

$$= 0.3802(39{,}244) + 0.6198(5{,}940) - 1.0\,(0)$$

$$= \boxed{18{,}602 \text{ J/h}}$$

$\text{HMIX}\,[T_F, P_F, \bar{X}_F]$

follow **Blue Crib** for the heat-of-reaction method

$\hat{H}_F$ Assumptions

1. ideal solution
2. Ref. state is T_F, P_F, liq. for BZ & TL.

Eq. 7.7

$$\hat{H}_F = 0.5\,\hat{H}_{BZ} + 0.5\,\hat{H}_{TL} + \cancelto{0}{\Delta\hat{H}_{MIX}}$$

$$= 0.5\,(0.0 \text{ J/mol}) + 0.5\,(0.0 \text{ J/mol})$$

$$= \boxed{0.0 \text{ J/mol}} \text{ for mixture F.}$$

Eq. 7.8

$$\hat{H}_{BZ} = \cancelto{0}{\hat{H}^o_{BZ}} + \Delta\hat{H}_{BZ}\,[10°\text{C}, P_F, \text{liq} \leftarrow 10°\text{C}, P_F, \text{liq}]$$

$$= \int_{10°\text{C}}^{10°\text{C}} \cancelto{0}{C^L_{P,BZ}}\,dT + \int_{1\text{atm}}^{1\text{atm}} \left[\hat{V} - \cancelto{0}{T\left(\frac{\partial\hat{V}}{\partial T}\right)_P}\right] dP = \boxed{0.0 \text{ J/mol}}$$

for Pure BZ

Eq. 7.8

$$\hat{H}_{TL} = \cancelto{0}{\hat{H}^o_{TL}} + \Delta\hat{H}_{TL}\,[10°\text{C}, P_F, \text{liq} \leftarrow 10°\text{C}, P_F, \text{liq}]$$

$$= \int_{10°\text{C}}^{10°\text{C}} \cancelto{0}{C^L_{P,TL}}\,dT + \int_{1\text{atm}}^{1\text{atm}} \left[\hat{V} - \cancelto{0}{T\left(\frac{\partial\hat{V}}{\partial T}\right)_P}\right] dP = \boxed{0.0 \text{ J/mol}}$$

for Pure TL

CM 200
Hanyak

Example 8.4-4
F&R, 2nd Ed.

11/25/90
3 of 5

HMIX $[T_L, P_L, \bar{X}_L]$

follow **Blue Crib** for the heat-of-reaction method

$\hat{H}_L$ Assumptions

1. ideal solution
2. incompressible liq; no P effect on $\Delta\hat{H}_j$.
3. Ref. state is T_F, P_F, liq. for BZ + TL.

Eq. 7.7 $\hat{H}_L = 0.4\,\hat{H}_{BZ} + 0.6\,\hat{H}_{TL} + \cancelto{0}{\Delta\hat{H}_{MIX}}$

$= 0.4\,(5339\text{ J/mol}) + 0.6\,(6,341)$

$= \boxed{5940\text{ J/mol}}$ for mixture L.

Eq. 7.8 $\hat{H}_{BZ} = \cancelto{0}{\hat{H}^o_{BZ}} + \Delta\hat{H}_{BZ}[50°C,\ P^*_{BZ}[50°C],\ \overset{\text{sat'd}}{\text{liq}} \leftarrow 10°C,\ 1\text{ atm},\ \text{liq}]$ {see PH diagram, p.5}

$$= \int_{10°C}^{50°C} c^L_{P,BZ}\,dT + \int_{1\text{atm}}^{271.3\text{ mmHg}} \left[\hat{V} - \cancelto{0}{T\left(\frac{\partial\hat{V}}{\partial T}\right)_P}\right] dP$$

where $c^L_{P,BZ} = 62.55 + 0.234T$ J/mol·K & T in K,
From Table B.2 in F&R.

$$= \int_{283.15K}^{323.15K} (62.55 + 0.234T)\,dT = 62.55T + \frac{0.234}{2}T^2 \Big|_{283.15K}^{323.15K}$$

$$= 62.55\,(323.15 - 283.15) + \frac{0.234}{2}\,(323.15^2 - 283.15^2)$$

$= 2502 + 2837 = \boxed{5339\text{ J/mol}}$ for pure BZ.

Eq. 7.8 $\hat{H}_{TL} = \cancelto{0}{\hat{H}^o_{TL}} + \Delta\hat{H}_{TL}[50°C,\ P^*_{TL}[50°C],\ \overset{\text{sat'd}}{\text{liq}} \leftarrow 10°C,\ 1\text{ atm},\ \text{liq}]$ {see PH diagram, p. 5}

$$= \int_{10°C}^{50°C} c^L_{P,TL}\,dT + \int_{1\text{atm}}^{92.11\text{ mmHg}} \left[\hat{V} - \cancelto{0}{T\left(\frac{\partial\hat{V}}{\partial T}\right)_P}\right] dP$$

where $c^L_{P,TL}$ = 148.8 J/mol·°C @ 0 °C
= 181.2 J/mol·°C @ 100 °C } Table B.2 in F&R

Assume $c^L_{P,TL}$ is linear function of T; that is,

$c^L_{P,TL} = a + b\,T$

Now 148.8 = a + b (0°C) & 181.2 = a + b (100°C)
and solve for a and b in these two equations.

$$= \int_{10°C}^{50°C} (148.8 + 0.324\,T)\,dT = 148.8\,T + \frac{0.324}{2}T^2 \Big|_{10°C}^{50°C}$$

$$= 148.8\,(50 - 10) + \frac{0.324}{2}\,(50^2 - 10^2)$$

$= \boxed{6341\text{ J/mol}}$ for pure TL.

CM 200 Example 8.4-4 11/15/90
Hanyak F&R, 2nd Ed. 4 of 5

HMIX $[T_V, P_V, \bar{X}_V]$ follow **Blue Crib** for the heat-of-reaction method

$\hat{H}_V$ Assumptions

1. ideal solution
2. vapor is ideal gas
3. ref. state is T_F, P_F, liq. for BZ & TL

Eq. 7.7

$$\hat{H}_V = 0.684\,\hat{H}_{BZ} + 0.316\,\hat{H}_{TL} + \cancelto{0}{\Delta\hat{H}_{mix}}$$

$$= 0.684\,(37{,}527) + 0.316\,(42{,}960)$$

$$= \boxed{39{,}244 \text{ J/mol}} \text{ for mixture V.}$$

Eq. 7.8

$$\hat{H}_{BZ} = \cancelto{0}{\hat{H}^{o}_{BZ}} + \Delta\hat{H}_{BZ}[50°c,\ P^{*}_{BZ}[50°c],\ \overset{\text{sat'd}}{\text{vap}} \leftarrow 10°c,\ 1\text{atm},\ \text{liq}] \qquad \left\{\begin{matrix}\text{See}\\ \text{PH diagram, p.5}\end{matrix}\right\}$$

$$= \Delta\hat{H}_{BZ}[80.1°c,\ 1\text{ atm},\ \overset{\text{sat'd}}{\text{liq}} \leftarrow 10°c,\ 1\text{atm},\ \text{liq}] + \qquad \left\{\begin{matrix}\text{sensible heat}\\ \text{of liq. at fix P}\end{matrix}\right\}$$

$$\Delta\hat{H}_{BZ}[80.1°c,\ 1\text{ atm},\ \overset{\text{sat'd}}{\text{vap}} \leftarrow 80.1°c,\ 1\text{atm},\ \overset{\text{sat'd}}{\text{liq}}] + \qquad \left\{\begin{matrix}\text{latent heat}\\ \text{of vaporization}\end{matrix}\right\}$$

$$\Delta\hat{H}_{BZ}[50°c,\ P^{*}_{BZ}[50°c],\ \overset{\text{sat'd}}{\text{vap}} \leftarrow 80.1°c,\ 1\text{atm},\ \overset{\text{sat'd}}{\text{vap}}] \qquad \left\{\begin{matrix}\text{sensible heat}\\ \text{of an ideal gas}\end{matrix}\right\}$$

$$= \int_{283.15K}^{353.25K} \underbrace{(62.55 + 0.234\,T)}_{c^{L}_{p,BZ}}\,dT \ +$$

Table B.2 in F&R, 3rd Ed.

$$\Delta\hat{H}_{vap} + \int_{80.1°c}^{50°c} \underbrace{(74.06 + 0.3295\,T - 25.2\times10^{-5}T^2 + 77.57\times10^{-9}T^3)}_{c^{V}_{p,BZ}}\,dT$$

Table B.1 in F&R, 3rd Ed. Table B.2 in F&R, 3rd Ed.

$$= \left[62.55\,(353.25 - 283.15) + \frac{0.234}{2}\,(353.25^2 - 283.15^2)\right]\frac{\text{J}}{\text{mol}} + 30{,}765\ \frac{\text{J}}{\text{mol}} +$$

$$\left[74.06\,(50-80.1) + \frac{0.3295}{2}\,(50^2 - 80.1^2) - \frac{25.2\times10^{-5}}{3}(50^3 - 80.1^3) + \frac{77.57\times10^{-9}}{4}(50^4 - 80.1^4)\right]$$

$$= 9{,}604 + 30{,}765 - 2{,}842 = \boxed{37{,}527 \text{ J/mol}} \text{ for pure BZ.}$$

Eq. 7.8

$$\hat{H}_{TL} = \cancelto{0}{\hat{H}^{o}_{TL}} + \Delta\hat{H}_{TL}[50°c,\ P^{*}_{TL}[50°c],\ \overset{\text{sat'd}}{\text{vap}} \leftarrow 10°c,\ 1\text{atm},\ \text{liq}] \qquad \left\{\begin{matrix}\text{See}\\ \text{PH diagram, p.5}\end{matrix}\right\}$$

$$= \Delta\hat{H}_{TL}[110.62°c,\ 1\text{atm},\ \overset{\text{sat'd}}{\text{liq}} \leftarrow 10°c,\ 1\text{atm},\ \text{liq}] + \Delta\hat{H}_{vap}[1\text{ atm}] +$$

$$\Delta\hat{H}_{TL}[50°c,\ P^{*}_{TL}[50°c],\ \overset{\text{sat'd}}{\text{vap}} \leftarrow 110.62°c,\ 1\text{atm},\ \overset{\text{sat'd}}{\text{vap}}]$$

$$= \int_{10°c}^{110.62°c} (148.8 + 0.324\,T)\,dT + \Delta\hat{H}_{vap} + \int_{110.62°c}^{50°c} (94.18 + 0.38\,T - 27.86\times10^{-5}T^2 + 80.33\times10^{-9}T^3)\,d$$

$$= \left[148.8(110.62 - 10) + \frac{0.324}{2}(110.62^2 - 10^2)\right] \text{J/mol} + 33{,}470 \text{ J/mol} +$$

$$\left[94.18(50 - 110.62) + \frac{0.38}{2}(50^2 - 110.62^2) - \frac{27.86\times10^{-5}}{3}(50^3 - 110.62^3) + \frac{80.33\times10^{-9}}{4}(50^4 - 110.62^4)\right]$$

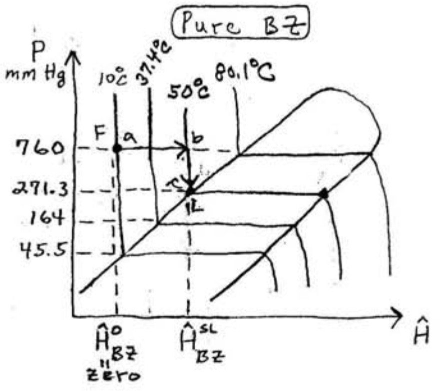
$$= 16{,}938 + 33{,}470 - 7{,}448 = \boxed{42{,}960 \text{ J/mol}} \text{ for pure TL.}$$

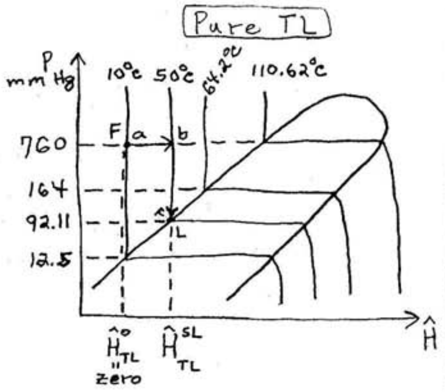
cm 200
Hanyak

Example 8.4-4
F&R, 2nd Ed.

11/15/90
5 of 5

PH Diagrams for Stream L





Sensible liq. $\Delta\hat{H}$: Path a → b → c

Sensible liq. $\Delta\hat{H}$: Path a → b → c

Raoult's: $y_{BZ} P = P^*_{BZ}[T]\, x_{BZ}$

$P^*_{BZ}[T] = \frac{y_{BZ}P}{x_{BZ}} = \frac{0.663(164)}{0.4}$

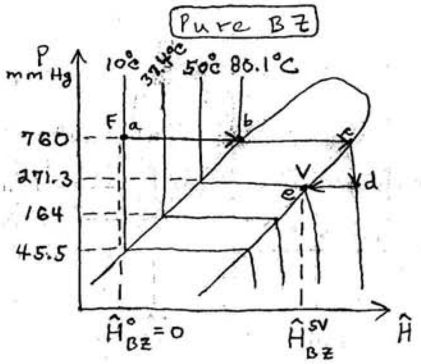
Antoine: $P^*_{BZ}[T] = 271.3$ mmHg for 50°C

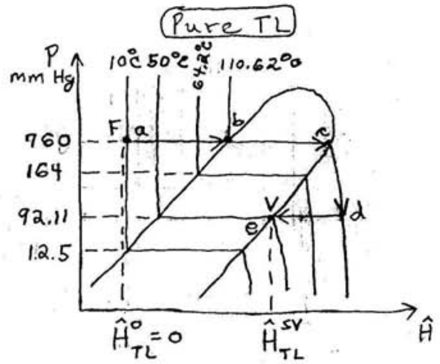
$y_{TL} = P^*_{TL}[T]\, x_{TL}$

$P^*_{TL}[T] = \frac{y_{TL}P}{x_{TL}} = \frac{0.337(164)}{0.6}$

$P^*_{T}[T] = 92.11$ mmHg for 50°C

PH Diagrams for Stream V





Sensible liq. $\Delta\hat{H}$: Path a → b
Latent $\Delta\hat{H}$: Path b → c
Sensible vap. $\Delta\hat{H}$: Path c → d → e.

Sensible liq $\Delta\hat{H}$: Path a → b
Latent $\Delta\hat{H}$: Path b → c
Sensible vap $\Delta\hat{H}$: Path c → d → e

Antoine Equations {Table B.4, F&R, 3rd Ed.}

BZ: $\log_{10} P^* = 6.89272 - \frac{1203.531}{T + 219.888}$

TL: $\log_{10} P^* = 6.95805 - \frac{1346.773}{T + 219.693}$

} P^* in mm Hg
T in °C

larger

CM 200 Hanyak	Example 8.5-1 F&R, 3rd Ed.	11/25/91 1 of 3

Problem Statement

Similar to Example 8.5-1 in F&R, 3rd Ed.

energy balancing with heat of mixing

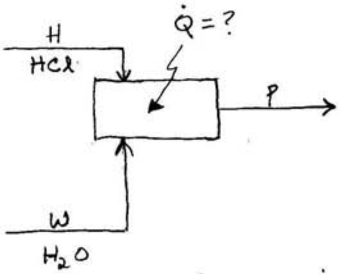
Gaseous hydrochloric acid at 100°C and liquid water at 25°C are fed to an absorption unit to produce 20 wt% HCl(aq) at 40°C. The absorption unit operates at a constant pressure of 1 atm. How much heat must be transferred to or from the unit to produce 1000 kg/h of aqueous HCl?

Diagram

label with molar quantities because enthalpies will be calculated as energy per unit mole.

T_H = 100°C
P_H = 1 atm
Ph_H = gas
$\dot{n}_H$ = ?
$x_{H,HC}$ = 1.0

T_W = 25°C
P_W = 1 atm
Ph_W = liq
$\dot{n}_W$ = ?
$x_{W,WA}$ = 1.0



T_P = 40°C
P_P = 1 atm
Ph_P = liq
$\dot{n}_P$ = ?
$x_{P,HC}$ = ?
$x_{P,WA}$ = ?

Given: $\dot{m}_P$ = 1000 kg/h
$w_{P,HC}$ = 0.20
$w_{P,WA}$ = 0.80

Find: $\dot{Q}$ in kJ/h

Assumptions

1. continuous process
2. steady state
3. no rxn
4. isobaric @ 1 atm
5. no shaft work.
6. neglect ΔKE & ΔPE
7. Ref. State for HCl is 25°C, 1 atm, gas
8. Ref. state for H_2O is 25°C, 1 atm, liq.

Model

① Total: $\dot{n}_H + \dot{n}_W - \dot{n}_P = 0$

② HCl: $\dot{n}_H - \dot{n}_{P,HC} = 0$

③ H_2O: $\dot{n}_W - \dot{n}_{P,WA} = 0$

check Mix P: $\dot{n}_P = \dot{n}_{P,HC} + \dot{n}_{P,WA}$

⑩ $\dot{n}_{P,HC} = \dot{n}_P \, x_{P,HC}$

⑪ $\dot{n}_{P,WA} = \dot{n}_P \, x_{P,WA}$

④ $\dot{n}_{P,HC} = 0.20 \, \dot{m}_P / M_{HCl}$

⑤ $\dot{n}_{P,WA} = 0.80 \, \dot{m}_P / M_{H_2O}$

⑥ $\dot{n}_H \hat{H}_H + \dot{n}_W \hat{H}_W - \dot{n}_P \hat{H}_P + \dot{Q} = 0$

Eq. 7.5d-a with no heat-of-reaction terms

⑦ $\hat{H}_H$ = HMIX[100°C, 1 atm, gas HCl]

⑧ $\hat{H}_W$ = HMIX[25°C, 1 atm, liq H_2O]

⑨ $\hat{H}_P$ = HMIX[40°C, 1 atm, $\bar{x}_P$]

\# vars = 12
\# eqns = 11
DOF = 1

Known $\dot{m}_P$

cm 200 | Example 8.5-1 | 11/25/91
Hanyak | F&R, 3rd Ed. | 2 of 3

Algorithm **Solution**

$[\dot{Q}] = f[\dot{m}_P]$ $\qquad \dot{m}_P = 1000$ kg/h

④ 1. $\dot{n}_{P,HC} \leftarrow 0.20\, \dot{m}_P / M_{HCl} \quad = 0.2\left(1000 \frac{kg}{h}\right)\left(\frac{10^3 \text{ gmol HCl}}{36.5 \text{ kg HCl}}\right) = 5480 \frac{\text{gmol HCl}}{h}$

⑤ 2. $\dot{n}_{P,WA} \leftarrow 0.80\, \dot{m}_P / M_{H_2O} \quad = 0.8\left(1000 \frac{kg}{h}\right)\left(\frac{10^3 \text{ gmol } H_2O}{18.02 \text{ kg } H_2O}\right) = 44{,}400 \frac{\text{gmol } H_2O}{h}$

② 3. $\dot{n}_H \leftarrow \dot{n}_{P,HC} \quad = 5480$ gmol HCl/h

③ 4. $\dot{n}_W \leftarrow \dot{n}_{P,WA} \quad = 44{,}400$ gmol H_2O/h

① 5. $\dot{n}_P \leftarrow \dot{n}_H + \dot{n}_W \quad = 5{,}480 + 44{,}400 = 49{,}880$ gmol/h

⑩ 6. $x_{P,HC} \leftarrow \dot{n}_{P,HC} / \dot{n}_P \quad = 5{,}480 / 49{,}880 = 0.1099$

⑪ 7. $x_{P,WA} \leftarrow \dot{n}_{P,WA} / \dot{n}_P \quad = 44{,}400 / 49{,}880 = 0.8901$

⑦ 8. $\hat{H}_H \leftarrow$ HMIX[100°C, 1 atm, gas HCl] $= 2.182$ kJ/gmol Stream H

⑧ 9. $\hat{H}_W \leftarrow$ HMIX[25°C, 1 atm, liq H_2O] $= 0.0$ kJ/gmol Stream W

⑨ 10. $\hat{H}_P \leftarrow$ HMIX[40°C, 1 atm, $\bar{X}_P$] $= -6.492$ kJ/gmol Stream P

⑥ 11. $\dot{Q} \leftarrow \dot{n}_P \hat{H}_P - \dot{n}_H \hat{H}_H - \dot{n}_W \hat{H}_W \quad = \left(49{,}880 \frac{gmol}{h}\right)\left(-6.492 \frac{kJ}{gmol}\right) - \left(5480 \frac{gmol}{h}\right)\left(2.182 \frac{kJ}{gmol}\right)$

Why is the heat negative? $= \boxed{-3.36 \times 10^5 \text{ kJ/h}}$

HMIX [T_H, P_H, gas HCl] follow **Blue Crib** for the heat-of-reaction method

Eq. 7.8

$$\hat{H}_H = \hat{H}^\circ_{HC}[25°C, 1 atm, gas] + \Delta\hat{H}_{HC}[100°C, 1 atm, gas \leftarrow 25°C, 1 atm, gas]$$

$$= 0.0 \text{ J/gmol} + \int_{25°C}^{100°C} \underbrace{(29.13 - 0.1341\times10^{-2}T + 0.9715\times10^{-5}T^2 - 4{,}335\times10^{-9}T^3)}_{\text{Table B.2}}\, dT$$

$$= 29.13(100-25) - \frac{0.1341\times10^{-2}}{2}(100^2 - 25^2) + \frac{0.9715\times10^{-5}}{3}(100^3 - 25^3) - \frac{4.335\times10^{-9}}{4}(100^4 - 25^4)$$

$$= 2185 - 6.3 + 3.2 - 0.1 = \boxed{2{,}182 \text{ J/gmol}} \text{ for Stream H.}$$

HMIX [T_W, P_W, liq H_2O] follow **Blue Crib** for the heat-of-reaction method

Eq. 7.8

$$\hat{H}_W = \hat{H}^\circ_{WA}[25°C, 1 atm, liq] + \Delta\hat{H}_{WA}[25°C, 1 atm, liq \leftarrow 25°C, 1 atm, liq]$$

$$= 0.0 \text{ J/gmol} + 0.0 \text{ J/gmol}$$

$$= \boxed{0.0 \text{ J/gmol}} \text{ for Stream W.}$$

CM 200 Hanyak	Example 8.5-1 F&R, 3rd Ed.	11/25/91 3 of 3

HMIX[T_P, P_P, $\bar{X}_P$] follow **Blue Crib** for the heat-of-reaction method but account for ΔH_{mix} effect as shown here:

click here

$$\hat{H}_P = \boxed{0.1099\,\hat{H}_{HC} + 0.8901\,\hat{H}_{WA} + \Delta\hat{H}_{MIX}[25°C,\ 1\,atm,\ \bar{X}_P,\ aq] + \Delta\hat{H}_P[40°C,\ 1\,atm,\ \bar{X}_P,\ aq \leftarrow 25°C,\ 1\,atm,\ \bar{X}_P,\ aq]}$$

$$= 0.0\ kJ/gmol + 0.0\ kJ/gmol - 7.410\ kJ/gmol + 0.9185\ kJ/gmol$$

$$= \boxed{-6.4915\ kJ/gmol} \text{ for Stream P.}$$

$$\hat{H}_{HC} = \hat{H}^{\circ}_{HC}[25°C,\ 1\,atm,\ gas] + \Delta\hat{H}_{HC}[25°C,\ 1\,atm,\ gas \leftarrow 25°C,\ 1\,atm,\ gas]$$

$$= 0.0\ kJ/gmol + 0.0\ kJ/gmol$$

$$= \boxed{0.0\ kJ/gmol} \text{ for pure HCl}$$

$$\hat{H}_{WA} = \hat{H}_{WA}[25°C,\ 1\,atm,\ liq] + \Delta\hat{H}_{WA}[25°C,\ 1\,atm,\ liq \leftarrow 25°C,\ 1\,atm,\ liq]$$

$$= 0.0\ kJ/gmol + 0.0\ kJ/gmol$$

$$= \boxed{0.0\ kJ/gmol} \text{ for pure } H_2O$$

$$\Delta\hat{H}_{MIX} = \Delta\hat{H}_s[25°C,\ 1\,atm,\ \bar{X}_P,\ aq] \text{ in kJ/gmol of mixture P.}$$

$$= \Delta\hat{H}_s\left[25°C,\ 1\,atm,\ \frac{(0.8901\,\dot{n}_P)\ mol\ H_2O}{(0.1099\,\dot{n}_P)\ mol\ HCl}\right] \cdot \left(\frac{0.1099\,\dot{n}_P\ mol\ HCl}{\dot{n}_P\ mol\ mix\ P}\right)$$

$$= \underbrace{\Delta\hat{H}_s[25°C,\ 1\,atm,\ 8.0992\ mol\ H_2O/mol\ HCl]}_{\text{Table B.11 in kJ soln/mol HCl, where soln is mix P.}} \cdot \left(\frac{0.1099\ mol\ HCl}{1.0\ mol\ mix\ P}\right)$$

$$= (-67.4\ kJ\ mix\ P/mol\ HCl)\left(\frac{0.1099\ mol\ HCl}{1.0\ mol\ mix\ P}\right) = \boxed{-7.410\ kJ/gmol} \text{ mix P}$$

$$\Delta\hat{H}_P = \int_{25°C}^{40°C} C_p^{soln}\, dT$$

← Sensible $\Delta\hat{H}$ of 10.99 mol % HCl-H_2O sol'n

C_p^{soln}: $0.73 \frac{kcal\ sol'n}{kg\ sol'n \cdot \Delta°C}$ ← from Perry's Chem. Eng. Handbook, p. 3-145, for 11 mol % HCl solution.

$$= \left(0.73\,\frac{\cancel{kcal}\ mix\ P}{\cancel{kg\ soln} \cdot \cancel{\Delta°C}}\right)(40-25)\cancel{\Delta°C}\ \underbrace{\left\langle\frac{1000\ \cancel{kg\ P/h}}{49,880\ gmol\ P/h}\right\rangle}_{\text{Mol. Wt. of P}} \left\langle\frac{4.184\ kJ}{\cancel{kcal}}\right\rangle$$

$$= \boxed{0.9185\ kJ/gmol} \text{ mix P.}$$

larger

cm 200
Hanyak

Example 8.5-5
F&R, 3rd Ed.

11/26/91
1 of 2

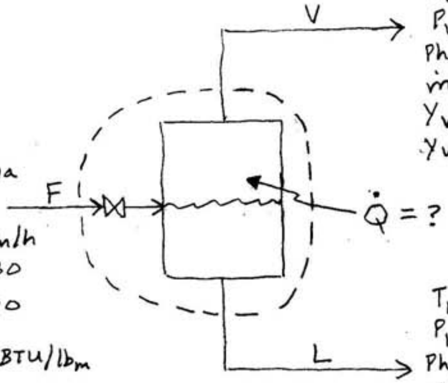
Problem Statement

Similar to Example 8.5-5 in F&R, 3rd Ed. energy balancing with HXY diagram

A liquid process stream at 100 psia and 100 lb_m/h contains 30.0 % ammonia and 70.0 % water on a mass basis. Its pressure is reduced through a valve to 1.0 atm and then fed to a tank where the solution is heated to form a vapor phase and liquid phase that are in equilibrium. For a vapor composition of 89.0 wt% of ammonia, what is the temperature in the tank, the mass flows of the liquid and vapor product streams, the composition of the ammonia in the liquid product, and the heat transfer into the vaporizer? Note that the specific enthalpy of the feed solution is 100 BTU/ lb_m relative to a reference state of -40°F, 1 atm, and liquid for NH_3 and a reference state of 32°F, 1 atm, and liquid for H_2O. These two reference states are the same ones used in the enthalpy-composition (HXY) diagram of Figure 8.5-2 found in the Felder and Rousseau textbook, 3rd Ed.

Diagram

T_F
$P_F = 100$ psia
$Ph_F =$ liq
$\dot{m}_F = 100\ \text{lb}_m/\text{h}$
$z_{F,Am} = 0.30$
$z_{F,WA} = 0.70$
$\hat{H}_F = 100\ \text{BTU}/\text{lb}_m$



$T_V = ?$
$P_V = 1$ atm
$Ph_V =$ sat'd vap
$\dot{m}_V = ?$
$Y_{V,Am} = 0.89$
$Y_{V,WA} = 0.11$

$T_L = T_V = ?$
$P_L = 1$ atm
$Ph_L =$ sat'd liq
$\dot{m}_L = ?$
$X_{L,Am} = ?$
$X_{L,WA} = ?$

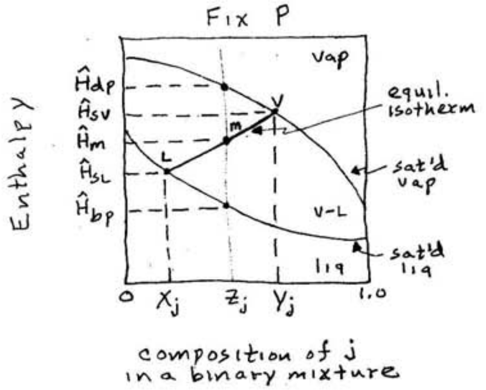
Assumptions

1. continuous process
2. steady state
3. no rxn; no shaft work; neglect ΔKE and ΔPE
4. Ref. State NH_3 is -40°F, 1 atm, liq.
5. Ref. State H_2O is 32°F, 1 atm, liq.

Find: T_V, $X_{L,Am}$, $\dot{m}_V$, $\dot{m}_L$, $\dot{Q}$

NOTE: $\bar{z}_F$, $\bar{Y}_V$, & $\bar{X}_L$ are mass fractions.

General HXY Diagram



HXY Algorithms

1. $[T_{bp}, Y_j, \hat{H}_{bp}] = HXY[P, V_f = 0, z_j]$
2. $[T_{dp}, X_j, \hat{H}_{dp}] = HXY[P, V_f = 1, z_j]$

3. $[T, X_j, Y_j, \hat{H}_{sv}, \hat{H}_{sL}] = HXY[P, V_f, z_j]$
4. $[V_f, X_j, Y_j, \hat{H}_{sv}, \hat{H}_{sL}] = HXY[T, P, z_j]$

5. $[T, X_j, \hat{H}_{sv}, \hat{H}_{sL}] = HXY[P, Y_j, \text{sat'd vap}]$
6. $[T, Y_j, \hat{H}_{sv}, \hat{H}_{sL}] = HXY[P, X_j, \text{sat'd liq}]$

Reverse Lever Rule

$$V_f = \frac{\overline{LM}}{\overline{LV}} = \frac{z_j - X_j}{Y_j - X_j} = \frac{\hat{H}_m - \hat{H}_{sL}}{\hat{H}_{sv} - \hat{H}_{sL}}$$

CM 200
Hanyak

Example 8.5-4
F+R, 2nd Ed

11/26/91
2 of 2

Model

① Total: $\dot{m}_F - \dot{m}_V - \dot{m}_L = 0$

② NH_3: $0.3\,\dot{m}_F - 0.89\,\dot{m}_V - \dot{m}_{L,AM} = 0$ ⑨ $\dot{m}_{L,Am} = \dot{m}_L X_{L,Am}$

③ H_2O: $0.7\,\dot{m}_F - 0.11\,\dot{m}_V - m_{L,WA} = 0$ ⑩ $\dot{m}_{L,WA} = \dot{m}_L X_{L,WA}$

check Mix L: $\dot{m}_L = \dot{m}_{L,Am} + \dot{m}_{L,WA}$

follow **Blue Crib** for the heat-of-reaction method

④ $\dot{m}_F \hat{H}_F - \dot{m}_V \hat{H}_V - \dot{m}_L \hat{H}_L + \dot{Q} = 0$

Eq. 7.5d-a with no heat-of-reaction terms

⑤ to ⑧ $[T_V, X_{L,Am}, \hat{H}_V, \hat{H}_L] = HXY[P_V, Y_{V,Am}, \text{sat'd vap}]$

Figure 8.5-2 in F&R, 3rd Ed., p. 403.

\# vars = 14
\# eqns = 10
DOF = 4

Algorithm

Solution

$[T_V, \text{etc.}] = f[\dot{m}_F, \hat{H}_F, P_V, Y_{V,Am}]$

⑤-⑧: 1. $[T_V, X_{L,Am}, \hat{H}_V, \hat{H}_L] \leftarrow HXY[P_V, Y_{V,Am}, \text{sat'd vap}]$ $= \left\{ \begin{array}{l} 120°F,\ X_{L,Am} = 0.185, \\ \hat{H}_V = 728\ BTU/lb_m \\ \hat{H}_L = 45\ BTU/lb_m \end{array} \right.$

2. SOLVE $\dot{m}_V$, $\dot{m}_L$ IN

①: $\dot{m}_V + \dot{m}_L = \dot{m}_F$

②: $0.89\,\dot{m}_V + X_{L,Am}\,\dot{m}_L = 0.3\,\dot{m}_F$

$= \left\{ \begin{array}{l} \text{Reverse Lever Rule} \\ \dot{m}_V = 16\ lb_m/h \\ \dot{m}_L = 84\ lb_m/h \end{array} \right.$

END

⑨ 3. $m_{L,Am} \leftarrow \dot{m}_L X_{L,Am}$

③ 4. $m_{L,WA} \leftarrow 0.7\,\dot{m}_F - 0.11\,\dot{m}_V$

⑩ 5. $X_{L,WA} \leftarrow \dot{m}_{L,WA} / \dot{m}_L$

} not needed!

④ 6. $\dot{Q} \leftarrow \dot{m}_V \hat{H}_V + \dot{m}_L \hat{H}_L - \dot{m}_F \hat{H}_F$ = 5428 BTU/h

= $\boxed{5400\ \text{BTU/h}}$

larger

CM 200 | Mixture Enthalpy | 11/27/91
Hanyak | | 1 of 2

HMIX$[T_i, P_i, \bar{X}_i]$ {for process units with no rxn, F+R, ch. 8}

heat-of-reaction method

Eq. 7.7 $$\hat{H}_i = \sum_{j=1}^{nc} X_{i,j}\, \hat{H}_j[T_i, P_i, Ph_i] + \Delta\hat{H}_{mix}[T_i, P_i, \bar{X}_i]$$

Eq. 7.8 $$\hat{H}_j = \overset{\text{zero}}{\cancel{\hat{H}^o_j}}\underbrace{[T^o_j, P^o_j, Ph^o_j]}_{\text{ref. state of pure } j} + \Delta\hat{H}_j[T_i, P_i, Ph_i \leftarrow T^o_j, P^o_j, Ph^o_j]$$

For example, $j = H_2O$ at 400°C, 3 atm, gas; with reference state of 25°C, 1 atm, liq. See PH Diagram A below for compound H_2O.

HMIX$[T_i, P_i, \bar{X}_i]$ {for reactions, F+R, 3rd Ed., ch. 9, p. 451}

heat-of-formation method

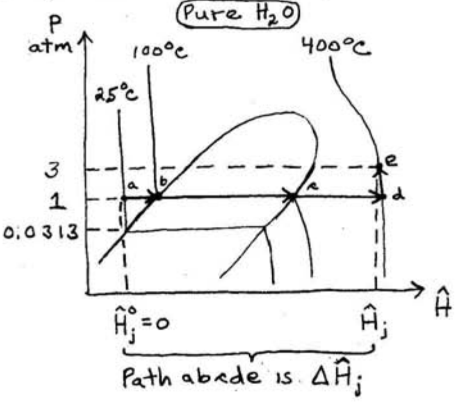
Eq. 7.3 $$\hat{H}_i = \sum_{j=1}^{nc} X_{i,j}\, \hat{H}_j[T_i, P_i, Ph_i] + \Delta\hat{H}_{mix}[T_i, P_i, \bar{X}_i]$$

Eq. 7.4 $$\hat{H}_j = \sum_{k=1}^{ne} a_{j,k}\, \overset{\text{zero}}{\cancel{\hat{H}^o_k}}[25°C, 1\text{ atm}, Ph^o_k] + \Delta\hat{H}^o_{f,j}[25°C, 1\text{ atm}, Ph^o_j]$$
$$+ \Delta\hat{H}_j[T_i, P_i, Ph_i \leftarrow 25°C, 1\text{ atm}, Ph_j]$$

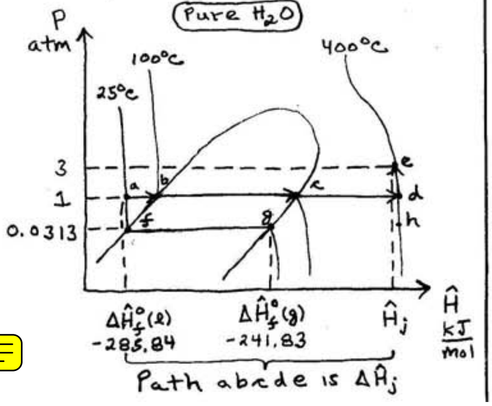
where $\hat{H}^o_k$ is molar enthalpy of Element k in Compound j.
Ph^o_k is stable phase of Element k at 25°C and 1 atm.
$\Delta\hat{H}^o_{f,j}$ is heat of formation of Compound at 25°C and 1 atm, found in Table B.1 of F+R, Third Ed.
Ph^o_j is stable phase of Compound j at 25°C and 1 atm.

For example, see PH diagram B below for compound H_2O and the explanation on Page 2.

PH Diagram A {no rxn}



PH Diagram B {rxn}



CM 200
Hanyak

Mixture Enthalpy

11/27/91
2 of 2

When chemical reaction is ocurring within the system boundary of an energy balance, the reference states <u>must</u> be the <u>pure</u> <u>elements</u> at 25°C, 1 atm, and their most stable phase at those conditions. For example, consider calculating the enthalpy of compound H_2O in a mixture at 400°C, 3 atm, and gas phase.

Eq. 7.4

$$\hat{H}_{H_2O} = \underbrace{\underbrace{a_{H_2O,H}}_{2}\,\cancelto{0}{\hat{H}^{\circ}_{H}}[25^\circ\text{C}, 1\text{ atm}, \text{gas}] + \underbrace{a_{H_2O,O}}_{1}\,\cancelto{0}{\hat{H}^{\circ}_{O}}[25^\circ\text{C}, 1\text{ atm}, \text{gas}]}_{\sum_{k=1}^{ne} a_{j,k}\,\hat{H}^{\circ}_{k}[25^\circ\text{C},\, 1\text{ atm},\, Ph^{\circ}_{k}] = 0} +$$

{reference enthalpies of elements arbitrarily set to zeros.}

$$\underbrace{\Delta\hat{H}^{\circ}_{f,H_2O}[25^\circ\text{C}, 1\text{ atm}, \text{liq}]}_{\text{standard heat of formation of water, from Table B.1}} + \Delta\hat{H}_{H_2O}\underbrace{[400^\circ\text{C}, 3\text{ atm}, \text{gas} \leftarrow 25^\circ\text{C}, 1\text{ atm}, \text{liq}]}_{\text{Path } a\to b\to c\to d\to e \text{ in PH Diagram B on Page 1.}}$$

$$= \underbrace{\Delta\hat{H}^{\circ}_{f}(\ell)}_{\substack{-285.84\\ \text{kJ/gmol}}} + \Delta\hat{H}[100^\circ\text{C}, 1\text{ atm}, \overset{\text{sat'd}}{\text{liq}} \leftarrow 25^\circ\text{C}, 1\text{ atm}, \text{liq}] \leftarrow \boxed{\text{Path } a\to b \text{ sensible } \Delta H}$$

$$+ \Delta\hat{H}[100^\circ\text{C}, 1\text{ atm}, \overset{\text{sat'd}}{\text{vap}} \leftarrow 100^\circ\text{C}, 1\text{ atm}, \overset{\text{sat'd}}{\text{liq}}] \leftarrow \boxed{\text{Path } b\to c \text{ latent } \Delta H}$$

$$+ \Delta\hat{H}[400^\circ\text{C}, 3\text{ atm}, \text{gas} \leftarrow 100^\circ\text{C}, 1\text{ atm}, \overset{\text{sat'd}}{\text{vap}}] \leftarrow \boxed{\text{Path } c\to d\to e \text{ sensible } \Delta H}$$

$$= \boxed{\underbrace{\Delta\hat{H}^{\circ}_{f}(\ell)}_{\text{Table B.1}} + \int_{25^\circ\text{C}}^{100^\circ\text{C}} \underbrace{C_p^{\text{liq}}}_{\text{Table B.2}}\,dT + \underbrace{\Delta\hat{H}_{\text{vap}}}_{\text{Table B.1}} + \int_{100^\circ\text{C}}^{400^\circ\text{C}} \underbrace{(a+bT+cT^2+dT^3)\,dT}_{\text{Table B.2}} + \int_{1\text{atm}}^{3\text{atm}} \underbrace{[\hat{V} - \cancelto{0}{T\left(\frac{\partial\hat{V}}{\partial T}\right)_p}]}_{\text{ideal gas}}\,dP}$$

OR, THE ABOVE IS EQUIVALENT TO

$$= \underbrace{\Delta\hat{H}^{\circ}_{f,H_2O}[25^\circ\text{C}, P^*[25^\circ\text{C}], \overset{\text{sat'd}}{\text{vap}}]}_{\text{Path } a\to f\text{-}g \text{ in PH Diagram B}} + \Delta\hat{H}_{H_2O}\underbrace{[400^\circ\text{C}, 3\text{ atm}, \text{gas} \leftarrow 25^\circ\text{C}, P^*[25^\circ\text{C}], \overset{\text{sat'd}}{\text{vap}}]}_{\text{Path } g\to h\to e \text{ in PH Diagram B on Page 1}}$$

$$= \boxed{\underbrace{\Delta\hat{H}_{f}(g)}_{\substack{-241.83\\ \text{kJ/gmol,}\\ \text{Table B.1}}} + \int_{25^\circ\text{C}}^{400^\circ\text{C}} \underbrace{(a+bT+cT^2+dT^3)\,dT}_{\text{Table B.2}} + \int_{P^*[25^\circ\text{C}]}^{3\text{atm}} \underbrace{[\hat{V} - \cancelto{0}{T\left(\frac{\partial\hat{V}}{\partial T}\right)_p}]}_{\text{ideal gas}}\,dP}$$

Why are two standard heats of formation tabulated for some compounds? Click here to resolve this conundrum.

larger

cM 200
Hanyak

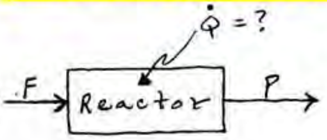
Energy Balance
Chemical Reactor

11/29/90
1 of 6

Diagram

Problem Statement: Water vapor is reacted with carbon monoxide to form hydrogen as shown in the diagram. How much heat must be transferred to or from the reactor?

$T_F = 315\,°C$
$P_F = 1$ atm
$\dot{n}_F = 100$ mol/h
$x_{F,cm} = 0.3$
$x_{F,wA} = 0.7$



$T_P = 400\,°C$
$P_P = 1$ atm
$\dot{n}_P = ?$
$x_{P,wA} = ?$
$x_{P,cD} = ?$
$x_{P,H2} = ?$

Given: 100% CO reacted

Find: $\dot{Q}$ in kJ/h

Assumptions

1. steady state
2. neglect ΔKE & ΔPE
3. no W_s
4. Rxn 100% completion

water-gas shift Rxn: $CO + H_2O(g) \rightarrow CO_2 + H_2$

What is its standard heat of reaction? See Eq. 7.5d-b in the **Blue Crib** master.

Model

① Total: $\dot{n}_F - \dot{n}_P + 0\,\dot{R} = 0$

② CO: $0.3\,\dot{n}_F - \dot{R} = 0$

③ H_2O: $0.7\,\dot{n}_F - \dot{n}_{P,wA} - \dot{R} = 0$

④ CO_2: $-\dot{n}_{P,cD} + \dot{R} = 0$

⑤ H_2: $-\dot{n}_{P,H2} + \dot{R} = 0$

# vars = 6
# eqns = 5
D.O.F. = 1

⑨ $\dot{n}_{P,wA} = \dot{n}_P\, x_{P,wA}$

⑩ $\dot{n}_{P,cD} = \dot{n}_P\, x_{P,cD}$

⑪ $\dot{n}_{P,H2} = \dot{n}_P\, x_{P,H2}$

check Mix P: $\dot{n}_P = \dot{n}_{P,wA} + \dot{n}_{P,cD} + \dot{n}_{P,H2}$

follow **Pink Crib** for the heat-of-formation method

⑥ $\dot{n}_F\,\hat{H}_F - \dot{n}_P\,\hat{H}_P + \dot{Q} = 0$ — Equation 7.1d, **heat-of-formation method**

⑦ $\hat{H}_F = \hat{H}[T_F, P_F, \bar{x}_F]$ — Eq. 7.2

⑧ $\hat{H}_P = \hat{H}[T_P, P_P, \bar{x}_P]$ — Eq. 7.2

Math Algorithm

$[\dot{Q}] = f\,[\,7 \text{ knowns}\,]$

①	1.	$\dot{n}_P$	←	$\dot{n}_F$	= 100 mol/h
②	2.	$\dot{R}$	←	$0.3\,\dot{n}_F$	= 30 g-rxns/h
③	3.	$\dot{n}_{P,wA}$	←	$0.7\,\dot{n}_F - R$	= 40 mol/h
④	4.	$\dot{n}_{P,cD}$	←	R	= 30 mol/h
⑤	5.	$\dot{n}_{P,H2}$	←	R	= 30 mol/h
⑨	6.	$x_{P,wA}$	←	$\dot{n}_{P,wA}/\dot{n}_P$	= 0.4
⑩	7.	$x_{P,cD}$	←	$\dot{n}_{P,cD}/\dot{n}_P$	= 0.3
⑪	8.	$x_{P,H2}$	←	$\dot{n}_{P,H2}/\dot{n}_P$	= 0.3
⑦	9.	$\hat{H}_F$	←	$\hat{H}[315°C, 1\text{ atm}, g]$	= -192.81 kJ/mol
⑧	10.	$\hat{H}_P$	←	$\hat{H}[400°C, 1\text{ atm}, g]$	= -201.35 kJ/mol
⑥	11.	$\dot{Q}$	←	$\dot{n}_P\,\hat{H}_P - \dot{n}_F\,\hat{H}_F$	= -854 kJ/h

Degrees of Freedom

# vars = 18
# eqns = 11
D.O.F. = 7

Know T_F, P_F, $\dot{n}_F$, $\bar{x}_F$
T_P, P_P

CM 200 Energy Balance 11/29/90
Hanyak Chemical Reactor 2 of 6

$\hat{H}[T_F, P_F, \bar{X}_F]$ follow **Pink Crib** for the heat-of-formation method

$\hat{H}_F$ Assumptions

1. ideal solution

Eq. 7.3 $\hat{H}_F = 0.3\,\hat{H}_{cm} + 0.7\,\hat{H}_{WA}$

$= 0.3\,(-101.89) + 0.7\,(-231.78)$

$= \boxed{-192.81 \text{ kJ/mol}}$ for mixture F.

Eq. 7.4 $\hat{H}_{cm} = \Delta\hat{H}^\circ_{f,cm}[25°C, 1 atm, gas] + \Delta\hat{H}_{cm}[315°C, 1 atm, gas \leftarrow 25°C, 1 atm, gas]$

$= \underbrace{\Delta\hat{H}^\circ_f(g)}_{\text{Table B.1}} + \underbrace{\Delta\hat{H}_{cp}[315°C]}_{\text{Table B.8}}$

$= -110.52 \text{ kJ/mol} + 8.63 \text{ kJ/mol}$

$= \boxed{-101.89 \text{ kJ/mol}}$ for pure cm.

Eq. 7.4 $\hat{H}_{WA} = \Delta\hat{H}^\circ_{f,WA}[25°C, 1 atm, liq] + \Delta\hat{H}_{WA}[315°C, 1 atm, gas \leftarrow 25°C, 1 atm, liq]$

or, the above is equivalent to

$= \Delta\hat{H}^\circ_{f,WA}[25°C, P^*[25°C], \text{sat'd vap}] + \Delta\hat{H}_{WA}[315°C, 1 atm, gas \leftarrow 25°C, P^*[25°C], \text{sat'd vap}]$

$= \underbrace{-241.83 \text{ kJ/mol}}_{\Delta H^\circ_f(g) \text{ from Table B.1}} + \left(\underbrace{3105 \text{ kJ/kg}}_{\text{Table B.7 assuming } 1 atm \approx 1 bar} - \underbrace{2547.3 \text{ kJ/kg}}_{\text{Table B.5}}\right)\left\langle\frac{18.016 \text{ kg}}{\text{kmol}}\right\rangle\left\langle\frac{\text{kmol}}{10^3 \text{ mol}}\right\rangle$

Why can we do this?

$= -241.83 + 10.05 = \boxed{-231.78 \text{ kJ/mol}}$ for pure WA.

Felder and Rousseau, 3rd Ed., Steam Tables (B.5, B.6, and B.7)

$$\hat{H}_{WA}[315°C, 1\,bar, gas] = \hat{H}^\bullet_{WA} + \Delta\hat{H}_{WA}[315°C, 1\,bar, gas \Leftarrow 0.01°C, 0.00611\,bar, sat'd\,liq]$$

$$\hat{H}_{WA}[25°C, 1\,bar, liq] = \hat{H}^\bullet_{WA} + \Delta\hat{H}_{WA}[25°C, 1\,bar, liq \Leftarrow 0.01°C, 0.00611\,bar, sat'd\,liq]$$

By subtracting the second equation from the first equation, you cancel out $\hat{H}^\bullet_{WA}$ in the steam tables and get

$$\Delta\hat{H}_{WA}[315°C \Leftarrow 25°C] = \hat{H}_{WA}[315°C, 1\,bar, gas] - \hat{H}_{WA}[25°C, 1\,bar, liq]$$

Note that $\hat{H}^\bullet_{WA} = \hat{U}^\bullet_{WA} + P\hat{V}^\bullet_{WA}$; and $\hat{U}^\bullet_{WA} = 0$ at the triple point condition of $0.01°C$, $0.00611\,bar$, *and saturated liquid*.

Using Table B.8 instead of the steam tables, the ΔH_{WA} is 10.119 kJ/mol for water at 1 atm. The steam tables gave ΔH_{WA} = 10.05 kJ/mol, because of the assumption that 1 atm is equivalent to 1 bar, negating any interpolation in the tables. Note that 1 atm = 1.01325 bar.

cm 200
Hanyak

Energy Balance
Chemical Reactor

11/29/90
3 of 6

$\hat{H}[T_P, P_P, \bar{X}_P]$ follow **Pink Crib** for the heat-of-formation method $\hat{H}_P$ Assumptions

1. ideal solution.

Eq. 7.3

$$\hat{H}_P = 0.4\,\hat{H}_{WA} + 0.3\,\hat{H}_{CD} + 0.3\,\hat{H}_{H2}$$

$$= 0.4(-228.67) + 0.3(-377.15) + 0.3(10.89)$$

$$= \boxed{-201.35 \text{ kJ/mol}} \text{ for mixture P.}$$

Eq. 7.4

$$\hat{H}_{WA} = \Delta\hat{H}^\circ_{f,WA}[25^\circ C, P^*, sv] + \Delta\hat{H}_{WA}[400^\circ C, 1\text{ atm}, g \leftarrow 25^\circ C, P^*, sv]$$

$$= \underbrace{-241.83 \text{ kJ/mol}}_{\substack{\Delta\hat{H}^\circ_f(g) \text{ from} \\ \text{Table B.1}}} + \Big(\underbrace{3278 \text{ kJ/kg}}_{\substack{\text{Table B.7} \\ 1\text{ atm} \approx 1\text{ bar}}} - \underbrace{2547.3 \text{ kJ/kg}}_{\text{Table B.5}}\Big)\left\langle\frac{18.016\text{ kg}}{\text{kmol}}\right\rangle\left\langle\frac{\text{kmol}}{10^3\text{ mol}}\right\rangle$$

$$= -241.83 + 13.16 = \boxed{-228.67 \text{ kJ/mol}} \text{ for pure WA.}$$

Eq. 7.4

$$\hat{H}_{CD} = \Delta\hat{H}^\circ_{f,CD}[25^\circ C, 1\text{ atm}, g] + \Delta\hat{H}_{CD}[400^\circ C, 1\text{ atm}, g \leftarrow 25^\circ C, 1\text{ atm}, g]$$

$$= \underbrace{\Delta\hat{H}^\circ_{f,CD}(g)}_{\text{Table B.1}} + \underbrace{\Delta\hat{H}_{CD}[400^\circ C]}_{\text{Table B.8}}$$

$$= -393.5 \text{ kJ/mol} + 16.35 \text{ kJ/mol}$$

$$= \boxed{-377.15 \text{ kJ/mol}} \text{ for pure CD.}$$

Eq. 7.4

$$\hat{H}_{H2} = \Delta\hat{H}^\circ_{f,H2}[25^\circ C, 1\text{ atm}, g] + \Delta\hat{H}_{H2}[400^\circ C, 1\text{ atm}, g \leftarrow 25^\circ C, 1\text{ atm}, g]$$

$$= \underbrace{\Delta\hat{H}^\circ_{f,H2}(g)}_{\text{Table B.1}} + \underbrace{\Delta\hat{H}_{H2}[400^\circ C]}_{\text{Table B.8}}$$

$$= 0.0 \text{ kJ/mol} + 10.89 \text{ kJ/mol}$$

$$= \boxed{10.89 \text{ kJ/mol}} \text{ for pure H2.}$$

Using the above problem, the heat-of-reaction method is derived from the heat-of-formation method, as shown next.

CM 200
Hanyak

Energy Balance
Chemical Reactor

11/29/90
4 of 6

Standard Heat of Reaction ($\Delta\hat{H}_r^o$) Derivation

Begin with the energy balance and the molar enthalpies of Streams F and P.

Since chemical reaction is occurring, we <u>must</u> pick as our reference states the pure elements at 25°C, 1 atm, and their stable phases.

Eq'n #

Eq. 7.1d ① $$\dot{n}_F \hat{H}_F - \dot{n}_P \hat{H}_P + \dot{Q} = 0$$

{Heat of Formation Method
$\Delta\dot{H} = \dot{n}_P \hat{H}_P - \dot{n}_F \hat{H}_F$
Eqn 9.5-2 in F+R, 3rd Ed., p. 452}

Eq. 7.3 ② $$\hat{H}_F = X_{F,cm} \hat{H}_{cm} + X_{F,WA} \hat{H}_{WA}$$

where $\hat{H}_{cm}$ and $\hat{H}_{WA}$ are for the pure compounds at T_F, P_F, Ph_F, referenced to their pure elements at 25°C, 1 atm, stable phases.

Multipling Eqn ② with $\dot{n}_F$ gives:

③ $$\dot{n}_F \hat{H}_F = \dot{n}_{F,cm} \hat{H}_{cm} + \dot{n}_{F,WA} \hat{H}_{WA}$$

Substituting expressions for $\hat{H}_{cm}$ and $\hat{H}_{WA}$ in Eqn ③: gives:

④ $$\dot{n}_F \hat{H}_F = \dot{n}_{F,cm}\left\{\Delta\hat{H}^o_{f,cm}[25°C, 1 atm, g] + \Delta\hat{H}_{cm}[315°C, 1 atm, g \leftarrow 25°C, 1 atm, g]\right\} + \dot{n}_{F,WA}\left\{\Delta\hat{H}^o_{f,WA}[25°C, P^*, sv] + \Delta\hat{H}_{WA}[315°C, 1 atm, g \leftarrow 25°C, P^*, sv]\right\}$$

Simplifying the notation in Eqn ④ gives

⑤ $$\dot{n}_F \hat{H}_F = \dot{n}_{F,cm} \Delta\hat{H}^o_{f,cm}(g) + \dot{n}_{F,cm} \Delta\hat{H}_{cm}[315°C] + \dot{n}_{F,WA} \Delta\hat{H}^o_{f,WA}(g) + \dot{n}_{F,WA} \Delta\hat{H}_{WA}[315°C]$$

Using the same procedure applied to Eqns ② thru ⑤, we can produce the following for the energy content ($\dot{n}_P \hat{H}_P$) of Stream P.

Eq. 7.3 ⑥ $$\hat{H}_P = X_{P,WA} \hat{H}_{WA} + X_{P,CD} \hat{H}_{CD} + X_{P,H2} \hat{H}_{H2} \quad @ \; T_P;\; P_P,\; Ph_P$$

⑦ $$\dot{n}_P \hat{H}_P = \dot{n}_{P,WA} \hat{H}_{WA} + \dot{n}_{P,CD} \hat{H}_{CD} + \dot{n}_{P,H2} \hat{H}_{H2}$$

$$⑧\quad \dot{n}_P \hat{H}_P = \dot{n}_{P,WA}\left\{ \Delta\hat{H}^{o}_{f,WA}[25°C, P^*, SV] + \Delta\hat{H}_{WA}[400°C, 1atm, g \leftarrow 25°C, P^*, SV] \right\} +$$
$$\dot{n}_{P,CD}\left\{ \Delta\hat{H}^{o}_{f,CD}[25°C, 1atm, g] + \Delta\hat{H}_{CD}[400°C, 1atm, g \leftarrow 25°C, 1atm, g] \right\} +$$
$$\dot{n}_{P,H2}\left\{ \Delta\hat{H}_{f,H2}[25°C, 1atm, g] + \Delta\hat{H}_{H2}[400°C, 1atm, g \leftarrow 25°C, 1atm, g] \right\}$$

Simplifying the notation in Eqn ⑧ gives:

$$⑨\quad \dot{n}_P \hat{H}_P = \dot{n}_{P,WA}\,\Delta\hat{H}^{o}_{f,WA}(g) + \dot{n}_{P,WA}\,\Delta\hat{H}_{WA}[400°C] +$$
$$\dot{n}_{P,CD}\,\Delta\hat{H}^{o}_{f,CD}(g) + \dot{n}_{P,CD}\,\Delta\hat{H}_{CD}[400°C] +$$
$$\dot{n}_{P,H2}\,\Delta\hat{H}^{o}_{f,H2}(g) + \dot{n}_{P,H2}\,\Delta\hat{H}_{H2}[400°C]$$

Substituting Eqn ⑤ and Eqn ⑨ into energy balance Eqn ①
and factoring the heats-of-formation terms gives:

$$⑩\quad \{\dot{n}_{F,CM}\}\,\Delta\hat{H}^{o}_{f,CM} + \{\dot{n}_{F,WA} - \dot{n}_{P,WA}\}\,\Delta\hat{H}^{o}_{f,WA} +$$
$$\{-\dot{n}_{P,CD}\}\,\Delta\hat{H}^{o}_{f,CD} + \{-\dot{n}_{P,H2}\}\,\Delta\hat{H}^{o}_{f,H2} +$$
$$\{\dot{n}_{F,CM}\,\Delta\hat{H}_{CM}[315°C] + \dot{n}_{F,WA}\,\Delta\hat{H}_{WA}[315°C]\} -$$
$$\{n_{P,WA}\,\Delta\hat{H}_{WA}[400°C] + n_{P,CD}\,\Delta\hat{H}_{CD}[400°C] + n_{P,H2}\,\Delta\hat{H}_{H2}[400°C]\} +$$
$$\dot{Q} = 0$$

Examining the fifth set of braces ({…}) in Eqn ⑩ gives:

$$⑪\quad \left\{ \begin{matrix}\text{fifth set}\\ \text{in Eqn ⑩}\end{matrix} \right\} = \dot{n}_F\underbrace{\left(\sum_{j=1}^{2} X_{F,j}\,\Delta H_j[315°C, 1atm, g \leftarrow T_j^o, P_j^o, Ph_j^o] \right)}_{\substack{\text{Let us call this } \hat{H}'_F \text{ and note that}\\ \text{it is calculated relative to the compounds}\\ \text{(and } \underline{\text{not}} \text{ the elements) at standard conditions.}}}$$

Similarly, the sixth set of braces ({…}) in Eqn ⑩ becomes:

$$⑫\quad \left\{ \begin{matrix}\text{sixth set}\\ \text{in Eqn ⑩}\end{matrix} \right\} = \dot{n}_P\underbrace{\left(\sum_{j=1}^{3} X_{P,j}\,\Delta H_j[400°C, 1atm, g \leftarrow T_j^o, P_j^o, Ph_j^o] \right)}_{\text{Let us call this } \hat{H}'_P.}$$

cm 200 Energy Balance 11/29/90
Hanyak Chemical Reactor 6 of 6

Substituting Eqns ⑪ and ⑫ into Eqn ⑩ gives:

$$(13)\quad \{\dot n_{F,cm}\}\,\Delta\hat H^\circ_{f,cm} + \{\dot n_{F,WA} - \dot n_{P,WA}\}\,\Delta\hat H^\circ_{f,WA} + \{-\dot n_{P,CD}\}\,\Delta\hat H^\circ_{f,CD} + \{-\dot n_{P,H2}\}\,\Delta\hat H^\circ_{f,H2} + \dot n_F \hat H'_F - \dot n_P \hat H'_P + \dot Q = 0$$

Let us examine the component balances for the reactor:

$$(14)\quad cm: \quad \dot n_{F,cm} + \nu_{cm}\dot R = 0$$

$$(15)\quad WA: \quad \dot n_{F,WA} - \dot n_{P,WA} + \nu_{WA}\dot R = 0$$

$$(16)\quad CD: \quad -\dot n_{P,CD} + \nu_{CD}\dot R = 0$$

$$(17)\quad H2: \quad -n_{P,H2} + \nu_{H2}\dot R = 0$$

ν_j is the stoichiometric coefficient for compound j in the reaction. It is negative for a reactant and positive for a product.

Substituting Eqns ⑭ to ⑰ into braces ({…}) of Eqn ⑬ gives:

$$(18)\quad \{-\nu_{cm}\dot R\}\,\Delta\hat H^\circ_{f,cm} + \{-\nu_{WA}\dot R\}\,\Delta\hat H^\circ_{f,WA} + \{-\nu_{CD}\dot R\}\,\Delta\hat H^\circ_{f,CD} + \{-\nu_{H2}\dot R\}\,\Delta\hat H^\circ_{f,H2} + \dot n_F \hat H'_F - \dot n_P \hat H'_P + \dot Q = 0$$

Simplifying Eqn ⑱ gives:

$$(19)\quad -\dot R \underbrace{\sum_{j=1}^{4}\left(\nu_j\,\Delta\hat H^\circ_{f,j}\right)} + \dot n_F \hat H'_F - \dot n_P \hat H'_P + \dot Q = 0$$

Eq. 7.5d-b This is ΔH°_r, Eqn 9.3-1 in F+R, 3rd Ed., p. 447, with units of energy per number of reactions, like kJ/kg-rxns

Rearranging Eqn ⑲ gives:

Eq. 7.5d-a
$$(20)\quad \dot Q = \underbrace{\dot n_P \hat H'_P - \dot n_F \hat H'_F + \dot R\,\Delta H^\circ_r}$$

$\dot R$ has units # rxns / time
ΔH°_r has units energy / # rxns

{Heat of rxn method} This is $\Delta\dot H$, Eqn 9.5-1a in F+R, 3rd Ed., p. 451.

Why is the heat-of-formation method a better strategy for a reactor energy balance than the heat-of-reaction method? **Click here** to see why.

larger

Energy Balance
Batch Reactor

11/30/90
1 of 4

Problem 9.15

Similar to Problem 9.15 in F&R, 3rd Ed.

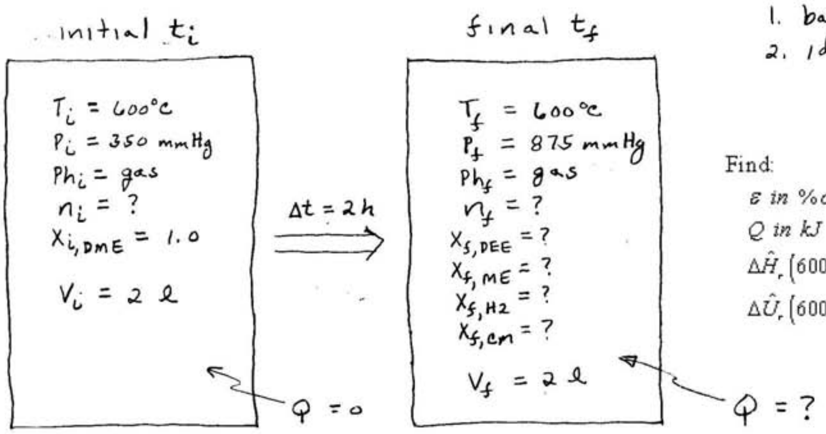
A two-liter laboratory reactor initially contains gaseous dimethyl ether at 600°C and 350 mm Hg. The reactor operates isothermally, and the dimethyl ether decomposes as follows:

$$(CH_3)_2O\ (g) \rightarrow CH_4\ (g) + H_2\ (g) + CO\ (g)$$

until the pressure in the closed vessel is 875 mm Hg after two hours. Has the reaction proceeded to completion? If not, what is the molar conversion of the dimethyl ether? How much heat is transferred into or from the reactor during the two-hour period? Finally, determine the molar enthalpy of reaction at 600°C and the molar internal energy of reaction at 600°C for the decomposition reaction.

Data for $(CH_3)_2O$ (g): Standard Heat of Formation = -180.16 kJ/mol
Heat Capacity (J/mol K) = $26.86 + 0.1659\ T(K) - 4.179 \times 10^{-5}\ T^2$

Diagram



Assumptions

1. batch process
2. ideal gas

Find:
ε in % conversion of $(CH_3)_2O$
Q in kJ
$\Delta\hat{H}_r\,(600°C)$ in kJ
$\Delta\hat{U}_r\,(600°C)$ in kJ

Additional Data

Rxn: $(CH_3)_2O(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$

Given: $\Delta\hat{H}^o_{f,DME}\,[25°c,\ 1\,atm,\ g] = -180.16\ kJ/mol$

$$\underset{\uparrow\ J/mol\cdot K}{C^g_{P,DME}} = 26.86 + 0.1659\ \underset{\uparrow\ K}{T} - 4.179 \times 10^{-5}\ T^2$$

$T_i = T_f = 600 + 273.16 = 873.16\ K$

$P_i = 350\ mmHg \left\langle \frac{1\ atm}{760\ mmHg} \right\rangle = 0.4605\ atm$

$P_f = 875\ mmHg \left\langle \frac{1\ atm}{760\ mmHg} \right\rangle = 1.1513\ atm$

CM 200
Hanyak

Energy Balance
Batch Reactor

11/30/90
2 of 4

Model {complete conversion}

① $P_i V_i = n_i R T_i$

② $P_f V_f = n_f R T_f$

③ Total: $2\,R'_I = n'_f - n_i$ Eq. 5.4i

④ $(CH_3)_2O$: $-R'_I = -n_i$ Eq. 5.5i

where prime (') means complete conversion

Know: $T_i, P_i, V_i, T_f, P_f, V_f$

D.O.F. = 10 − 4 = 6

Solution {complete conversion}

$$n_i = \frac{P_i V_i}{R T_i} = \frac{(0.4605\ \text{atm})(2\ell)}{(873.16\ \text{K})}\left(\frac{\text{mol K}}{0.08206\ \ell\cdot\text{atm}}\right)$$

$$= 0.01285\ \text{mol}$$

$$n_f = \frac{P_f V_f}{R T_f} = \frac{(1.1513\ \text{atm})(2\ell)}{(873.16\ \text{K})}\left(\frac{\text{mol K}}{0.08206\ \ell\cdot\text{atm}}\right)$$

$$= 0.03202\ \text{mol}$$

$R'_I = 1\,n_i = 0.01285$ g-rxn

$n'_f = 3\,R'_I = 0.03855$ mol

Since $n'_f > n_f$, the reaction goes to partial conversion.

Model {partial conversion}

① Total: $2\,R_I = n_f - n_i$ Eq. 5.4i

② $(CH_3)_2O$: $-R_I = n_{f,DME} - n_i$

③ CH_4: $R_I = n_{f,ME}$

④ H_2: $R_I = n_{f,H2}$

⑤ CO: $R_I = n_{f,CO}$ Eq. 5.5i

check $n_f = n_{f,DME} + \cdots + n_{f,CO}$

⑥ $\varepsilon = \dfrac{n_i - n_{f,DME}}{n_i}$

D.O.F. = # vars − # eqns
= 8 − 6 = 2

Known n_i, n_f

Solution {partial conversion}

$$R_I = \frac{n_f - n_i}{2} = \frac{0.03202 - 0.01285}{2}$$

$= 0.009585$ g-rxn

$n_{f,DME} = n_i - R_I = 0.01285 - 0.009585$
$= 0.003265$ mol

$n_{f,ME} = R_I = 0.009585$ mol

$n_{f,H2} = R_I = 0.009585$ mol

$n_{f,CO} = R_I = 0.009585$ mol

$$\varepsilon = \frac{0.01285 - 0.003265}{0.01285} * 100 = \boxed{75\ \%}$$

Check: $n_f = 0.003265 + 3 * 0.009585 = 0.03202$ mol
OK!

follow **Pink Crib** for the heat-of-formation method

Equation 7.1i-a and 7.1i-b, integral energy balance

Energy: $\underbrace{\int_{t_i}^{t_f} \dot{Q}\,dt}_{Q} = U_f - U_i$ but $H = U + PV$

⑦ $Q = (H_f - H_i) - (P_f V_f - P_i V_i)$ (kJ, see Page 4 of 4)

⑧ $H_f = H[T_f, P_f, \bar{n}_f]$ (kJ, see Page 3 of 4)

⑨ $H_i = H[T_i, P_i, n_i]$ (kJ, see Page 4 of 4)

see solution of energy balance on Page 4 of 4

CM 200
Hanyak

Energy Balance
Batch Reactor

11/30/90
3 of 4

$H[T_f, P_f, \bar{n}_f]$ follow **Pink Crib** for the heat-of-formation method

H_f Assumptions

1. Reference state is pure elements at 25°C, 1 atm, stable phase.
2. ideal gas
3. The pressure effect on the gas sensible ΔH is zero for ideal gas.

Eq. 7.3

$$H_f = n_{f,DME}\,\hat{H}_{DME} + n_{f,ME}\,\hat{H}_{ME} + n_{f,H_2}\,\hat{H}_{H_2} + n_{f,CO}\,\hat{H}_{CO}$$

$$= 0.003265(-117.75) + 0.009585(-45.39) + 0.009585(16.81) + 0.009585(-92.95)$$

$$= \boxed{-1.5493 \text{ kJ}} \quad \text{for mixture } f.$$

Eq. 7.4

$$\hat{H}_{DME} = \Delta\hat{H}^{o}_{f,DME}[25°C, 1\text{ atm}, g] + \Delta\hat{H}_{DME}[600°C, 875\text{ mmHg}, g \leftarrow 25°C, 1\text{ atm}, g]$$

$$= \Delta\hat{H}^{o}_{f,DME} + \int_{298.16\text{K}}^{873.16\text{K}} (26.86 + 0.1659\,T - 4.179\times10^{-5}T^2)\,dT$$

$$= -180.16\text{ kJ/mol} + \left[26.86(873.16-298.16) + \frac{0.1659}{2}(873.16^2 - 298.16^2) - \frac{4.179\times10^{-5}}{3}(873.16^3 - 298.16^3)\right]\frac{\text{J}}{\text{mol}\cdot\text{K}}\left\langle\frac{\text{kJ}}{10^3\text{ J}}\right\rangle$$

$$= -180.16 + 62.41 = \boxed{-117.75\text{ kJ/mol}} \quad \text{for pure DME.}$$

Eq. 7.4

$$\hat{H}_{ME} = \Delta\hat{H}^{o}_{f,ME} + \Delta\hat{H}_{ME}[600°C, 875\text{ mmHg}, g \leftarrow 25°C, 1\text{ atm}, g]$$

$$= \underbrace{-74.85\text{ kJ/mol}}_{\text{Table B.1}} + \int_{298.16\text{K}}^{873.16\text{K}} \underbrace{(19.87 + 0.05021\,T + 1.268\times10^{-5}T^2 - 11.00\times10^{-9}T^3)}_{\text{Table B.2, J/mol}\cdot\text{K}}\,dT$$

$$= -74.85\text{ kJ/mol} + \left[19.87(873.16-298.16) + \frac{0.05021}{2}(873.16^2 - 298.16^2) + \frac{1.268\times10^{-5}}{3}(873.16^3 - 298.16^3) - \frac{11\times10^{-9}}{4}(873.16^4 - 298.16^4)\right]\left\langle\frac{\text{kJ}}{10^3\text{ J}}\right\rangle$$

$$= -74.85 + 29.46 = \boxed{-45.39\text{ kJ/mol}} \quad \text{for pure ME.}$$

Eq. 7.4

$$\hat{H}_{H_2} = \Delta\hat{H}^{o}_{f,H_2} + \Delta\hat{H}_{H_2}[600°C, 875\text{ mmHg}, g \leftarrow 25°C, 1\text{ atm}, g]$$

$$= 0 + \underbrace{29.23\frac{\text{J}}{\text{mol}\cdot°C}}_{\text{Table B.3-1}}(600 - 25°C)\left\langle\frac{\text{kJ}}{10^3\text{ J}}\right\rangle = \boxed{16.81\text{ kJ/mol}} \quad \text{for } H_2.$$

Eq. 7.4

$$\hat{H}_{CO} = \Delta\hat{H}^{o}_{f,CO} + \Delta\hat{H}_{CO}[600°C, 875\text{ mmHg}, g \leftarrow 25°C, 1\text{ atm}, g]$$

$$= -110.52\text{ kJ/mol} + 30.56\frac{\text{J}}{\text{mol}\cdot°C}(600 - 25°C)\left\langle\frac{\text{kJ}}{10^3\text{ J}}\right\rangle$$

$$= -110.52 + 17.57 = \boxed{-92.95\text{ kJ/mol}} \quad \text{for pure CO.}$$

CM 200
Hanyak

Energy Balance
Batch Reactor

11/30/90
4 of 4

H [T_i, P_i, n_i] follow **Pink Crib** for the heat-of-formation method

H_i Assumptions

1. Reference state is pure elements at 25°C, 1 atm, stable phase
2. ideal gas
3. The pressure effect on the gas sensible ΔH is zero for ideal gas.

Eq. 7.3

$$H_i = n_i \hat{H}_{DME}$$

$$= 0.01285 \text{ mol } (-117.75 \text{ kJ/mol})$$

$$= \boxed{-1.5131 \text{ kJ}} \text{ for mixture } i.$$

Eq. 7.4

$$\hat{H}_{DME} = \Delta\hat{H}^{o}_{f,DME} + \Delta\hat{H}_{DME}[600°C, 350 \text{ mmHg}, g \leftarrow 25°C, 1 \text{ atm}, g]$$

$$= \underbrace{-180.16 + 62.41}_{\text{taken from } H_f \text{ calculation}} = \boxed{-117.75 \text{ kJ/mol}} \text{ for pure DME.}$$

Energy Balance **Solution:**

$$(P_f V_f - P_i V_i) = V_i(P_f - P_i) = (2\ell)(875-350 \text{ mmHg})\left\langle\frac{1.01325 \text{ bar}}{760 \text{ mmHg}}\right\rangle\left\langle\frac{100 \text{ J}}{1 \ \ell\cdot\text{bar}}\right\rangle\left\langle\frac{\text{kJ}}{10^3 \text{J}}\right\rangle$$

$$= 0.14 \text{ kJ}$$

Eq. 7 in math model

$$Q = (H_f - H_i) - (P_f V_f - P_i V_i)$$

$$Q = (-1.5493 \text{ kJ} + 1.5131 \text{ kJ}) - 0.14 \text{ kJ}$$

$$= -0.1762 \text{ kJ} = \boxed{-176.2 \text{ J}}$$

Heat of Rxn @ 600°C and 1 atm

$$\Delta H_r = \nu_{ME}\hat{H}_{ME} + \nu_{H2}\hat{H}_{H2} + \nu_{co}\hat{H}_{co} - \nu_{DME}\hat{H}_{DME} \quad @ \ 600°C + 1 \text{ atm}$$

$$= -45.39 + 16.81 - 92.95 - (-117.75) = -3.78 \text{ kJ / g-rxn}$$

$$\Delta U_r = \Delta H_r - (\nu_{ME} + \nu_{H2} + \nu_{co} - \nu_{DME}) RT$$

$$= -3.78 \frac{\text{kJ}}{\text{g-rxn}} - \left(2 \frac{\text{mol}}{\text{g-rxn}}\right)\left(\frac{\cancel{0.08206} \ \cancel{\ell\cdot\text{atm}}}{\cancel{\text{mol}}\cdot\cancel{K}}\right)(873.16 \ \cancel{K})\left\langle\frac{8.314 \ \cancel{J}}{\cancel{0.08206} \ \cancel{\ell\cdot\text{atm}}}\right\rangle\left\langle\frac{\text{kJ}}{10^3 \cancel{J}}\right\rangle$$

$$= -3.78 - 14.52 = -18.3 \text{ kJ / g-rxn}$$

larger

eLEAPS How To

Adiabatic T

An eLEAPS Session

eLEAPS script

1 of 9

Problem Statement

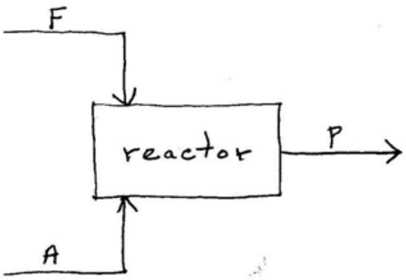
Similar to Example 9.6-2 in F&R, 3rd Ed.

Pure methanol at 25°C and 1 atm is to be fed to a furnace. Air in 100% excess at 100°C is also to be fed into the furnace. If you are to select the material of construction for the furnace, what is the highest temperature that the furnace walls will have to withstand?

Conceptual Model

$T_F = 25°C$
$P_F = 1$ atm
$Ph_F =$ liquid
$\dot{n}_F = 100$ mol/h
$X_{F,MH} = 1.0$

$T_A = 100°C$
$P_A = 1$ atm
$Ph_A =$ gas
$\dot{n}_A =$?
$X_{A,O2} = 0.21$
$X_{P,N2} = 0.79$



$T_P =$?
$P_P = 1$ atm
$Ph_P =$?
$\dot{n}_P =$?
$X_{P,O2} =$?
$X_{P,N2} =$?
$X_{P,CD} =$?
$X_{P,WA} =$?

Finds: T_P in °C

Other Givens: 100% excess air

Rxn I: $2\,CH_3OH + 3\,O_2 \longrightarrow 2\,CO_2 + 4\,H_2O$

$$\Delta\hat{H}_r^o = -2\,\Delta\hat{H}^o_{f,MH}(l) - 3\,\Delta\hat{H}^o_{f,O2}(g) + 2\,\Delta\hat{H}^o_{f,CD}(g) + 4\,\Delta\hat{H}^o_{f,WA}(l)$$

$$= -\frac{2\text{ g-mol MH}}{\text{g-rxn}}\left(-238.6\,\frac{\text{kJ}}{\text{g-mol MH}}\right) - \frac{3\text{ g-mol O2}}{\text{g-rxn}}\left(0.0\,\frac{\text{kJ}}{\text{g-mol O2}}\right)$$

$$+ \frac{2\text{ g-mol CD}}{\text{g-rxn}}\left(-393.5\,\frac{\text{kJ}}{\text{g-mol CD}}\right) + \frac{4\text{ g-mol WA}}{\text{g-rxn}}\left(-285.84\,\frac{\text{kJ}}{\text{g-mol WA}}\right)$$

$$= -1453.16\,\frac{\text{kJ}}{\text{g-rxn}} \cdot \frac{\text{g-rxn}}{2\text{ g-mol MH}} = -726.58\,\frac{\text{kJ}}{\text{g-mol MH}}$$

∴, exothermic

Do this to determine if $T_P < T_A$ or $T_P > T_F$.

Assumptions

1. complete combustion of MeOH
2. Streams F, A, & P at 1 atm
3. Stream A is 21/79 mol % O_2/N_2
4. Continuous process; adiabatic
5. steady state
6. neglect ΔKE & ΔPE
7. no shaft work
8. Basis: $\dot{n}_F = 100$ mol/h

Popup notes and/or web links on Pages 7-60 to 7-67 can be accessed through the above web link for the **eLEAPS script**.

Introduction

In this instructional companion, Appendices A, B, and C review the definitions of pertinent variables, the conversion of units, and the fundamentals of algebra. Basically, these three appendices cover knowledge you have gained in your previous encounters with mathematics, chemistry, and physics. These appendices serve to reacquaint you with this knowledge and to focus that knowledge as it relates to chemical engineering. With time you will **obtain mastery** of the information in these three appendices, because this information is fundamental to doing material and energy balances. You should refer to these appendices often whenever the need arises.

The basic definitions covered in Appendix A are of quantities commonly needed to solve the material and energy balances of chemical process units. These quantities are associated with **the chemical substances** found in process streams and process units. They are categorized as follows:
{use the **LoQ** link to return to this list of quantities.}

- Primary quantities - length, mass, time, temperature, and mass-mole.
- General quantities - area, volume, velocity, acceleration, and gravity.
- Chemical entities - atom, molecule, compound, mixture, component, and reaction.
- Chemical quantities - stoichiometric ratio, mass-atom, atomic weight, molecular weight of j, and molecular weight.
- Force quantities - force, weight, and pressure.
- Physical quantities - density, specific gravity, specific volume, molar density, and molar volume.
- Composition quantities - mass fraction, ppm or ppb, mole fraction, volume fraction, mass concentration, and molar concentration.
- Rate quantities - mass flow, molar flow, volumetric flow, mass velocity, and molar flux.

These quantities have dimensions and units, and they are represented by symbolic names called variables, such as **L** for length, **m** for mass, and **T** for temperature. The dimensions are the basic concepts of measurement, such as length, time, mass, temperature, etc. The units are means of expressing the dimensions.

In the definitions of this appendix, the variable names for quantities conform, with slight modifications, to the convention adopted by the American Institute of Chemical Engineering (AIChE), as described in their document entitled "Letter Symbols for Chemical Engineering" [AIChE, 1979a]. Also, the magnitudes and units of these variable quantities follow the convention described in the AIChE document entitled "SI for AIChE: A Guide for the Implementation of the International System of Units by the Chemical Engineering Profession" [AIChE, 1979b].

As a chemical engineer, you must be conversant in three different systems of units—the **cgs**, **mks**, and **fps** systems. The **cgs** (or centimeter-gram-second) system is the formerly-used common scientific system of units. The **mks** (or meter-kilogram-second) system is the SI (Systèm International) system of units, adopted as the international standard. The United States is the last large country that is slowly converting to the SI standard. The **fps** (or foot-pound-second) system is the American engineering system of units, currently used by engineers in the United States. You must master these three systems of units, since the information needed to solve any chemical engineering problem may be expressed in all three systems of units.

To aid your learning process, a common format has been adopted for the basic definitions found in this appendix. Each definition begins with a header line that contains the name of the quantity, its variable symbol, and its dimensions. This line is then followed by several sets of ordered paragraphs, whose purposes are as follows:

- A conceptual definition of the quantity.
- Examples of its variable and possible values in the **cgs**, **mks**, and **fps** systems of units, in that order.
- A mathematical definition of the quantity, wherever appropriate.
- A visual description of the quantity.
- The interrelationship of various quantities, wherever appropriate.
- Pertinent information for your enlightenment, wherever appropriate.

These sets of ordered paragraphs are separated by double-spaced lines.

In the definitions that follow, the terms chemical substance and substance are used extensively, and they are synonymous. In general, a **chemical substance** is any physical matter containing one or more chemical components at a definite composition. A **component** can be one of the following three chemical entities:

• a free element,	such as aluminum (Al), carbon (C), or radon (Rn);
• an elemental compound,	such as hydrogen (H_2), nitrogen (N_2), or sulfur (S_8);
• a chemical compound,	such as carbon dioxide (CO_2) or water (H_2O).

Of the 118 elements, elemental compounds are those nine elements—Br, Cl, F, H, I, N, O, P, and S—that exist as either diatomic or polyatomic molecules in their natural form. The remaining elements are free, since they are considered to occur naturally as one-atom molecules. Chemical compounds contain two or more elements chemically united in fixed proportions, such as CO_2 and H_2O. Although elemental compounds have multiple atoms of the **same** element, we will treat them as a special subclass of chemical compounds.

The **composition** of a chemical substance is the formulas and amounts of the chemical components within that substance. The amounts are commonly expressed on a relative basis in percentages. For example, the chemical substance of dry air contains approximately 21 volume percent O_2 (oxygen) and 79 volume percent N_2 (nitrogen). When a chemical substance contains only one chemical component, that component is called a **pure** component, because the composition of that component is 100 percent. Likewise, the chemical substance is also referred to as a pure substance. Deionized water *in vacuo* (i.e., in isolation) is an example of a pure substance; it contains only one component (H_2O).

Primary Quantities

Length, **L**, "length". LoQ

It is a measure of the distance between two points. The dimension for quantity **L** is "length".

For example, **L** = 1000 centimeters
or **L** = 1000 cm

For example, **L** = 10 meters
or **L** = 10 m

For example, **L** = 32.808 feet
or **L** = 32.808 ft

The distance across your knuckles on your hand is approximately 3 inches. Although two hands make a pair, four hands make a foot.

The symbols **D** and **r** are used for the special lengths called diameter and radius, respectively. Also, the symbols **H**, **h**, and **z** are used to represent height.

Mass, **m**, "mass". LoQ

It is a measure of the amount of matter in a physical object. The dimension for quantity **m** is "mass".

For example, **m** = 10 000 grams
or **m** = 10 000 g

For example, **m** = 10 kilograms
or **m** = 10 kg

For example, **m** = 22.0462 pound-mass
or **m** = 22.0462 lb_m

A physical object is a chemical substance in a particular state of aggregation (solid, liquid, or gas) and is stable in form. It can be either (1) a solid such as a block of aluminum or 100 grains of salt, (2) a liquid such as 2 liters of water, or (3) a gas such as 10 liters of methane contained in a tank.

When two or more states (also called phases) of a substance coexist (i.e., at the same time), each phase is a separate object. For the chemical substance of water at atmospheric pressure, the phases of water and ice coexist at 0˚C; therefore, two objects—water and ice—are present. Likewise, two objects are present when water and steam coexist at 100˚C.

The mass of a non-reacting object remains **constant**. A liter of water has the same amount of mass at New York City, as it does in the "Mile-High" City of Denver, Colorado.

Time, **t**, "time". LoQ

It is a measure of the finite duration of an event or process. The dimension for quantity **t** is "time". The base unit of time in all three systems of units is seconds.

For example, **t** = 54 seconds
or **t** = 54 s

Other units of time are often used like minute (min), day (d), and year (yr).

Running the 100-meter dash requires a certain amount of time, say 10 seconds, if you are in excellent condition.

Temperature, **T**, "temperature". LoQ

It is a measure of the average internal energy possessed by the molecules of a chemical substance in a particular state of aggregation (solid, liquid, or gas). The dimension for quantity **T** is "temperature".

For example, **T** = 25.00 Celsius
or **T** = 25.00˚C

For example, **T** = 298.15 Kelvin
or **T** = 298.15 K

For example, **T** = 77.00 Fahrenheit
or **T** = 77.00˚F
or **T** = 536.67 Rankine
or **T** = 536.67˚R

The internal energy of a substance is due to the rotational, translational, and vibrational motion of that substance's molecules, as well as the chemical bonding between atoms of the molecules. As the temperature of a substance increases, the internal energy of the substance increases resulting in the molecules growing farther apart. The most abrupt changes in molecular distance occur at phase transitions, such as from a solid to a liquid and from a liquid to a gas.

For example, the chemical substance of water at atmospheric pressure exists as a solid (called ice) below 0˚C, exists as a liquid (called water) between 0˚C and 100˚C, and exists as a gas (called steam) above 100˚C. The phase transitions of substance water occur at 0˚C, where ice and water coexist, and 100˚C, where water and steam coexist.

Mass-Mole, **n**, "mass-mole". LoQ

It represents Avogadro's number (N_A) of molecules of a chemical substance, when the mass of those N_A molecules is expressed in grams. This collection of molecules has a finite mass, whose magnitude depends upon the chemical substance. In other words, N_A molecules of water has a different mass than N_A molecules of carbon dioxide.

The dimension for quantity **n** is "mass-mole", where the prefix "mass-" can be either "gram-", "kilogram-", or "pound-". This prefix indicates the unit in which the mass of a chemical substance is to be expressed.

For example, $\mathbf{n} = 2$ gram-mole H_2O
or $\mathbf{n} = 2$ g-mol H_2O
or $\mathbf{n} = 2\cdot(6.022 \text{ x } 10^{23})$ molecules H_2O.

For example, $\mathbf{n} = 2$ kilogram-mole H_2O
or $\mathbf{n} = 2$ kg-mol H_2O
or $\mathbf{n} = 2\cdot1000\cdot(6.022 \text{ x } 10^{23})$ molecules H_2O.

For example, $\mathbf{n} = 2$ pound-mole H_2O
or $\mathbf{n} = 2$ lb-mol H_2O
or $\mathbf{n} = 2\cdot453.592\cdot(6.022 \text{ x } 10^{23})$ molecules H_2O.

As a **standard definition**, one gram-mole (also called a mole) of any substance is equivalent to $(6.022\ 141\ 79 \pm 0.000\ 000\ 30) \text{ x } 10^{23}$ molecules of that substance, where the mass of those molecules is to be expressed in grams. This standard for Avogadro’s number (N_A) is reported by the Physical Measurement Laboratory of the United States National Institute of Standards and Technology (NIST). The definitions for the kilogram-mole and pound-mole are derived from this standard definition for the gram-mole, as described on the next page†.

The precise, International System of Units (SI) definition of the mole is “the amount of a substance that contains as many elementary entities as there are atoms in 0.012 kilogram of pure carbon-12.” The elementary entities—atoms, molecules, ions, etc.—for that substance <u>must</u> be identified when the mole is used. The SI unit for the mass-mole is "mol", which also means "g-mol". For our purposes, the elementary entities are atoms, molecules, and reaction events.

Pure carbon-12 contains $6.022 \text{ x } 10^{23}$ molecules per gram-mole. Since one molecule of pure carbon-12 contains one atom, pure carbon-12 also contains $6.022 \text{ x } 10^{23}$ atoms per gram-mole.

As indicated in the above examples, three basic **mass-moles** exist, depending upon how the mass of a chemical substance is to be expressed. Their definitions are:

$$1 \text{ g-mol} \equiv (6.022 \text{ x } 10^{23}) \text{ molecules,}$$
$$1 \text{ kg-mol} \equiv 1000\cdot(6.022 \text{ x } 10^{23}) \text{ molecules,}$$
$$1 \text{ lb-mol} \equiv 453.592\cdot(6.022 \text{ x } 10^{23}) \text{ molecules.}$$

The kilogram-mole is 1000 times more molecules than the gram-mole, while the pound-mole is 453.592 times more molecules than the gram-mole.

† The definitions for one kilogram-mole and one pound-mole are selected so that the magnitudes for the mass of molecules expressed in kilograms and pounds-mass are identical to the magnitude of the standard mass of a chemical substance expressed in grams. In general,

1 g-mol of **j** = $(6.022 \text{ x } 10^{23})$ molecules of **j** = Y g of **j**,
1 kg-mol of **j** = $1000 \cdot (6.022 \text{ x } 10^{23})$ molecules of **j** = Y kg of **j**,
1 lb-mol of **j** = $453.592 \cdot (6.022 \text{ x } 10^{23})$ molecules of **j** = Y lb_m of **j**,

where the symbol **j** represents a chemical substance, and the magnitude Y is the same no matter what mass units are used. For the chemical substance of water, Y equals 18.0153. As we will see later, this magnitude Y is called the molecular weight of a chemical substance.

General Quantities

Area, A, "length^2". LoQ

It is the 2-dimensional space formed by the intersection of an imaginary plane that cuts through the mass of an object. This planar space could be a square, a rectangle, a circle, a triangle, etc., depending upon the 3-dimensional shape of the object. The dimension for quantity **A** is "length^2".

For example, **A** = 10 x 10^4 square centimeters
or **A** = 10 x 10^4 cm^2

For example, **A** = 10 square meters
or **A** = 10 m^2

For example, **A** = 107.639 square feet
or **A** = 107.639 ft^2

The cross-sectional area of a fluid, like water, held in a cylindrical container is a circular plane that is parallel to the cylinder's base. This area is equal to "$\pi \cdot D^2/4$", where D is the inside diameter of the cylinder.

Unlike a solid substance, a fluid substance, by definition, takes the shape of its container and is capable of flowing. This fact is true for both liquid and gaseous substances. Therefore, to determine the cross-sectional area of a fluid object, one must measure the inside planar dimensions of the container holding that fluid.

Volume, V, "length^3". LoQ

It is the 3-dimensional space occupied by the mass of an object. The dimension for quantity **V** is "length^3".

For example, **V** = 10 x 10^6 cubic centimeters
or **V** = 10 x 10^6 cm^3
or **V** = 10 x 10^3 liters
or **V** = 10 x 10^3 L

For example, **V** = 10 cubic meters
or **V** = 10 m^3

For example, **V** = 353.1467 cubic feet
or **V** = 353.1467 ft^3

The volume of a rectangular solid is equal to the width times the height times the depth of the rectangle; that is, $V = w \cdot h \cdot d$. A red brick that is 0.2 meter wide, 0.05 meter high, and 0.1 meter deep has a volume of 0.001 m^3.

The volume of a fluid object is determined by using the inside dimensions of the container holding that fluid substance.

As a general (or first) principle, **the volume of any solid, liquid, or gaseous substance is a function of that substance's temperature, pressure, chemical composition, and mass**. For example, when the temperature of 10 kg of water increases from 25˚C to 75˚C, the water's volume increases from 10 liters to 10.3 liters. Because of the temperature rise, the internal energy of the water increases, causing the molecular distances to expand, and thus the volume to increase. An increase in pressure causes the molecular distances to compress, and the volume to decrease. Changes in composition cause the molecules to attract or repel one another, and the volume to either decrease or increase.

Velocity, **u** or **v**, "length / time". LoQ

It is a rate at which an object moves, expressed as distance per unit of time. The dimensions for quantity **u** or **v** are "length per time".

For example, **u** = 1000 centimeters per second
or **u** = 1000 cm/s

For example, **u** = 10 meters per second
or **u** = 10 m/s

For example, **u** = 32.808 feet per second
or **u** = 32.808 ft/s

If a car travels a distance of 447 meters in 100 seconds at a uniform speed, then the car's velocity is 4.47 m/s, which is 14.67 ft/s or 10 miles per hour (mph).

Acceleration, **a**, "length / time^2". LoQ

It is a rate of change of an object's velocity with respect to time. The dimensions for quantity **a** are "length per time^2".

For example, **a** = 1000 centimeters per square second
or **a** = 1000 cm/s^2

For example, **a** = 10 meters per square second
or **a** = 10 m/s^2

For example, **a** = 32.808 feet per square second
or **a** = 32.808 ft/s^2

If a car is traveling at an initial velocity of 5 m/s, and it begins to accelerate at a uniform rate of 1 m/s^2 for 10 seconds, then the car's new speed or velocity is 15 m/s.

Gravitational Acceleration, **g**, "length / $time^2$". LoQ

It is an acceleration experienced by an object due to that object's presence in a gravitational field, such as Earth's gravity. The dimensions for quantity **g** are "length per $time^2$".

For example, **g** = 980.665 centimeters per square second
g = 980.665 cm/s^2

For example, **g** = 9.806 65 meters per square second
g = 9.806 65 m/s^2

For example, **g** = 32.1740 feet per square second
g = 32.1740 ft/s^2

The gravitational acceleration acting on an object is a function of that object's distance from the center of the gravitational field, such as Earth's center. An object at sea level and 45° latitude would experience a **g** of 980.665 cm/s^2, while that same object at Denver, Colorado would experience a **g** of 979.696 cm/s^2.

The value of **g** at any location on Earth is given by the Helmert's equation:

$$\mathbf{g} = 980.665 - 2.5928 \text{ Cos } 2\theta + 0.0069 \text{ Cos}^2 2\theta - 3.086 \times 10^{-6} \text{ H}$$

where **g** is the acceleration due to Earth's gravity at a location, cm/s^2;
θ is the location's latitude on the Earth's surface, degrees;
H is the location's height above sea level, centimeters.

The International Standard (SI) value of the acceleration due to gravity is 9.806 65 m/s^2, measured at sea level and 45° latitude.

Chemical Entities

Atom

LoQ

It is a chemical element of which 118 are now recognized, as of 2011. An atom cannot be separated into simpler entities by chemical means.

For example,	Element **C**	is one atom of carbon;
and	Element **H**	is one atom of hydrogen;
and	Element **Au**	is one atom of gold;
and	Element **Pb**	is one atom of lead.

The Periodic Table of the Elements defines the names, symbols, atomic numbers, and atomic weights of all 118 elements.

All of the elements are regarded as free elements, except for nine of them—Br, Cl, F, H, I, N, O, P, and S—(i.e., bromine, chlorine, fluorine, hydrogen, iodine, nitrogen, oxygen, phosphorus, and sulfur, respectively). Free elements are considered to occur naturally as one-atom molecules. The nine exceptions exist as either diatomic or polyatomic molecules in their natural form.

Molecule

LoQ

It is the smallest aggregate of atoms considered to be an electrically-neutral chemical substance. A molecule of a chemical substance is represented symbolically by a chemical formula. This formula specifies the number of elemental atoms in that molecule.

For example,	**C**, **Au**, and **Ar**	are atom molecules for carbon, gold, and argon;
and	$\mathbf{Cl_2}$ and $\mathbf{H_2S}$	are molecules for chlorine and hydrogen sulfide.

The formula **Ar** implies that one molecule of argon contains one atom of argon, while the formula H_2S implies that one molecule of hydrogen sulfide contains two atoms of hydrogen and one atom of sulfur.

Compound

LoQ

It is a chemical substance composed of two or more atoms chemically united in a fixed proportion and represented symbolically by a chemical formula.

For example,	compound $\mathbf{N_2}$	means one molecule of nitrogen contains two atoms of elemental nitrogen;
and	compound $\mathbf{H_2O}$	means one molecule of water contains two atoms of hydrogen and one atom of oxygen.

In other words, a compound is a chemical substance that has more than one atom. Free elements are not chemical compounds.

Mixture

LoQ

It is an aggregate of two or more chemical substances that are not chemically united and that exist in relative amounts to each other. The formulas of these chemical substances and their relative amounts are called the mixture's **composition**.

For example, a mixture of **dry air** near sea level contains the following chemical substances:

Substance	Formula	Mole Percent
Nitrogen	N_2	78.03%
Oxygen	O_2	20.99%
Argon	Ar	0.94%
Carbon Dioxide	CO_2	0.03%
Others	--	0.01%

		100.00%

The other substances are neon, helium, methane, krypton, nitrous oxide, hydrogen, xenon, ozone, ammonia, carbon monoxide, iodine, nitrogen dioxide, and sulfur dioxide. They are called **trace** substances, because their composition is very small (less than 1/100 of a mole percent). The "Formula" and "Mole Percent" columns represent the **composition** of the dry air mixture.

Component

LoQ

It is one of the chemical substances (either a free element or a compound) in a chemical mixture.

For example, element **Ar** is one component in the dry-air mixture,
and compound $\mathbf{O_2}$ is another component in the dry-air mixture,
and compound $\mathbf{CO_2}$ is another component in the dry-air mixture.

A mixture is often referred to as a chemical substance, because it is an aggregate of chemical components (i.e., substances).

Reaction

LoQ

It is a balanced chemical relationship that indicates the combining ratios between reacting substances and their products. This relationship is called the stoichiometry of the reaction, or the stoichiometric balance. The general format for the stoichiometric balance is either "reactants → products" for an irreversible reaction or "reactants ⇄ products" for a reversible reaction.

For example, $2\ H_2 + O_2 \rightarrow 2\ H_2O$ implies that two molecules of hydrogen react with one molecule of oxygen to produce two molecules of water.

In the stoichiometric relationship for the water reaction, the "2" for hydrogen, the implied "1" for oxygen, and the "2" for water are called the **stoichiometric coefficients**. Their values are chosen to balance the number of atoms for each element appearing in the reactants with those appearing in the products. For the above water reaction, the elemental atoms balance is as follows:

	reactant side	product side
Element **H**	4 atoms	4 atoms
Element **O**	2 atoms	2 atoms

The stoichiometric relationship for a chemical reaction must be balanced before it can be used.

The coefficients in a stoichiometric balance have units. For the above water reaction, the units are as follows:

$$2\ \frac{molecules\ H_2}{reaction\ \ event} + 1\ \frac{molecules\ O_2}{reaction\ \ event} \rightarrow 2\ \frac{molecules\ H_2O}{reaction\ \ event}$$

Thus, each reaction event combines 2 molecules of H_2 and 1 molecule of O_2 to form 2 molecules of H_2O. If Avogadro's number ($N_A = 6.022 \times 10^{23}$) of reaction events is occurring simultaneously, then the units are expressed as follows:

$$2\ \frac{N_A\ molecules\ H_2}{N_A\ reaction\ \ events} + 1\ \frac{N_A\ molecules\ O_2}{N_A\ reaction\ \ events} \rightarrow 2\ \frac{N_A\ molecules\ H_2O}{N_A\ reaction\ \ events}$$

$$2\ \frac{g-mol\ H_2}{g-rxn} + 1\ \frac{g-mol\ O_2}{g-rxn} \rightarrow 2\ \frac{g-mol\ H_2O}{g-rxn}$$

This stoichiometric balance is read as two gram-moles of hydrogen react with one gram-mole of oxygen to produce two gram-moles of water per gram-reaction events. From the above relationships, one can deduce the following conversion factors:

1 g-mol ≡ 6.022×10^{23} molecules,
1 g-rxn ≡ 6.022×10^{23} reaction events.

Since the terms "mole" and "gram-mole" are synonymous, the gram-mole version of the stoichiometric balance can also be read as two moles of hydrogen react with one mole of oxygen to produce two moles of water per gram-reaction events.

If (1000·N_A) reaction events are occurring simultaneously, then the units are expressed as follows:

$$2\,\frac{1000\cdot N_A\ molecules\ H_2}{1000\cdot N_A\ reaction\ \ events} + 1\,\frac{1000\cdot N_A\ molecules\ O_2}{1000\cdot N_A\ reaction\ \ events} \rightarrow 2\,\frac{1000\cdot N_A\ molecules\ H_2O}{1000\cdot N_A\ reaction\ \ events}$$

$$2\,\frac{kg-mol\ H_2}{kg-rxn} + 1\,\frac{kg-mol\ O_2}{kg-rxn} \rightarrow 2\,\frac{kg-mol\ H_2O}{kg-rxn}$$

This stoichiometric balance is read as two kilogram-moles of hydrogen react with one kilogram-mole of oxygen to produce two kilogram-moles of water per kilogram-reaction events. From the above relationships, one can deduce the following conversion factors:

1 kg-mol ≡ 1000 g-mol ≡ 1000·(6.022 x 10^{23}) molecules,
1 kg-rxn ≡ 1000 g-rxn ≡ 1000·(6.022 x 10^{23}) reaction events.

Since the terms "kmol" and "kilogram-mole" are synonymous, the kilogram-mole version of the stoichiometric balance can also be read as two kmoles of hydrogen react with one kmole of oxygen to produce two kmoles of water per kilogram-reaction events.

If (453.592·N_A) reaction events are occurring simultaneously, then the units are expressed as follows:

$$2\,\frac{453.592\cdot N_A\ molecules\ H_2}{453.592\cdot N_A\ reaction\ \ events} + 1\,\frac{453.592\cdot N_A\ molecules\ O_2}{453.592\cdot N_A\ reaction\ \ events} \rightarrow 2\,\frac{453.592\cdot N_A\ molecules\ H_2O}{453.592\cdot N_A\ reaction\ \ events}$$

$$2\,\frac{lb-mol\ H_2}{lb-rxn} + 1\,\frac{lb-mol\ O_2}{lb-rxn} \rightarrow 2\,\frac{lb-mol\ H_2O}{lb-rxn}$$

This stoichiometric balance is read as two pound-moles of hydrogen react with one pound-mole of oxygen to produce two pound-moles of water per pound-reaction events. From the above relationships, one can deduce the following conversion factors:

1 lb-mol ≡ 453.592 g-mol ≡ 453.592·(6.022 x 10^{23}) molecules,
1 lb-rxn ≡ 453.592 g-rxn ≡ 453.592·(6.022 x 10^{23}) reaction events,

Based on the four forms of the stoichiometric balance described above, all coefficients in any balance can be read as either molecules per reaction event, g-mol (or mol) per g-rxn, kg- mol (kmol) per kg-rxn, or lb-mol per lb-rxn. In general, the molar units on any stoichiometric coefficient must be expressed per number of reaction events.

When balancing a stoichiometric relationship, the stoichiometric coefficients should be expressed using the lowest common denominator of one for all of the coefficients. Thus, the following is the preferred form for the water reaction balance:

$$2\ H_2 + 1\ O_2 \rightarrow 2\ H_2O$$

while these are not:

$$1\ H_2 + \tfrac{1}{2}\ O_2 \rightarrow 1\ H_2O$$
$$4\ H_2 + 2\ O_2 \rightarrow 4\ H_2O$$

The last two expressions for the stoichiometric balance are very awkward to work with because of how the units must be expressed for the coefficients. They <u>must be interrupted</u> as follows for the "g-mol" form:

$$1\ \frac{g-mol\ H_2}{\tfrac{1}{2}\ g-rxn} + \tfrac{1}{2}\ \frac{g-mol\ O_2}{\tfrac{1}{2}\ g-rxn} \rightarrow 1\ \frac{g-mol\ H_2O}{\tfrac{1}{2}\ g-rxn}$$

$$4\ \frac{g-mol\ H_2}{2\ g-rxn} + 2\ \frac{g-mol\ O_2}{2\ g-rxn} \rightarrow 4\ \frac{g-mol\ H_2O}{2\ g-rxn}$$

Similar interruptions exist for the "kg-mol" and "lb-mol" forms. Basically, the denominator of each unit must contain that number that would result in the coefficients having the lowest common denominator of one. Thus, the <u>preferred form</u> for the stoichiometric balance should be used since each coefficient is automatically expressed per 1 g-rxn, 1 kg-rxn, or 1 lb-rxn.

The stoichiometric balance is a <u>concise</u> statement that implies "total mass is conserved during a chemical reaction." For example, when two gram-moles of hydrogen completely reacts with one gram-mole of oxygen, two gram-moles of water are produced. According to the stoichiometric balance, the combined mass of the reactants (i.e., H_2 and O_2) must equal the combined mass of the products (i.e., H_2O). The table below shows this equality for g-mol units, kg-mol units, and lb-mol units.

	Reactant Side		Product Side
2 g-mol **H_2**	4.031 88 g		
1 g-mol **O_2**	31.998 80 g		
2 g-mol **H_2O**			36.030 68 g
	36.030 68 g	=	36.030 68 g
2 kg-mol **H_2**	4.031 88 kg		
1 kg-mol **O_2**	31.998 80 kg		
2 kg-mol **H_2O**			36.030 68 kg
	36.030 68 kg	=	36.030 68 kg
2 lb-mol **H_2**	4.031 88 lb_m		
1 lb-mol **O_2**	31.998 80 lb_m		
2 lb-mol **H_2O**			36.030 68 lb_m
	36.030 68 lb_m	=	36.030 68 lb_m

where the molecular weights of H_2, O_2, and H_2O were used to convert molar to mass units:

M_{H2} = 2.015 94 g/g-mol or kg/kg-mol or lb_m/lb-mol,
M_{O2} = 31.998 80 g/g-mol or kg/kg-mol or lb_m/lb-mol,
M_{WA} = 18.015 34 g/g-mol or kg/kg-mol or lb_m/lb-mol.

Chemical Quantities

Stoichiometric Ratio, $\mathbf{SR}_{j1/j2} = \nu_{j1} / \nu_{j2}$, "mass-moles j1 / mass-moles j2". LoQ

It is a dimensionless ratio of the stoichiometric coefficient of one chemical substance to the stoichiometric coefficient of another chemical substance, where both substances appear in a balanced stoichiometric relationship. The dimensions for quantity $\mathbf{SR}_{j1/j2}$ are "mass-moles of j1 per mass-moles of j2".

For example,	$\mathbf{SR}_{H_2/H_2O}$	= 2 g-mol H_2 / 2 g-mol H_2O	in the water reaction,
and	$\mathbf{SR}_{O_2/H_2O}$	= 1 g-mol O_2 / 2 g-mol H_2O	in the water reaction.
For example,	$\mathbf{SR}_{H_2/H_2O}$	= 2 kg-mol H_2 / 2 kg-mol H_2O	in the water reaction,
and	$\mathbf{SR}_{O_2/H_2O}$	= 1 kg-mol O_2 / 2 kg-mol H_2O	in the water reaction.
For example,	$\mathbf{SR}_{H_2/H_2O}$	= 2 lb-mol H_2 / 2 lb-mol H_2O	in the water reaction,
and	$\mathbf{SR}_{O_2/H_2O}$	= 1 lb-mol O_2 / 2 lb-mol H_2O	in the water reaction,

where the magnitude of ratio $\mathbf{SR}_{j1/j2}$ is the same no matter what mass-mole units are used.

Mathematically, the stoichiometric ratio ($\mathbf{SR}_{j1/j2}$) is equal to the stoichiometric coefficient of one chemical substance (ν_{j1}) divided by the stoichiometric coefficient of another chemical substance (ν_{j2}); that is, $\mathbf{SR}_{j1/j2} = \nu_{j1} / \nu_{j2}$.

The symbol ν, used for the stoichiometric coefficient, is the lower-case letter for nu in the Greek alphabet. Nu corresponds to the letter "n" in the English alphabet.

Mass-Atom of k, $\mathbf{a}_{j,k}$, "mass-atoms k / mass-mole j". LoQ

It represents Avogadro's number (N_A) of atoms of an element **k** in a chemical substance **j**, when the mass-mole for that substance is expressed as one gram-mole. A chemical substance can be either a free element or a compound.

The dimensions for quantity $\mathbf{a}_{j,k}$ are "mass-atoms of k per mass-mole of j", where the prefix "mass-" can be either "gram-", "kilogram-", or "pound-". This prefix indicates the unit in which the mass of chemical substance **j** is to be expressed.

For example,	$\mathbf{a}_{H_2O,H}$	= 2	g-atom H / 1 g-mol H_2O
or	$\mathbf{a}_{H_2O,H}$	= $2 \cdot (6.022 \times 10^{23})$	atoms H / 1 g-mol H_2O.
For example,	$\mathbf{a}_{H_2O,H}$	= 2	kg-atom H / 1 kg-mol H_2O
or	$\mathbf{a}_{H_2O,H}$	= $2 \cdot 1000 \cdot (6.022 \times 10^{23})$	atoms H / 1 kg-mol H_2O.

For example, $\mathbf{a}_{H_2O,H} = 2$ lb-atom H / 1 lb-mol H_2O

or $\mathbf{a}_{H_2O,H} = 2 \cdot 453.592 \cdot (6.022 \text{ x } 10^{23})$ atoms H / 1 lb-mol H_2O.

The magnitudes of quantity $\mathbf{a}_{j,k}$ are identical when its units are either "g-atom k / g-mol j", "kg-atom k / kg-mol j", or "lb-atom k / lb-mol j".

In the double subscripts on the symbol **a**, the first one (**j**) is for the chemical substance, and the second (**k**) is for an element in that substance. The convention for double subscripts is that the second subscript is for a sub-entity of the entity represented by the first subscript. For example, subscript **j** might represent a blue, orange, or brown basket, while subscript **k** might be the green, red, or yellow apples in that basket.

As indicated in the above examples, three basic **mass-atoms** exist, depending upon the mass-mole being used for a chemical substance. Their definitions are:

$$1 \text{ g-atom} \equiv (6.022 \text{ x } 10^{23}) \text{ atoms},$$
$$1 \text{ kg-atom} \equiv 1000 \cdot (6.022 \text{ x } 10^{23}) \text{ atoms},$$
$$1 \text{ lb-atom} \equiv 453.592 \cdot (6.022 \text{ x } 10^{23}) \text{ atoms}.$$

The kilogram-atom is 1000 times more atoms than the gram-atom, while the pound-atom is 453.592 times more atoms than the gram-atom.

These three definitions for mass-atoms are based on the fact that a fixed number of atoms of element **k** exist in a molecule of chemical substance **j**. For example, the chemical substance of water always has two hydrogen atoms per molecule of water. In general, their definitions are selected so that the magnitude of quantity $\mathbf{a}_{j,k}$ is the same in all three definitions, as illustrated below:

$$\mathbf{a}_{j,k} = Y \frac{6.022 \times 10^{23} \text{ atoms k}}{6.022 \times 10^{23} \text{ molecules j}} = Y \frac{\text{g-atom k}}{\text{g-mol j}}$$

$$\mathbf{a}_{j,k} = Y \frac{1000 \cdot 6.022 \times 10^{23} \text{ atoms k}}{1000 \cdot 6.022 \times 10^{23} \text{ molecules j}} = Y \frac{\text{kg-atom k}}{\text{kg-mol j}}$$

$$\mathbf{a}_{j,k} = Y \frac{453.592 \cdot 6.022 \times 10^{23} \text{ atoms k}}{453.592 \cdot 6.022 \times 10^{23} \text{ molecules j}} = Y \frac{\text{lb-atom k}}{\text{lb-mol j}}$$

where the symbol **j** represents a chemical substance, the symbol **k** represents an element in that substance, and the magnitude Y is the same no matter which definition is used for mass-atoms.

The chemical formula for H_2O means that one molecule of water contains two atoms of hydrogen and one atom of oxygen. It can also be read as one gram-mole (or one mole) of water contains 2 g-atoms of hydrogen and one g-atom of oxygen. Alternately, the formula H_2O can be read as one kilogram-mole of water contains 2 kg-atoms of hydrogen and one kg-atom of oxygen. Also, it can be read as one pound-mole of water contains 2 lb-atoms of hydrogen and one lb-atom of oxygen.

The quantity $\mathbf{a}_{j,k}$ for one gram-mole of chemical substance **j** can be derived from the molecular quantity $\mathbf{a}'_{j,k}$, which is based on <u>one</u> molecule of that substance. Quantity $\mathbf{a}'_{j,k}$ is the number of atoms of an element **k** in a molecule of substance **j**, expressed in units of "atoms of k per molecule of j". By applying the following conversion factors to $\mathbf{a}'_{j,k}$,

$$1 \text{ gram-atom} \equiv 6.022 \times 10^{23} \text{ atoms,}$$
$$1 \text{ gram-mole} \equiv 6.022 \times 10^{23} \text{ molecules,}$$

one can derive the quantity $\mathbf{a}_{j,k}$, expressed in units of "g-atom of **k** per g-mol of **j**".

For example, $\mathbf{a}'_{H_2O,H}$ = 2 atoms H / molecule H_2O
or $\mathbf{a}_{H_2O,H}$ = 2 g-atom H / g-mol H_2O.

Both quantities have the same magnitude but different units. One is based on a single molecule, while the other is based on Avogadro's number of molecules.

Atomic Weight, $\mathbf{A}_k$, "mass k/ mass-atom k". LoQ

It is the mass of one mass-atom of chemical element **k**, where the mass can be in either grams, kilograms, or pounds. The dimensions for quantity $\mathbf{A}_k$ are "mass of k per mass-atom of k"

For example, $\mathbf{A}_H$ = 1.007 97 g H / g-atom H
or $\mathbf{A}_H$ = 1.007 97 kg H / kg-atom H
or $\mathbf{A}_H$ = 1.007 97 lb_m H / lb-atom H

where the magnitude of $\mathbf{A}_H$ is the same no matter what mass units are used.

The quantity $\mathbf{A}_k$ for one gram-atom of chemical element **k** can be derived from the atomic quantity $\mathbf{A}'_k$, which is based on <u>one</u> atom of that element. Quantity $\mathbf{A}'_k$ is the number of atomic mass units (**amu**) in an atom of element **k**, expressed in units of "amu of k per atom of k". By applying the following conversion factors to $\mathbf{A}'_k$,

$$1 \text{ amu} \equiv 1.661 \times 10^{-24} \text{ grams,}$$
$$1 \text{ gram-atom} \equiv 6.022 \times 10^{23} \text{ atoms,}$$

one can derive the quantity $\mathbf{A}_k$, expressed in units of "g of **k** per g-atom of **k**".

For example, $\mathbf{A}'_H$ = 1.007 97 amu H / atom H
and $\mathbf{A}_H$ = 1.007 97 g H / g-atom H.

Both quantities have the same magnitude but different units. One is based on a single atom, while the other is based on Avogadro's number of atoms.

The Periodic Table of Elements defines the atomic mass units (amu) for each elemental atom. The "amu" is a relative scale that assigns pure carbon-12 a mass of 12.011 15 amu. The **standard** for one "amu" is equivalent to (1.660 538 782 ± 0.000 000 083) x 10^{-27} kg, as reported by the Physical Measurement Laboratory of the United States National Institute of Standards and Technology (NIST).

Molecular Weight of j, $\mathbf{M_j}$, "mass j / mass-mole j". LoQ

It is the mass of one mass-mole of chemical substance **j**, where the mass can be in either grams, kilograms, or pounds. Chemical substance **j** is either a free element or a compound. The dimensions for quantity $\mathbf{M_j}$ are "mass of j per mass-mole of j".

For example, $\mathbf{M_{H_2O}}$ = 18.0153 g H_2O / g-mol H_2O

or $\mathbf{M_{H_2O}}$ = 18.0153 kg H_2O / kg-mol H_2O

or $\mathbf{M_{H_2O}}$ = 18.0153 lb_m H_2O / lb-mol H_2O.

where the magnitude of $\mathbf{M_{H_20}}$ is the same no matter what mass units are used.

Mathematically, the molecular weight of a chemical substance **j** can be calculated from the atomic weights of the elements in that substance, as given by the following general equation:

$$\mathbf{M_j} = \sum_{k=1}^{ne} \mathbf{a}_{j,k} \cdot \mathbf{A_k} \qquad \text{(A.1)}$$

where $\mathbf{M_j}$ is the molecular weight of substance **j** in "mass j / mass-mole j",

$\mathbf{a_{j,k}}$ is the number of mass-atoms of element **k** per mass-mole of substance **j** in "mass-atoms k / mass-mole j",

$\mathbf{A_k}$ is the atomic weight of element **k** in "mass k / mass-atom k",

ne is the number of different elements in chemical substance **j**.

For example, the equation for the molecular weight of carbon dioxide is as follows:

$$\mathbf{M_{CO_2}} = \mathbf{a_{CO_2,C}}\,\mathbf{A_C} + \mathbf{a_{CO_2,O}}\,\mathbf{A_O}$$

$$\mathbf{M_{CO_2}} = 1\,\frac{\text{kg-atom C}}{\text{kg-mol CO}_2}\left(12.01115\,\frac{\text{kg C}}{\text{kg-atom C}}\right) + 2\,\frac{\text{kg-atom O}}{\text{kg-mol CO}_2}\left(15.9994\,\frac{\text{kg O}}{\text{kg-atom O}}\right)$$

$$= 44.01\,\frac{\text{kg CO}_2}{\text{kg-mol CO}_2}$$

where the unit prefix "mass-" can be expressed in either grams, kilograms, or pounds. In other words, the molecular weight of carbon dioxide can be read as either 44.01 g/g-mol, 44.01 kg/kg-mol, or 44.01 lb_m/lb-mol.

The quantity $\mathbf{M_j}$ for one gram-mole of chemical substance **j** can be derived from the molecular quantity $\mathbf{M_j'}$, which is based on one molecule of that substance. Quantity $\mathbf{M_j'}$ is the number of atomic mass units (**amu**) in a molecule of substance **j**, expressed in units of "amu of j per molecule of j". By applying the following conversion factors to $\mathbf{M}_j'$,

$$1 \text{ amu} \equiv 1.661 \times 10^{-24} \text{ grams,}$$
$$1 \text{ gram-mole} \equiv 6.022 \times 10^{23} \text{ molecules,}$$

one can derive the quantity $\mathbf{M}_j$, expressed in units of "g of **j** per g-mol of **j**".

For example, $\mathbf{M}_{H_2O}' = 18.0153$ amu H_2O / molecule H_2O
and $\mathbf{M}_{H_2O} = 18.0153$ g H_2O / g-mol H_2O.

Both quantities have the same magnitude but different units. One is based on a single molecule, while the other is based on Avogadro's number of molecules.

The molecular weights for all free elements and most chemical substances are tabulated in literature sources (such as textbooks, handbooks, or technical journals). If not, the above equation can be used to calculate the molecular weight of a chemical substance from the atomic weights of the elements in that substance.

The terms molecular weight and atomic weight are misnomers. The more accurate terms for these quantities are <u>molecular mass</u> and <u>atomic mass</u>. Because of tradition, the misnomers are universally used by chemists and engineers. We will follow tradition and still use the terms molecular weight and atomic weight, but remember that they represent masses and <u>not</u> weights.

Molecular Weight, $\mathbf{M} = \mathbf{m} / \mathbf{n}$, "mass / mass-mole".

LoQ

It is the mass of one mass-mole of a chemical substance, where the mass can be in either grams, kilograms, or pounds. The chemical substance is either a free element, a compound, or a mixture. The dimensions for quantity **M** are "mass per mass-mole".

For example, $\mathbf{M} = 28.0855$ g Si / g-mol Si for element silicon,
or $\mathbf{M} = 253.8089$ g I_2 / g-mol I_2 for compound iodine,
or $\mathbf{M} = 18.0153$ g H_2O / g-mol H_2O for compound water,
or $\mathbf{M} = 28.9669$ g air / g-mol air for mixture air.

For example, $\mathbf{M} = 28.0855$ kg Si / kg-mol Si for element silicon,
or $\mathbf{M} = 253.8089$ kg I_2 / kg-mol I_2 for compound iodine,
or $\mathbf{M} = 18.0153$ kg H_2O / kg-mol H_2O for compound water,
or $\mathbf{M} = 28.9669$ kg air / kg-mol air for mixture air.

For example, $\mathbf{M} = 28.0855$ lb_m Si / lb-mol Si for element silicon,
or $\mathbf{M} = 253.8089$ lb_m I_2 / lb-mol I_2 for compound iodine,
or $\mathbf{M} = 18.0153$ lb_m H_2O / lb-mol H_2O for compound water,
or $\mathbf{M} = 28.9669$ lb_m air / lb-mol air for mixture air,

where the magnitude of $\mathbf{M}$ for any chemical substance is the same no matter what mass units are used.

In the above example, the air mixture is assumed to contain only nitrogen, oxygen, argon, and carbon dioxide, and the trace compounds in air have been lumped with nitrogen (i.e., they are treated as being nitrogen). Of the 6.022 x 10^{23} molecules in a gram-mole of air, 78.04% of them are N_2, 20.99% of them are O_2, 0.94% of them are Ar, and 0.03% of them are CO_2.

Mathematically, the molecular weight of a substance ($\mathbf{M}$) is equal to the mass of that substance ($\mathbf{m}$) divided by the mass-moles of that substance ($\mathbf{n}$); that is, $\mathbf{M} = \mathbf{m} / \mathbf{n}$.

For a chemical substance that is a mixture, a subscript notation is used to refer to the molecular weight ($\mathbf{M}_j$) of pure component $\mathbf{j}$ of the mixture. Pure component $\mathbf{j}$ is associated with component $\mathbf{j}$ in the mixture.

For example,	$\mathbf{M}$	might be the molecular weight of an air mixture,
while	$\mathbf{M}_{N_2}$	would be the molecular weight of pure component N_2, and it is associated with component N_2 in the air mixture;
and	$\mathbf{M}_{CO_2}$	would be the molecular weight of pure component CO_2, and it is associated with component CO_2 in the air mixture.

The subscripted equation $\mathbf{M}_j = \mathbf{m}_j / \mathbf{n}_j$ means that the molecular weight of pure component $\mathbf{j}$ is equal to the mass of pure $\mathbf{j}$ per unit mass-mole of pure $\mathbf{j}$. Note that the symbol $\mathbf{M}$ applies to the total mixture, while the subscripted symbol $\mathbf{M}_j$ for pure $\mathbf{j}$ is associated with component $\mathbf{j}$ in that mixture.

Force Quantities

Force, $\mathbf{F} = \mathbf{m} \cdot \mathbf{a}$, "mass·length / time^2" or "force". LoQ

It is a physical influence exerted by somebody or something on an object, producing or tending to produce a change in the movement or in the shape of that object. The dimensions for quantity **F** are either "mass·length per time^2" or "force".

For example,	$\mathbf{F} = 10 \times 10^3 \cdot (200)$	grams·centimeters per square second
or	$\mathbf{F} = 10 \times 10^3 \cdot (200)$	$g \cdot cm/s^2$
or	$\mathbf{F} = 20 \times 10^5$	dyne
For example,	$\mathbf{F} = 10 \cdot (2.0)$	kilograms·meters per square second
or	$\mathbf{F} = 10 \cdot (2.0)$	$kg \cdot m/s^2$
or	$\mathbf{F} = 20$	Newtons
or	$\mathbf{F} = 20$	N
For example,	$\mathbf{F} = 22.0462 \cdot (6.5616)$	pounds-mass·feet per square second
or	$\mathbf{F} = 22.0462 \cdot (6.5616)$	$lb_m \cdot ft/s^2$
or	$\mathbf{F} = 4.4961$	pounds-force†
or	$\mathbf{F} = 4.4961$	lb_f

where the symbols—**N** and **lb_f**—are the commonly-used units for force.

In these examples, the object has a mass of 10 000 g (= 10 kg = 22.0462 lb_m), and it is accelerating at 2 m/s^2 (= 200 cm/s^2 = 6.5616 ft/s^2).

Mathematically, force (**F**) is equal to the product of the mass (**m**) and acceleration (**a**) of an object; that is, $\mathbf{F} = \mathbf{m} \cdot \mathbf{a}$. This equation is Newton's second law of motion.

Since the units of force (mass·length / time^2) are cumbersome to work with, a derived force unit is defined to equal the basic units. By definition, the three force units are:

$$1 \text{ dyne} \equiv 1 \; g \cdot cm / s^2,$$
$$1 \text{ newton (N)} \equiv 1 \; kg \cdot m / s^2,$$
$$1 \; lb_f \equiv 32.174 \; lb_m \cdot ft / s^2,$$

where lb_f and lb_m are not the same units. Symbol **lb_f is a force** unit, while symbol **lb_m is a mass** unit.

When you push a book, initially at rest on top of a table, your finger tips exert a force on the book and cause it to move.

† Because one dyne and one newton are equivalent to their basic units, the magnitudes of the force units in the first two examples are identical to that of their basic units. However, the magnitudes of the force unit and the basic units in the third example differ by a factor of 32.174.

Why is 32.174 used in the definition of the $\mathbf{lb_f}$ unit? This question will be answered when we examine the quantity of weight.

Weight, $\mathbf{W} = \mathbf{m \cdot g}$, "mass·length / time^2" or "force". LoQ

It is that force exerted on an object by the gravitational field in which the object resides. The dimensions for quantity **W** are either "mass·length per time^2" or "force".

For example, $\mathbf{W} = 980.665 \times 10^5$ dynes

For example, $\mathbf{W} = 980.665$ Newtons
or $\mathbf{W} = 980.665$ N

For example, $\mathbf{W} = 220.463$ pounds-force
or $\mathbf{W} = 220.463$ $\mathrm{lb_f}$

where the symbols—**N** and $\mathbf{lb_f}$—are the commonly-used units for weight.

In these examples, the object has a mass of 100 000 g (= 100 kg = 220.462 $\mathrm{lb_m}$) and experiences Earth's gravitational pull **g** at sea level and 45° latitude. At this location on the Earth's surface, the quantity **g** equals 980.665 cm/s^2 (= 9.806 65 m/s^2 = 32.174 ft/s^2).

Mathematically, weight (**W**) is equal to the mass of an object (**m**) in a gravitational field times the acceleration due to that gravitational field (**g**); that is, $\mathbf{W = m \cdot g}$. This equation is a specific application of Newton's second law of motion.

The gravitational acceleration **g** is a function of the object's distance from the center of the gravitational field. For example, water in the amount of 56.50 kg weighs 554.1 N at sea level and 45° latitude but weighs 553.5 N at Denver, Colorado; because, the Earth's gravitational acceleration **g** is 9.806 65 m/s^2 at sea level and 45° latitude and 9.796 96 m/s^2 at Denver. However, the mass of the water is **constant**, because it is not affected by location. This same amount of water (56.50 kg) on the moon would weigh approximately 92 N, since the moon's gravitational acceleration is one-sixth of the Earth's.

In the above examples, an object's weight is calculated using $\mathbf{W = m \cdot g}$, as follows:

$$\mathbf{m} = (100\,000\ g)\cdot\left(980.665\,\frac{cm}{s^2}\right)\cdot\left\langle \frac{1\,dyne}{1\,\frac{g\cdot cm}{s^2}} \right\rangle = 980.665\times 10^5\ dynes$$

$$\mathbf{m} \;=\; (100\,kg)\cdot\left(9.806\,65\,\frac{m}{s^2}\right)\cdot\left\langle\frac{1\,N}{1\,\dfrac{kg\cdot m}{s^2}}\right\rangle \;=\; 980.665\,N$$

$$\mathbf{m} \;=\; (220.463\,lb_m)\cdot\left(32.174\,\frac{ft}{s^2}\right)\cdot\left\langle\frac{1\,lb_f}{32.174\,\dfrac{lb_m\cdot ft}{s^2}}\right\rangle \;=\; 220.463\,lb_f$$

Thus, the weight of 100 000 g is 980.665 x 10^5 dynes, and the weight of 100 kg is 980.665 N. However, the weight of 220.463 lb_m is 220.463 lb_f. In the third example, the magnitudes of the weight and mass are identical; but, their units are different—one is force, and the other is mass. Since the object is at sea level and 45° latitude, the gravitational acceleration **g** acting on the object is 32.174 ft/s^2. This 32.174 cancels the 32.174 appearing in the conversion factor for the **lb_f** unit, and thus the magnitudes for weight and mass are identical. The third example illustrates why the definition for the **lb_f** unit contains the constant 32.174. This constant was selected so that the magnitudes of weight and mass are identical **at sea level and 45° latitude**. Their magnitudes are usually different, because the value of **g** varies depending upon the object's distance from the center of the Earth.

When you read your weight on the bathroom scale (say 220 lb_f), you can immediately estimate what your mass is (roughly 220 lb_m), since **g** does not vary that much on the Earth's surfaces (by less than 0.5%). Your weight and mass would be exact in value (but not units), if the bathroom scale was at sea level and 45° latitude.

Pressure, **P** = **F / A**, "force / length^2" or "pressure". LoQ

It is the exertion of a perpendicular force upon a surface by an object in contact with that surface. The dimensions for quantity **P** are either "force per length^2" or "pressure".

For example, $\mathbf{P} = 1.013\,25 \times 10^6$ dyne per square centimeter
or $\mathbf{P} = 1.013\,25 \times 10^6$ dyne/cm^2
or $\mathbf{P} = 760$ mm Hg at 0°C
or $\mathbf{P} = 1.0$ atmosphere or atm

For example, $\mathbf{P} = 1.013\,25 \times 10^5$ newton per square meter
or $\mathbf{P} = 1.013\,25 \times 10^5$ N/m^2
or $\mathbf{P} = 1.013\,25 \times 10^5$ pascal
or $\mathbf{P} = 101.325$ kPa.
or $\mathbf{P} = 1.0$ atmosphere or atm

For example, $\mathbf{P} = 2116.22$ pounds-force per square foot
or $\mathbf{P} = 2116.22$ lb_f/ft^2
or $\mathbf{P} = 14.696$ lb_f/in^2 or psi or psia
or $\mathbf{P} = 1.0$ atmosphere or atm

where the symbols—**atm**, **kPa**, **psi**, **mm Hg**—are the commonly-used units for pressure.

The prefixed unit "kPa" is a kilopascal (1000 Pa), and the **standard atmosphere** (1 atm) is defined to be either 101.325 kPa, 760 mm Hg at 0˚C, or 14.696 psi.

Two commonly-used, derived **pressure** units exist. By definition, they are:

$$1 \ \mathrm{N} / \mathrm{m}^2 \equiv 1 \ \text{Pascal},$$
$$1 \ \mathrm{lb_f} / \mathrm{in}^2 \equiv 1 \ \text{psi or psia},$$

where the pressure units **psi** and **psia** mean pounds-force per square inch absolute.

Mathematically, pressure (**P**) is equal to the force (**F**) exerted by an object divided by the contact area (**A**) of that object on a surface; that is, **P = F / A**. The pressure is the same at all points within the surface area contacted by the object.

When you push a book, initially at rest on top of a table, your finger tips exert a pressure on the side of the book and cause it to move. This pressure is equal to the force exerted by your finger tips divided by the contact area on your finger tips.

A column of liquid, such as water, sitting in a graduated cylinder exerts a pressure on the base of that cylinder. The force exerted on the cylinder's base by the liquid is "m·g"; that is, the weight of the liquid caused by Earth's gravitational pull. The pressure exerted by the liquid on the cylinder's base is the liquid's weight divided by the cross-sectional area of the cylinder.

A volume of gas, such as propane, contained in a closed tank exerts a pressure on the inside surface of that tank. The movement of the gaseous molecules impacts an averaged force (m·a) on the tank's surface. This force when divided by the tank's surface area represents the pressure exerted by the gas on the tank's steel wall.

If the propane tank were to be heated, say by the radiation from the sun, the internal energies of both the steel tank and the gas would increase, as well as their temperatures. Therefore, the motion of the gaseous molecules would increase and cause them to impact the closed-tank's surface with greater force. This effect would cause the gas pressure to rise inside of the tank.

Physical Quantities

Density, $\rho = \mathbf{m} / \mathrm{V}$, "mass / length^3". LoQ

It is the mass of a chemical substance per unit volume of that chemical substance in a particular state of aggregation (solid, liquid, or gas). The chemical substance is either a free element, a compound, or a mixture. The dimensions for quantity ρ are "mass per length^3".

For example, for elemental copper (**Cu**) as a **solid** at 101.325 kPa (1 atm) and
20°C, ρ = 8.960 grams per cubic centimeter
or ρ = 8.960 g/cm^3
or ρ = 8.960 grams per milliliter
or ρ = 8.960 g/mL;
and 25°C, ρ = 8.920 g/cm^3
or ρ = 8.920 g/mL

For example, for compound water (**H_2O**) as a **liquid** at 1 atm and
4°C, ρ = 1000.0 kilograms per cubic meter
or ρ = 1000.0 kg/m^3
or ρ = 1.0000 kilogram per liter
or ρ = 1.0000 kg/L or g/mL;
and 75°C, ρ = 970.90 kg/m^3
or ρ = 0.9709 kg/ L or g/mL

For example, for a mixture of air as a **gas** at 44.088 psi (3 atm) and
25°C, ρ = 0.2217 pound-mass per cubic foot
or ρ = 0.2217 lb$_m$/ft^3
or ρ = 0.0296 pound-mass per US gallon
or ρ = 0.0296 lb$_m$/gal;
and 75°C, ρ = 0.1899 lb$_m$/ft^3
or ρ = 0.0254 lb$_m$/gal

where the symbols—**g/cm^3**, **kg/L**, **lb$_m$/ft^3**—are the commonly-used units for density.

Mathematically, the density of a substance (ρ) is equal to the mass of that substance (**m**) divided by the volume of that substance (V); that is, $\rho = \mathbf{m} / \mathrm{V}$.

As a general (or first) principle, **the density of a chemical substance is a function of the temperature, pressure, and chemical composition of that substance**. When the temperature of a substance increases and causes the molecular distances to expand, the density of that substance decreases, assuming the pressure and composition are constant. When the pressure increases and causes the molecular distances to compress, the density of the substance will increase, assuming the temperature and composition are constant. When the composition changes and causes the molecules to attract or repel one another, the density of the substance will either increase or decrease, assuming the temperature and pressure are constant.

In the above examples, copper, water, and air are three representative substances for a solid, a liquid, and a gas, respectively, at a pressure of one atmosphere. Their densities at 25˚C are:

Substance	Formula	Phase	Density kg/L = g/cm^3
Copper	Cu	solid	8.92
Water	H_2O	liquid	0.9971
Air Mixture	air	gas	0.003 552

As implied by this example, a solid is more dense than a liquid, and a liquid is more dense than a gas, where dense means more mass per unit of volume. Also, the density of a solid is about one order of magnitude greater than that of a liquid, while the density of a liquid is about 100 orders of magnitude greater than that of a gas.

Unlike the **extensive** quantity of volume whose magnitude depends upon the amount of substance present, density is an **intensive** quantity, one that does not depend upon the amount of substance present. For example, 10.0 kg of water at 4˚C and 1 atm has a volume of 10.0 L, while 200 kg of water at the same T and P conditions has a volume of 200 L. Therefore, the density of liquid water at 4˚C and 1 atm is 1.00 kg/L, no matter how much mass of water is present.

These general observations about the extensive volume and the intensive density of a chemical substance are expressed concisely by the following functional equations:

$$\mathbf{V} = \mathit{vol}[\, \mathbf{T}, \mathbf{P}, \mathbf{comp}, \mathbf{m} \,]$$
$$\rho = \mathit{rho}[\, \mathbf{T}, \mathbf{P}, \mathbf{comp} \,]$$

where *vol*[…] and *rho*[…] are called functional forms. The functional equation for density states that the density (ρ) of a chemical substance is a function of the temperature (**T**), pressure (**P**), and composition (**comp**) of that substance. In other words, one must know the **T**, **P**, and **comp** of a substance, before one can determine the density of that substance. The function *rho*[…] is a **concise and general notation** for either (1) a table of density found in a literature source (such as a textbook, handbook, or technical journal), (2) a graph of density versus temperature also found in a literature source, (3) a mathematical algorithm which states how equations are solved to determine the density of a substance, or (4) a software program that implements the mathematical algorithm.

For a chemical substance that is a mixture at temperature **T** and pressure **P**, a subscript notation is used to refer to the density (ρ_j) of pure component **j** existing at the **T** and **P** of the mixture. Pure component **j** is associated with component **j** in the mixture.

For example, ρ might be the density of an air mixture at temperature **T** and pressure **P**, while ρ_{N_2} would be the density of pure component N_2 at **T** and **P**, and it is associated with component N_2 in the air mixture;

and ρ_{CO_2} would be the density of pure component CO_2 at **T** and **P**, and it is associated with component CO_2 in the air mixture.

The subscripted equation $\rho_j = m_j / V_j$ means that the density of pure component **j** is equal to the mass of pure **j** per unit volume of pure **j**. Note that the symbol **ρ** applies to the total mixture, while the subscripted symbol ρ_j for pure **j** is associated with component **j** in that mixture.

Specific Gravity, $sg = \rho / \rho_{ref}$, "density @ T & P / density @ T_{ref} & P_{ref}". LoQ

It is a dimensionless ratio of the density of a chemical substance of interest (at temperature T and pressure P) to the density of a reference substance (at temperature T_{ref} and pressure P_{ref}). The substance of interest is in a particular state of aggregation (solid, liquid, or gas) and is either a free element, a compound, or a mixture. The dimensions for quantity **sg** are "density of substance at T and P over density of reference at T_{ref} and P_{ref}".

The commonly-used reference substance for **solids and liquids** is pure water at 4˚C and 1 atm, and for **gases** is air at **standard conditions** (0˚C and 1 atm).

For example, element copper (**Cu**) as a **solid** has a

$$sg = 8.92 \, \frac{25^\circ}{4^\circ}$$

This notation means that the specific gravity of copper at 25˚C with reference to water at 4˚C is 8.92. The pressures for the substance and reference are <u>implied</u> to be 1 atm.

For example, compound isopropyl alcohol (C_3H_8O) as a **liquid** has a

$$sg = 0.7851 \, \frac{20^\circ}{4^\circ}$$

This notation means that the specific gravity of isopropyl alcohol at 20˚C with reference to water at 4˚C is 0.7851. The pressures for the substance and reference are <u>implied</u> to be 1 atm.

For example, a mixture of natural **gas** has a

$$sg = 2.3538 \, \frac{75^\circ \text{ \& } 3 \text{ atm}}{0^\circ \text{ \& } 1 \text{ atm}} ,$$

where this natural gas is found in Oil City, PA with a composition of 1.1% nitrogen (N_2), 67.6% methane (CH_4), and 31.3% ethane (C_2H_6) on a volume basis. This notation means that the specific gravity of natural gas at 75˚C and 3 atm with reference to air at 0˚C and 1 atm is 2.3538. Unlike solids and liquids, the two pressures for the substance and reference <u>must</u> be specified for gases. The reference density of air at 0˚C and 1 atm is 1.2923 g/L.

Mathematically, the specific gravity of a substance (**sg**) is equal to the density of that substance (ρ) divided by the density of a reference substance (ρ_{ref}); that is, $\mathbf{sg} = \rho / \rho_{ref}$, with units of "density at T and P per density at T_{ref} and P_{ref}".

A **proper value** for the specific gravity of a substance is given, when the temperatures and pressures of both the substance and reference accompany that value. When they are not, the following assumptions are commonly made for these temperatures and pressures:

Phase	T	P	T_{ref}	P_{ref}	reference	ρ_{ref}	
solid	20˚C	1 atm	4˚C	1 atm	pure H_2O	1.0000 g/cm^3	= 1.000 kg/L
liquid	20˚C	1 atm	4˚C	1 atm	pure H_2O	1.0000 g/cm^3	= 62.43 lb$_m$/ft^3
gas	0˚C	1 atm	0˚C	1 atm	air mixture	1.2923 g/L	

Since solids and liquids are fairly incompressible (i.e., are not greatly affected by pressure changes), their reported values of specific gravity commonly do not indicate the pressures. These pressures are implied to be 1 atm. Since gases are greatly affected by pressure changes, their reported values of specific gravity must indicate the pressures.

Specific gravity is a convenient notation for tabulating, indirectly, the densities of substance in literature sources (such as textbooks, handbooks, or technical journals). Because **sg** is a dimensionless ratio of densities, the value of **sg** is **constant** no matter what system of units is used to express the density. Most literature sources not only give the value of a specific gravity, but they also indicate the temperatures and sometimes the pressures for both the substance of interest and the reference substance.

For a chemical substance that is a mixture at temperature **T** and pressure **P**, a subscript notation is used to refer to the specific gravity ($\mathbf{sg}_j$) of pure component **j** existing at the **T** and **P** of the mixture. Pure component **j** is associated with component **j** in the mixture.

For example,	**sg**	might be the specific gravity of an air mixture at temperature **T** and pressure **P**,
while	$\mathbf{sg}_{N_2}$	would be the specific gravity of pure component N_2 at **T** and **P**, and it is associated with component N_2 in the air mixture;
and	$\mathbf{sg}_{CO_2}$	would be the specific gravity of pure component CO_2 at **T** and **P**, and it is associated with component CO_2 in the air mixture.

The subscripted equation $\mathbf{sg}_j = \rho_j / \rho_{ref}$ means that the specific gravity of pure component **j** is equal to the density of pure **j** divided by a reference density. Note that the symbol **sg** applies to the total mixture, while the subscripted symbol $\mathbf{sg}_j$ for pure **j** is associated with component **j** in that mixture.

Specific Volume, $\hat{\mathbf{V}}' = \mathbf{V} / \mathbf{m}$, "length^3 / mass". LoQ

It is the volume of a chemical substance per unit mass of that chemical substance in a particular state of aggregation (solid, liquid, or gas). The chemical substance is either a free element, a compound, or a mixture. The specific volume and density of a chemical substance are the reciprocal of one another. The dimensions for quantity $\hat{\mathbf{V}}'$ are "length^3 per mass".

For example, for elemental copper (**Cu**) as a **solid** at 101.325 kPa (1 atm) and

20°C, $\hat{\mathbf{V}}' = 0.1116$ cubic centimeter per gram
or $\hat{\mathbf{V}}' = 0.1116$ cm^3/g
or $\hat{\mathbf{V}}' = 0.1116$ milliliter per gram
or $\hat{\mathbf{V}}' = 0.1116$ mL/g;
and 25°C, $\hat{\mathbf{V}}' = 0.1121$ cm^3/g
or $\hat{\mathbf{V}}' = 0.1121$ mL/g

For example, for compound water (**H_2O**) as a **liquid** at 1 atm and

4°C, $\hat{\mathbf{V}}' = 0.001$ cubic meter per kilogram
or $\hat{\mathbf{V}}' = 0.001$ m^3/kg
or $\hat{\mathbf{V}}' = 1.000$ liter per kilogram
or $\hat{\mathbf{V}}' = 1.000$ L/kg;
and 75°C, $\hat{\mathbf{V}}' = 0.001\ 03$ m^3/kg
or $\hat{\mathbf{V}}' = 1.030$ L/kg

For example, for a mixture of air as a **gas** at 44.088 psi (3 atm) and

25°C, $\hat{\mathbf{V}}' = 4.5106$ cubic feet per pound-mass
or $\hat{\mathbf{V}}' = 4.5106$ ft^3/lb_m
or $\hat{\mathbf{V}}' = 33.7838$ US gallons per pound-mass
or $\hat{\mathbf{V}}' = 33.7838$ gal/lb_m;
and 75°C, $\hat{\mathbf{V}}' = 5.2660$ ft^3/lb_m
or $\hat{\mathbf{V}}' = 39.3701$ gal/lb_m

where the symbols—**cm^3/g**, **L/kg**, **ft^3/lb_m**—are the commonly-used units for specific volume.

Mathematically, the specific volume of a substance ($\hat{\mathbf{V}}'$) is equal to the volume of that substance (**V**) divided by the mass of that substance (**m**); that is, $\hat{\mathbf{V}}' = \mathbf{V} / \mathbf{m}$.

Alternately, the specific volume of a chemical substance is the reciprocal of the density of that substance; that is, $\hat{\mathbf{V}}' = 1 / \rho$.

Like density, the specific volume of a chemical substance is also a function of the temperature, pressure, and chemical composition of that substance. Since the specific volume is the reciprocal of the density, the effect of temperature, pressure, and composition on the magnitude of the specific volume is opposite to that on the density. When the specific volume of a chemical substance can not be found in a literature source (such as a textbook, handbook, or technical journal), it can be calculated from the density of that substance; that is, $\hat{\mathbf{V}}' = 1/\rho$.

For a chemical substance that is a mixture at temperature **T** and pressure **P**, a subscript notation is used to refer to the specific volume ($\hat{\mathbf{V}}'_j$) of pure component **j** existing at the **T** and **P** of the mixture. Pure component **j** is associated with component **j** in the mixture.

For example,	$\hat{\mathbf{V}}'$	might be the specific volume of an air mixture at temperature **T** and pressure **P**,
while	$\hat{\mathbf{V}}'_{N_2}$	would be the specific volume of pure component N_2 at **T** and **P**, and it is associated with component N_2 in the air mixture;
and	$\hat{\mathbf{V}}'_{CO_2}$	would be the specific volume of pure component CO_2 at **T** and **P**, and it is associated with component CO_2 in the air mixture.

The subscripted equation $\hat{\mathbf{V}}'_j = \mathbf{V}_j / \mathbf{m}_j$ means that the specific volume of pure component **j** is equal to the volume of pure **j** per unit mass of pure **j**. Note that the symbol $\hat{\mathbf{V}}'$ applies to the total mixture, while the subscripted symbol $\hat{\mathbf{V}}'_j$ for pure **j** is associated with component **j** in that mixture.

Molar Density, $\hat{\rho} = \mathbf{n} / \mathbf{V}$, "mass-mole / length^3". LoQ

It is the mass-mole of a chemical substance per unit volume of that chemical substance in a particular state of aggregation (solid, liquid, or gas). The chemical substance is either a free element, a compound, or a mixture. The dimensions for quantity $\hat{\rho}$ are "mass-mole per length^3".

For example, for elemental copper (**Cu**) as a **solid** at 101.325 kPa (1 atm) and

	20˚C,	$\hat{\rho}$ =	0.1410	gram-mole per cubic centimeters
or		$\hat{\rho}$ =	0.1410	g-mol/cm^3
or		$\hat{\rho}$ =	0.1410	gram-mole per milliliters
or		$\hat{\rho}$ =	0.1410	g-mol/mL;
and	25˚C,	$\hat{\rho}$ =	0.1404	g-mol/cm^3
or		$\hat{\rho}$ =	0.1404	g-mol/mL

For example, for compound water (**H_2O**) as a **liquid** at 1 atm and

	4˚C,	$\hat{\rho}$ =	55.5093	kilogram-mole per cubic meter
or		$\hat{\rho}$ =	55.5093	kg-mol/m^3

or $\hat{\rho}$ = 0.0555 kilogram-mole per liters
or $\hat{\rho}$ = 0.0555 kg-mol/L;
and 75˚C, $\hat{\rho}$ = 55.5093 kg-mol/m^3
or $\hat{\rho}$ = 0.0555 kg-mol/L

For example, for a mixture of air as a **gas** at 44.088 psi (3 atm) and
25˚C, $\hat{\rho}$ = 0.007 654 pound-mole per cubic feet
or $\hat{\rho}$ = 0.007 654 lb-mol/ft^3
or $\hat{\rho}$ = 0.001 022 pound-mole per USA gallons
or $\hat{\rho}$ = 0.001 022 lb-mol/gal;
and 75˚C, $\hat{\rho}$ = 0.006 556 lb-mol/ft^3
or $\hat{\rho}$ = 0.000 877 lb-mol/gal

where the symbols—**g-mol/cm^3**, **kg-mol/L**, **lb-mol/ft^3**—are the commonly-used units for molar density.

Mathematically, the molar density of a substance ($\hat{\rho}$) is equal to the mass-mole of that substance (**n**) divided by the volume of that substance (**V**); that is, $\hat{\rho} = \mathbf{n} / \mathbf{V}$.

Alternately, the molar density of a chemical substance is equal to the density divided by the molecular weight of that substance; that is, $\hat{\rho} = \rho / \mathbf{M}$.

Like density, the molar density of a chemical substance is also a function of the temperature, pressure, and chemical composition of that substance. Since the molar density is proportional to the density, the effect of temperature, pressure, and composition on the magnitude of the molar density is the same as that on the density. When the molar density of a chemical substance can not be found in a literature source (such as a textbook, handbook, or technical journal), it can be calculated from the density of that substance; that is, $\hat{\rho} = \rho / \mathbf{M}$.

For a chemical substance that is a mixture at temperature **T** and pressure **P**, a subscript notation is used to refer to the molar density ($\hat{\rho}_j$) of pure component **j** existing at the **T** and **P** of the mixture. Pure component **j** is associated with component **j** in the mixture.

For example,	$\hat{\rho}$	might be the molar density of an air mixture at temperature **T** and pressure **P**,
while	$\hat{\rho}_{N_2}$	would be the molar density of pure component N_2 at **T** and **P**, and it is associated with component N_2 in the air mixture;
and	$\hat{\rho}_{CO_2}$	would be the molar density of pure component CO_2 at **T** and **P**, and it is associated with component CO_2 in the air mixture.

The subscripted equation $\hat{\rho}_j = \mathbf{n}_j / \mathbf{V}_j$ means that the molar density of pure component **j** is equal to the mass-mole of pure **j** per unit volume of pure **j**. Note that the symbol $\hat{\rho}$ applies to the total mixture, while the subscripted symbol $\hat{\rho}_j$ for pure **j** is associated with component **j** in that mixture.

Molar Volume, $\hat{\mathbf{V}} = \mathbf{V} / \mathbf{n}$, "length^3 / mass-mole". LoQ

It is the volume of a chemical substance per unit mass-mole of that chemical substance in a particular state of aggregation (solid, liquid, or gas). The chemical substance is either a free element, a compound, or a mixture. The dimensions for quantity $\hat{\mathbf{V}}$ are "length^3 per mass-mole".

For example, for elemental copper (**Cu**) as a **solid** at 101.325 kPa (1 atm) and
20°C, $\hat{V}$ = 7.092 cubic centimeters per gram-mole
or $\hat{V}$ = 7.092 cm^3/g-mol
or $\hat{V}$ = 7.092 milliliters per gram-mole
or $\hat{V}$ = 7.092 mL/g-mol;
and 25°C, $\hat{V}$ = 7.124 cm^3/g-mol
or $\hat{V}$ = 7.124 mL/g-mol

For example, for compound water (**H_2O**) as a **liquid** at 1 atm and
4°C, $\hat{V}$ = 0.018 015 cubic meter per kilogram-mole
or $\hat{V}$ = 0.018 015 m^3/kg-mol
or $\hat{V}$ = 18.015 liters per kilogram-mole
or $\hat{V}$ = 18.015 L/kg-mol;
and 75°C, $\hat{V}$ = 0.018 555 m^3/kg-mol
or $\hat{V}$ = 18.555 L/kg-mol

For example, for a mixture of air as a **gas** at 44.088 psi (3 atm) and
25°C, $\hat{V}$ = 130.658 cubic feet per pound-mole
or $\hat{V}$ = 130.658 ft^3/lb-mol
or $\hat{V}$ = 978.611 USA gallons per pound-mole
or $\hat{V}$ = 978.611 gal/lb-mol;
and 75°C, $\hat{V}$ = 152.538 ft^3/lb-mol
or $\hat{V}$ = 1140.429 gal/lb-mol

where the symbols—**cm^3/g-mol**, **L/kg-mol**, **ft^3/lb-mol**—are the commonly-used units for molar volume.

Mathematically, the molar volume of a substance ($\hat{\mathbf{V}}$) is equal to the volume of that substance ($\mathbf{V}$) divided by the mass-mole of that substance ($\mathbf{n}$); that is, $\hat{\mathbf{V}} = \mathbf{V} / \mathbf{n}$.

Alternately, the molar volume of a chemical substance is equal to the molecular weight divided by the density of that substance; that is, $\hat{\mathbf{V}} = \mathbf{M} / \boldsymbol{\rho}$.

Like density, the molar volume of a chemical substance is also a function of the temperature, pressure, and chemical composition of that substance. Since the molar volume is proportional to the reciprocal of the density, the effect of temperature, pressure, and composition on the magnitude of the molar volume is opposite to that on the density. When the molar volume of a chemical substance can not be found in a literature source (such as a textbook, handbook, or technical journal), it can be calculated from the density of that substance; that is, $\hat{\mathbf{V}} = \mathbf{M}/\rho$.

For a chemical substance that is a mixture at temperature **T** and pressure **P**, a subscript notation is used to refer to the molar volume ($\hat{\mathbf{V}}_j$) of pure component **j** existing at the **T** and **P** of the mixture. Pure component **j** is associated with component **j** in the mixture.

For example,	$\hat{\mathbf{V}}$	might be the molar volume of an air mixture at temperature **T** and pressure **P**,
while	$\hat{\mathbf{V}}_{N_2}$	would be the molar volume of pure component N_2 at **T** and **P**, and it is associated with component N_2 in the air mixture;
and	$\hat{\mathbf{V}}_{CO_2}$	would be the molar volume of pure component CO_2 at **T** and **P**, and it is associated with component CO_2 in the air mixture.

The subscripted equation $\hat{\mathbf{V}}_j = \mathbf{V}_j / \mathbf{n}_j$ means that the molar volume of pure component **j** is equal to the volume of pure **j** per unit mass-mole of pure **j**. Note that the symbol $\hat{\mathbf{V}}$ applies to the total mixture, while the subscripted symbol $\hat{\mathbf{V}}_j$ for pure **j** is associated with component **j** in that mixture.

Some textbooks use the same symbol for molar volume and specific volume, namely $\hat{\mathbf{V}}$. Usually, the context of the problem will indicated whether the units of $\hat{\mathbf{V}}$ are volume per unit mass-mole or volume per mass. If quantities in the problem are in molar units, then $\hat{\mathbf{V}}$ will have units of volume per unit mass-mole. If quantities in the problem are in mass units, then $\hat{\mathbf{V}}$ will have units of volume per unit mass. When a problem requires that both sets of units are needed, then $\hat{\mathbf{V}}$ will be use for molar volume, and $\hat{\mathbf{V}}'$ will be use for specific volume.

Mixture Composition Quantities

Mass Fraction, $w_j = m_j / m$, "mass j / mass mix". LoQ

It is a dimensionless ratio of the mass of component **j** in a chemical mixture per total mass of that mixture in a particular state of aggregation (solid, liquid, or gas). By definition, a mixture is chemically inert; that is, no chemical reactions are occurring. The dimensions for quantity w_j are "mass of j per mass of mixture".

For example, $w_{N_2} = 0.0150$ g N_2 / g gas
and $w_{CH_4} = 0.5274$ g CH_4 / g gas
and $w_{C_2H_6} = \underline{0.4576}$ g C_2H_6 / g gas.
1.0000

For example, $w_{N_2} = 0.0150$ kg N_2 / kg gas
and $w_{CH_4} = 0.5274$ kg CH_4 / kg gas
and $w_{C_2H_6} = \underline{0.4576}$ kg C_2H_6 / kg gas.
1.0000

For example, $w_{N_2} = 0.0150$ lb_m N_2 / lb_m gas
and $w_{CH_4} = 0.5274$ lb_m C_2H_6 / lb_m gas
and $w_{C_2H_6} = \underline{0.4576}$ lb_m C_2H_6 / lb_m gas.
1.0000

where the mixture of the three chemical components (nitrogen, methane, and ethane) is that of natural gas found in Oil City, PA.

The **composition** of a mixture is the chemical formulas and mass fractions of the components in that mixture, and these mass fractions **must** sum to one. As illustrated in the above examples, the magnitude of a mass fraction (w_j) for any component in a mixture is the same no matter what mass units are used.

Mathematically, the mass fraction of component **j** in a mixture (w_j) is equal to the mass of that component (m_j) divided by the total mass of the mixture (m); that is, $w_j = m_j / m$.

Alternately, the mass of component **j** (m_j) is equal to the product of the total mass of the mixture (m) and the mass fraction of component **j** in that mixture (w_j); that is, $m_j = m \cdot w_j$.

A mixture can be visualized as being formed from the **pure components**; that is, the pure substances at the temperature (**T**) and pressure (**P**) of the mixture. For example, a mixture of 100 kg of natural gas at 25°C and 1 atm can be visualized as being formed by mixing the following pure gases:

Container	Pure **j**	Formula	Mix **T**	Mix **P**	$\mathbf{m_j}$
Tank 1	nitrogen	N_2	25˚C	1 atm	1.50 kg
Tank 2	methane	CH_4	25˚C	1 atm	52.74 kg
Tank 3	ethane	C_2H_6	25˚C	1 atm	45.76 kg
			Total mixture **m** =		100.00 kg

Thus, the total mass of a mixture can be visualized as being the sum of the masses of the pure components.

As a general (or first) principle for mixtures, **the total mass of a chemically-inert mixture is equal to the sum of its component masses**. Mathematically, this principle is:

$$\mathbf{m} = \sum_{j=1}^{nc} \mathbf{m_j} = \mathbf{m_1} + \mathbf{m_2} + \ldots + \mathbf{m_j} + \ldots + \mathbf{m_{nc}} \qquad (A.2)$$

where $\mathbf{m}$ is the total mass of the mixture in "mass mix",
$\mathbf{m_j}$ is the mass of component **j** in the mixture in "mass j",
$\mathbf{nc}$ is the number of chemical components in the mixture.

Equation A.2 is read as the total mass ($\mathbf{m}$) of the mixture is equal to the mass of the first component ($\mathbf{m_1}$) plus the mass of the second component ($\mathbf{m_2}$) plus all the component masses up to and including that for the "**nc**" component ($\mathbf{m_{nc}}$). In the example, the first component is nitrogen, the second component is methane, and the third (or "**nc**") component is ethane.

If both sides of Equation A.2 are divided by the total mass **m** of the mixture, the resulting equation is:

$$1.0 = \sum_{j=1}^{nc} \frac{\mathbf{m_j}}{\mathbf{m}} = \frac{\mathbf{m_1}}{\mathbf{m}} + \frac{\mathbf{m_2}}{\mathbf{m}} + \ldots + \frac{\mathbf{m_j}}{\mathbf{m}} + \ldots + \frac{\mathbf{m_{nc}}}{\mathbf{m}} \qquad (A.3)$$

Substituting $\mathbf{w_j} = \mathbf{m_j} / \mathbf{m}$ into Equation A.3 produces the following equation:

$$1.0 = \sum_{j=1}^{nc} \mathbf{w_j} = \mathbf{w_1} + \mathbf{w_2} + \ldots + \mathbf{w_j} + \ldots + \mathbf{w_{nc}} \qquad (A.4)$$

Therefore, the sum of the component mass fractions for a chemical mixture must be equal to one.

The amounts of the chemical components in a chemical mixture are commonly reported on a relative basis in percentages. For example, the component amounts of two similar mixtures of natural gas at 25˚C and 1 atm are as follows:

Substance	Formula	Mixture A	Mixture B	w_j	mass %
nitrogen	N_2	1.50 kg	2.25 kg	0.0150	1.50
methane	CH_4	52.74 kg	79.11 kg	0.5274	52.74
ethane	C_2H_6	45.76 kg	68.64 kg	0.4576	45.76
mixture		100.00 kg	150.00 kg	1.0000	100.00

Although Mixtures A and B have different masses, they have the same mass fractions. This example illustrates that mass fractions are **intensive** quantities; their magnitudes are independent of the amount of substance present. A mixture of 100 kg and a mixture of 150 kg can have the same component mass fractions. As illustrated in this example, the component composition can be expressed as either mass fractions or mass percentages. Component mass percents are the respective mass fractions times 100. Conversely, component mass fractions are the respective mass percents divided by 100.

The compositions of solid and liquid mixtures are commonly given in mass percent, but occasionally in mole percent. When the basis of the percentage is not given, mass percent is assumed. The composition of gas mixtures is commonly given in mole or volume percent, but is assumed to be mole percent when the basis of the percentage is not given.

The term **part per million (ppm)** is a convenient way to express the mass fraction of a component **j**, whose magnitude is on the order of 10^{-6} (e.g., 10^{-6} kg of **j** in 1 kg of mixture). For gases, **ppm** is usually on a molar basis. By definition, a part per million is

$$\text{1 part per million (ppm)} \equiv 10^{-6}\ \frac{\textit{mass of } \mathbf{j}}{\textit{mass of mix}} \quad \textit{or} \quad \frac{\textit{mole of } \mathbf{j}}{\textit{mole of mix}}.$$

For liquid mixtures, **ppm** is usually on a mass basis. For example, if 0.000 040 kg of carbon monoxide (CO) existed in 1 kg of air, then the mass fraction of CO becomes:

$$\mathbf{w_{co}} = 0.000\,040\,\frac{kg\ CO}{kg\ air}\left\langle \frac{1\ ppm}{10^{-6}\,\dfrac{kg\ CO}{kg\ air}} \right\rangle = 40\ \text{ppm} \quad \text{or} \quad 40{,}000\ \text{ppb}$$

The composition unit of **ppm** (10^{-6}) and **ppb** (10^{-9}) are commonly used by the Environmental Protection Agency (EPA) to report the toxicity levels of dangerous substances in air and water.

In place of the term mass fraction, engineers and chemist often use the term weight fraction. Since a mixture and its components are subject to the same gravitational pull **g**, the equation for the mass fraction of component **j** can be algebraically manipulated as follows:

$$\mathbf{w_j} = \frac{\mathbf{m_j}}{\mathbf{m}}\frac{\mathbf{g}}{\mathbf{g}} = \frac{\mathbf{W_j}}{\mathbf{W}}$$

where $\mathbf{W_j}$ is the weight of component **j** in the mixture in "force j",
W is the total weight of the mixture in "force mix".

Thus, quantity $\mathbf{w_j}$ can be called either a mass fraction or a weight fraction. Since the term weight fraction is a misnomer for a composition quantity, you should always interpret a weight fraction as a mass fraction.

Mole Fraction, $\mathbf{x_j = n_j / n}$, "mass-mole j / mass-mole mix". LoQ

It is a dimensionless ratio of the mass-mole of component **j** in a chemical mixture per total mass-mole of that mixture in a particular state of aggregation (solid, liquid, or gas). By definition, a mixture is chemically inert; that is, no chemical reactions are occurring. The dimensions for quantity $\mathbf{x_j}$ are "mass-mole of j per mass-mole of mixture".

For example, $x_{N_2} = 0.0110$ g-mol N_2 / g-mol gas
and $x_{CH_4} = 0.6760$ g-mol CH_4 / g-mol gas
and $x_{C_2H_6} = \underline{0.3130}$ g-mol C_2H_6 / g-mol gas.
1.0000

For example, $x_{N_2} = 0.0110$ kg-mol N_2 / kg-mol gas
and $x_{CH_4} = 0.6760$ kg-mol CH_4 / kg-mol gas
and $x_{C_2H_6} = \underline{0.3130}$ kg-mol C_2H_6 / kg-mol gas.
1.0000

For example, $x_{N_2} = 0.0110$ lb-mol N_2 / lb-mol gas
and $x_{CH_4} = 0.6760$ lb-mol C_2H_6 / lb-mol gas
and $x_{C_2H_6} = \underline{0.3130}$ lb-mol C_2H_6 / lb-mol gas.
1.0000

where the mixture of the three chemical components (nitrogen, methane, and ethane) is that of natural gas found in Oil City, PA.

The **composition** of a mixture is the chemical formulas and mole fractions of the components in that mixture, and these mole fractions **must** sum to one. As illustrated in the above examples, the magnitude of a mole fraction ($\mathbf{x_j}$) for any component in a mixture is the same no matter what mass-mole units are used.

Mathematically, the mole fraction of component **j** in a mixture ($\mathbf{x_j}$) is equal to the mass-moles of that component ($\mathbf{n_j}$) divided by the total mass-moles of the mixture ($\mathbf{n}$); that is, $\mathbf{x_j = n_j / n}$.

Alternately, the mass-mole of component **j** ($\mathbf{n_j}$) is equal to the product of the total mass-mole of the mixture ($\mathbf{n}$) and the mole fraction of component **j** in that mixture ($\mathbf{x_j}$); that is, $\mathbf{n_j = n \cdot x_j}$.

A mixture can be visualized as being formed from the **pure components**; that is, the pure substances at the temperature (**T**) and pressure (**P**) of the mixture. For example, a mixture of

100 kg-mol of natural gas at 25˚C and 1 atm can be <u>visualized</u> as being formed by mixing the following pure gases:

Container	Pure **j**	Formula	Mix **T**	Mix **P**	n_j
Tank 1	nitrogen	N_2	25˚C	1 atm	1.10 kg-mol
Tank 2	methane	CH_4	25˚C	1 atm	67.60 kg-mol
Tank 3	ethane	C_2H_6	25˚C	1 atm	31.30 kg-mol
				Total mixture **n** =	100.00 kg-mol

Thus, the total mass-mole of the mixture can be visualized as being the sum of the mass-moles of the pure components.

As a general (or first) principle for mixtures, **the total mass-mole of a chemically-inert mixture is equal to the sum of its component mass-moles**. Mathematically, this principle is:

$$\mathbf{n} = \sum_{j=1}^{nc} \mathbf{n}_j = \mathbf{n}_1 + \mathbf{n}_2 + \ldots + \mathbf{n}_j + \ldots + \mathbf{n}_{nc} \tag{A.5}$$

where **n** is the total mass-mole of the mixture in "mass-mole mix",
$\mathbf{n}_j$ is the mass-mole of component **j** in the mixture in "mass-mole j",
nc is the number of chemical components in the mixture.

Equation A.5 is read as the total mass-mole (**n**) of the mixture is equal to the mass-mole of the first component ($\mathbf{n}_1$) plus the mass-mole of the second component ($\mathbf{n}_2$) plus all the component mass-moles up to and including that for the "nc" component ($\mathbf{n}_{nc}$). In the example, the first component is nitrogen, the second component is methane, and the third (or "nc") component is ethane.

If both sides of Equation A.5 are divided by the total mass-mole **n** of the mixture, the resulting equation is:

$$1.0 = \sum_{j=1}^{nc} \frac{\mathbf{n}_j}{\mathbf{n}} = \frac{\mathbf{n}_1}{\mathbf{n}} + \frac{\mathbf{n}_2}{\mathbf{n}} + \ldots + \frac{\mathbf{n}_j}{\mathbf{n}} + \ldots + \frac{\mathbf{n}_{nc}}{\mathbf{n}} \tag{A.6}$$

Substituting $\mathbf{x}_j = \mathbf{n}_j / \mathbf{n}$ into Equation A.6 produces the following equation:

$$1.0 = \sum_{j=1}^{nc} \mathbf{x}_j = \mathbf{x}_1 + \mathbf{x}_2 + \ldots + \mathbf{x}_j + \ldots + \mathbf{x}_{nc} \tag{A.7}$$

Therefore, the sum of the component mole fractions for a chemical mixture must be equal to one.

The amounts of the chemical components in a chemical mixture are commonly reported on a relative basis in percentages. For example, the component amounts of two similar mixtures of natural gas at 25˚C and 1 atm are as follows:

Substance	Formula	Mixture A	Mixture B	x_j	mole %
nitrogen	N_2	1.10 kg-mol	1.65 kg-mol	0.0110	1.10
methane	CH_4	67.60 kg-mol	101.40 kg-mol	0.6760	67.60
ethane	C_2H_6	31.30 kg-mol	46.95 kg-mol	0.3130	31.30
mixture		100.00 kg-mol	150.00 kg-mol	1.0000	100.00

Although Mixtures A and B have different mass-moles, they have the same mole fractions. This example illustrates that mole fractions are **intensive** quantities; their magnitudes are independent of the amount of substance present. A mixture of 100 kg-mol and a mixture of 150 kg-mol can have the same component mole fractions. As illustrated in this example, the component composition can be expressed as either mole fractions or mole percentages. Component mole percents are the respective mole fractions times 100. Conversely, component mole fractions are the respective mole percents divided by 100.

The composition of gas mixtures is commonly given in mole or volume percent, but is assumed to be mole percent when the basis of the percentage is not given. The compositions of solid and liquid mixtures are commonly given in mass percent, but occasionally in mole percent. When the basis of the percentage is not given, mass percent is assumed.

Volume Fraction, $y_j = V_j / V$, "length^3 j / length^3 mix". LoQ

It is a dimensionless ratio of the volume of pure component **j** at the temperature and pressure of a chemical mixture per total volume of that mixture in a particular state of aggregation (solid, liquid, or gas). By definition, a mixture is chemically inert; that is, no chemical reactions are occurring. The dimensions for quantity y_j are "volume of pure j at mixture T and P per volume of mixture".

For example, $y_{C_3H_8O}$ = 0.7174 cm^3 C_3H_8O / cm^3 mix

and y_{H_2O} = $\underline{0.3074}$ cm^3 H_2O / cm^3 mix.

1.0248

For example, $y_{C_3H_8O}$ = 0.7174 m^3 C_3H_8O / m^3 mix.

and y_{H_2O} = $\underline{0.3074}$ m^3 H_2O / m^3 mix

1.0248

For example, $y_{C_3H_8O}$ = 0.7174 ft^3 C_3H_8O / ft^3 mix

and y_{H_2O} = $\underline{0.3074}$ ft^3 H_2O / ft^3 mix.

1.0248

where the mixture of 2-propanol and water is isopropyl rubbing alcohol, found in most drug stores. The compound 2-propanol is also called isopropanol or isopropyl alcohol.

The **composition** of a mixture is the chemical formulas and volume fractions of the components in that mixture, and these volume fractions may or may not sum to one[†]. As illustrated in the above examples, the magnitude of a volume fraction (y_j) for any component in a mixture is the same no matter what volume units are used.

Mathematically, the volume fraction of component **j** in a mixture (y_j) is equal to the volume of the **pure** component (V_j) at the temperature (**T**) and pressure (**P**) of the mixture divided by the total volume of the mixture (**V**); that is, $y_j = V_j / V$, where $V_j = vol_j[\,T, P, \text{pure } j, m_j\,]$. The function *volj* means the volume of pure substance **j** is determined at the temperature, pressure, and amount of **j** found in the mixture.

Alternately, the volume of the **pure** component (V_j) at the temperature (**T**) and pressure (**P**) of the mixture is equal to the product of the total volume of the mixture (**V**) and the volume fraction of component **j** in that mixture (y_j); that is, $V_j = V \cdot y_j$.

[†] A mixture can be visualized as being formed from the **pure components**; that is, the pure substances at the temperature (**T**) and pressure (**P**) of the mixture. For example, a mixture of 97.58 mL of rubbing alcohol at 25˚C and 1 atm can be visualized as being formed by mixing the following pure liquids:

Container	Pure **j**	Formula	Mix **T**	Mix **P**	V_j	Pure sg_j	m_j
Beaker 1	2-propanol	C_3H_8O	25˚C	1 atm	70.00 mL	0.7851	54.96 g
Beaker 2	water	H_2O	25˚C	1 atm	30.00 mL	0.9982	29.95 g
			Total mixture **V** =		97.58 mL	and **m** =	84.91 g

where the specific gravity sg_j is for pure **j** at 20˚C and 1 atm referenced to pure water at 4˚C and 1 atm. The specific gravity of the mixture obtained by mixing 70 mL of 2-propanol with 30 mL of water is $0.8702\,\frac{20^\circ}{4^\circ}$. The total mass of the mixture is 84.91 g, and the composition of the 2-propanol is roughly 65 mass percent. The total volume of this mixture is 97.58 mL, not 100 mL.

Unlike the total mass of a mixture, the total volume of a mixture is **not** necessarily equal to the sum of the volumes of the pure components. If the pure component volumes were additive upon mixing, then the mixture volume would be 100 mL. Because the molecules of 2-propanol and water are attracted to one another, the molecular distances decrease and produce a mixture volume of 97.58 mL. If these molecules had repelled one another, the mixture volume would have been greater than 100 mL. When the component molecules of a mixture do not interact with one another, the mixture is called an **ideal solution** and the pure component volumes are additive.

In general, the pure component volumes of gas mixtures are additive, when the pressure is below 3 atm or the temperature is very high. At these conditions, a gas mixture behaves like an ideal solution and is called an **ideal gas** mixture. The pure component volumes of solid and liquid mixtures, in general, are **not** additive. As a first approximation, these types of mixtures are commonly assumed to behave as ideal solutions.

As a general (or first) principle for mixtures, **the total volume of a chemically-inert mixture is not equal to the sum of its pure component volumes**. Mathematically, this principle is:

$$\mathbf{V} = \sum_{j=1}^{nc} \mathbf{V_j} + \Delta\mathbf{V_{mix}} = \mathbf{V_1} + \mathbf{V_2} + \ldots + \mathbf{V_j} + \ldots + \mathbf{V_{nc}} + \Delta\mathbf{V_{mix}} \qquad (A.8)$$

$$\mathbf{V_j} = vol_j[\ \mathbf{T}, \mathbf{P}, \textbf{pure j}, \mathbf{m_j}\ ] \qquad \text{for } j = 1, 2, \ldots, nc \qquad (A.9)$$

where			
	$\mathbf{V}$	is	the total volume of the mixture in units of "length^3 mix",
	$\mathbf{V_j}$	is	the volume of pure component **j** in units of "length^3 j",
	$\Delta\mathbf{V_{mix}}$	is	the volume change on mixing in units of "length^3",
	nc	is	the number of chemical components in the mixture,
	T	is	the temperature of the mixture in units of "temperature",
	P	is	the pressure of the mixture in units of "pressure",
	$\mathbf{m_j}$	is	the mass of component **j** in the mixture in units of "mass",
	$vol_j[\ ]$	is	the volume function for pure substance **j** at the conditions of the mixture.

Equation A.8 means that the total volume (**V**) of the mixture is equal to the pure volume of the first component ($\mathbf{V_1}$) plus the pure volume of the second component ($\mathbf{V_2}$) plus all the pure component volumes up to and including that for the "**nc**" component ($\mathbf{V_{nc}}$) plus the volume change on mixing ($\Delta\mathbf{V_{mix}}$). In the example, the first component is 2-propanol (also called isopropyl alcohol) and the second (or "**nc**") component is water. Click here to view a presentation about the volume-of-mixing effect [Brown and Hanyak, 1998].

If both sides of Equation A.8 are divided by the total volume **V** of the mixture, the resulting equation is:

$$1.0 = \sum_{j=1}^{nc} \frac{\mathbf{V_j}}{\mathbf{V}} + \frac{\Delta\mathbf{V_{mix}}}{\mathbf{V}} = \frac{\mathbf{V_1}}{\mathbf{V}} + \frac{\mathbf{V_2}}{\mathbf{V}} + \ldots + \frac{\mathbf{V_j}}{\mathbf{V}} + \ldots + \frac{\mathbf{V_{nc}}}{\mathbf{V}} + \frac{\Delta\mathbf{V_{mix}}}{\mathbf{V}} \qquad (A.10)$$

Substituting $\mathbf{y_j} = \mathbf{V_j} / \mathbf{V}$ into Equation A.10 produces the following equation for **real mixtures**:

$$1.0 = \sum_{j=1}^{nc} \mathbf{y_j} + \frac{\Delta\mathbf{V_{mix}}}{\mathbf{V}} = \mathbf{y_1} + \mathbf{y_2} + \ldots + \mathbf{y_j} + \ldots + \mathbf{y_{nc}} + \frac{\Delta\mathbf{V_{mix}}}{\mathbf{V}} \qquad (A.11)$$

When a real mixture behaves like an ideal solution, the $\Delta\mathbf{V_{mix}}$ **equals zero**, and Equation A.11 reduces to:

$$1.0 = \sum_{j=1}^{nc} \mathbf{y_j} = \mathbf{y_1} + \mathbf{y_2} + \ldots + \mathbf{y_j} + \ldots + \mathbf{y_{nc}} \qquad (A.12)$$

Therefore, the sum of the component volume fractions for a **real mixture** may not necessarily equal one, but the sum of the component volume fractions for an **ideal mixture** will be equal to one. For the isopropanol-water mixture given above,

$$1.0 = \frac{V_1}{V} + \frac{V_2}{V} + \frac{\Delta V_{mix}}{V} = \frac{70.00\,mL}{97.58\,mL} + \frac{30.00\,mL}{97.58\,mL} + \frac{(97.58-100.00)\,mL}{97.58\,mL}$$

$$1.0 = \quad = 0.7174 + 0.3074 - 0.0248 = 1.0000$$

where the volume of mixing is negative since the total volume decreases after mixing the two component volumes of 70 mL of pure isopropanol with 30 mL of pure water.

The amounts of the chemical components in a chemical mixture are commonly reported on a relative basis in percentages. For example, the component amounts of two similar **ideal** mixtures of natural gas at 25˚C and 1 atm are as follows:

Substance	Formula	Mixture A	Mixture B	y_j	vol %
nitrogen	N_2	26.91 m^3	40.37 m^3	0.0110	1.10
methane	CH_4	1653.91 m^3	2480.87 m^3	0.6760	67.60
ethane	C_2H_6	765.79 m^3	1148.69 m^3	0.3130	31.30
mixture		2446.61 m^3	3669.93 m^3	1.0000	100.00

Although Mixtures A and B have different volumes, they have the same volume fractions. This example illustrates that volume fractions are **intensive** quantities; their magnitudes are independent of the amount of substance present. A mixture of 2446.61 m^3 and a mixture of 3669.93 m^3 can have the same component volume fractions. As illustrated in this example, the component composition can be expressed as either volume fractions or volume percentages. Component volume percents are the respective volume fractions times 100. Conversely, component volume fractions are the respective volume percents divided by 100.

The composition of gas mixtures is commonly given in volume or mole percent, but is assumed to be mole percent when the basis of the percentage is not given. If a gas mixture behaves like an ideal solution (i.e., an ideal gas), then its volume and mole percents are identical. The compositions of solid and liquid mixtures are commonly given in mass percent, but occasionally in mole percent, and rarely in volume percent. When the basis of the percentage is not given, mass percent is assumed.

Mass Concentration, $\hat{c}'_j = m_j / V$, "mass j / length^3 mix". LoQ

It is a ratio of the mass of component **j** in a chemical mixture per unit volume of that mixture in a particular state of aggregation (solid, liquid, or gas). By definition, a mixture is chemically inert; that is, no chemical reactions are occurring. The dimensions for quantity $\hat{c}'_j$ are "mass of j per length^3 of mixture".

For example, $\hat{c}'_{C_3H_8O} = 0.5632$ g C_3H_8O / cm^3 mix
and $\hat{c}'_{H_2O} = 0.3069$ g H_2O / cm^3 mix.
$\rho = 0.8701$ g mix / cm^3 mix.

For example, $\hat{\mathbf{c}}'_{C_3H_8O} = 563.20 \text{ kg } C_3H_8O \text{ / m}^3 \text{ mix}$

and $\hat{\mathbf{c}}'_{H_2O} = \underline{306.90} \text{ kg } H_2O \text{ / m}^3 \text{ mix.}$

$\rho = 870.10 \text{ kg mix / m}^3 \text{ mix.}$

For example, $\hat{\mathbf{c}}'_{C_3H_8O} = 35.1596 \text{ lb}_m \; C_3H_8O \text{ / ft}^3 \text{ mix}$

and $\hat{\mathbf{c}}'_{H_2O} = \underline{19.1592} \text{ lb}_m \; H_2O \text{ / ft}^3 \text{ mix.}$

$\rho = 54.3188 \text{ lb}_m \text{ mix / ft}^3 \text{ mix.}$

where the mixture of 2-propanol and water is isopropyl rubbing alcohol, found in most drug stores.

The **composition** of a mixture is the chemical formulas and mass concentrations of the components in that mixture, and these mass concentrations **must** sum to the density (ρ) of the total mixture. As illustrated in the above examples, the magnitude of a mass concentration ($\hat{\mathbf{c}}'_j$) for any component in a mixture **differs** depending upon the mass and volume units used.

Mathematically, the mass concentration of component **j** in a mixture ($\hat{\mathbf{c}}'_j$) is equal to the mass of that component ($\mathbf{m_j}$) divided by the total volume of the mixture (**V**); that is, $\hat{\mathbf{c}}'_j = \mathbf{m_j / V}$.

Alternately, the mass of component **j** ($\mathbf{m_j}$) is equal to the product of the total volume of the mixture (**V**) and the mass concentration of component **j** in that mixture ($\hat{\mathbf{c}}'_j$); that is, $\mathbf{m_j = V \cdot \hat{c}'_j}$.

The component mass concentrations of a chemical mixture are related to the density of that mixture. This relationship is derived from the general principle for mixtures; that is, **the total mass of a chemically-inert mixture is equal to the sum of its component masses**. Mathematically, this principle is:

$$\mathbf{m} = \sum_{j=1}^{nc} \mathbf{m_j} = \mathbf{m_1 + m_2 + \ldots + m_j + \ldots + m_{nc}}$$

where $\mathbf{m}$ is the total mass of the mixture in "mass mix",
$\mathbf{m_j}$ is the mass of component **j** in the mixture in "mass j",
$\mathbf{nc}$ is the number of chemical components in the mixture.

If both sides of this general equation are divided by the total volume **V** of the mixture, the resulting equation is:

$$\frac{\mathbf{m}}{\mathbf{V}} = \sum_{j=1}^{nc} \frac{\mathbf{m_j}}{\mathbf{V}} = \frac{\mathbf{m_1}}{\mathbf{V}} + \frac{\mathbf{m_2}}{\mathbf{V}} + \ldots + \frac{\mathbf{m_j}}{\mathbf{V}} + \ldots + \frac{\mathbf{m_{nc}}}{\mathbf{V}} \tag{A.13}$$

Substituting $\boldsymbol{\rho} = \mathbf{m / V}$ and $\hat{\mathbf{c}}'_j = \mathbf{m_j / V}$ into Equation A.13 produces the following equation:

$$\rho \;=\; \sum_{j=1}^{nc} \hat{c}'_j = \;\; \hat{c}'_1 \;+\; \hat{c}'_2 \;+\; \ldots \;+\; \hat{c}'_j \;+\; \ldots \;+\; \hat{c}'_{nc} \qquad \text{(A.14)}$$

Dividing both sides of Equation A.14 by the density of the mixture produces the following equation:

$$1.0 \;=\; \sum_{j=1}^{nc} \frac{\hat{c}'_j}{\rho} = \;\; \frac{m_1}{V} \cdot \frac{V}{m} \;+\; \ldots \;+\; \frac{m_j}{V} \cdot \frac{V}{m} \;+\; \ldots \;+\; \frac{m_{nc}}{V} \cdot \frac{V}{m} \qquad \text{(A.15)}$$

Substituting $w_j = m_j / m$ into Equation A.15 produces the following equation:

$$1.0 \;=\; \sum_{j=1}^{nc} w_j \;\;=\;\; w_1 \;+\; w_2 \;+\; \ldots \;+\; w_j \;+\; \ldots \;+\; w_{nc}$$

Therefore, the component mass fractions (w_j) and mass concentrations ($\hat{c}'_j$) of a chemical mixture are related by the equation $w_j = \hat{c}'_j \;/\; \rho$.

Molar Concentration, $\hat{c}_j \;=\; n_j / V$, "mass-mole j / length^3 mix". LoQ

It is a ratio of the mass-moles of component **j** in a chemical mixture per unit volume of that mixture in a particular state of aggregation (solid, liquid, or gas). By definition, a mixture is chemically inert; that is, no chemical reactions are occurring. The dimensions for quantity $\hat{c}_j$ are "mass-moles of j per length^3 of mixture".

For example, $\hat{c}_{C_3H_8O} \;=\; 0.009\,372$ g-mol C_3H_8O / cm^3 mix
and $\hat{c}_{H_2O} \;=\; \underline{0.017\,035}$ g-mol H_2O / cm^3 mix.
$\hat{\rho} \;=\; 0.026\,407$ g-mol mix / cm^3 mix.

For example, $\hat{c}_{C_3H_8O} \;=\; 9.372$ kg-mol C_3H_8O / m^3 mix
and $\hat{c}_{H_2O} \;=\; \underline{17.035}$ kg-mol H_2O / m^3 mix.
$\hat{\rho} \;=\; 26.407$ kg-mol mix / m^3 mix.

For example, $\hat{c}_{C_3H_8O} \;=\; 0.5851$ lb-mol C_3H_8O / ft^3 mix
and $\hat{c}_{H_2O} \;=\; \underline{1.0635}$ lb-mol H_2O / ft^3 mix.
$\hat{\rho} \;=\; 1.6486$ lb-mol mix / ft^3 mix.

where the mixture of 2-propanol and water is isopropyl rubbing alcohol, found in most drug stores.

The **composition** of a mixture is the chemical formulas and molar concentrations of the components in that mixture, and these molar concentrations **must** sum to the molar density of the total mixture. As illustrated in the above examples, the magnitude of a molar concentration

($\hat{c}_j$) for any component in a mixture **differs** depending upon the mass-mole and volume units used.

Mathematically, the molar concentration of component **j** in a mixture ($\hat{c}_j$) is equal to the mass-moles of that component (n_j) divided by the total volume of the mixture (**V**); that is, $\hat{c}_j = n_j / V$.

Alternately, the mass-moles of component **j** (n_j) is equal to the product of the total volume of the mixture (**V**) and the molar concentration of component **j** in that mixture ($\hat{c}_j$); that is, $n_j = V \cdot \hat{c}_j$.

The component molar concentrations of a chemical mixture are related to the molar density of that mixture. This relationship is derived from the general principle for mixtures; that is, **the total mass-mole of a chemically-inert mixture is equal to the sum of its component mass-moles**. Mathematically, this principle is:

$$n = \sum_{j=1}^{nc} n_j = n_1 + n_2 + \ldots + n_j + \ldots + n_{nc}$$

where n is the total mass-mole of the mixture in "mass-mole mix",
n_j is the mass-mole of component **j** in the mixture in "mass-mole j",
nc is the number of chemical components in the mixture.

If both sides of this principle equation are divided by the total volume **V** of the mixture, the resulting equation is:

$$\frac{n}{V} = \sum_{j=1}^{nc} \frac{n_j}{V} = \frac{n_1}{V} + \frac{n_2}{V} + \ldots + \frac{n_j}{V} + \ldots + \frac{n_{nc}}{V} \qquad \text{(A.16)}$$

Substituting $\hat{\rho} = n / V$ and $\hat{c}_j = n_j / V$ into Equation A.16 produces the following equation:

$$\hat{\rho} = \sum_{j=1}^{nc} \hat{c}_j = \hat{c}_1 + \hat{c}_2 + \ldots + \hat{c}_j + \ldots + \hat{c}_{nc} \qquad \text{(A.17)}$$

Dividing both sides of Equation A.17 by the molar density of the mixture produces the following equation:

$$1.0 = \sum_{j=1}^{nc} \frac{\hat{c}_j}{\hat{\rho}} = \frac{n_1}{V} \cdot \frac{V}{n} + \ldots + \frac{n_j}{V} \cdot \frac{V}{n} + \ldots + \frac{n_{nc}}{V} \cdot \frac{V}{n} \qquad \text{(A.18)}$$

Substituting $x_j = n_j / n$ into Equation A.18 produces the following equation:

$$1.0 = \sum_{j=1}^{nc} x_j = x_1 + x_2 + \ldots + x_j + \ldots + x_{nc}$$

Therefore, the component mole fractions (x_j) and molar concentrations ($\hat{c}_j$) of a chemical mixture are related by the equation $x_j = \hat{c}_j / \hat{\rho}$.

The **molarity** (M) of a solution is the gram-moles of a solute in one liter of solution, where the solvent in that solution is a liquid. In other words, the molarity is a molar concentration with units of "g-mol / L". In the above example, the mixture of 2-propanol and water has a molarity of 9.372 M C_3H_8O, where water is the solvent.

Some textbooks use the same symbol for molar and mass concentrations, namely $\hat{c}_j$. Usually, the context of the problem will indicated whether the units of $\hat{c}_j$ are mass-mole per unit volume or mass per volume. If quantities in the problem are in molar units, then $\hat{c}_j$ will have units of mass-mole per unit volume. If quantities in the problem are in mass units, then $\hat{c}_j$ will have units of mass per unit volume. When a problem requires that both sets of units are needed, then $\hat{c}_j$ will be use for molar concentration, and $\hat{c}'_j$ will be use for mass concentration.

Rate Quantities

Mass Flow, $\dot{m} = m / t$, "mass / time". LoQ

It is the rate at which the mass of a chemical substance flows per unit of time past a cross-sectional area of the transporting medium, such as a conveyor belt for a solid, a square channel for a liquid, or a cylindrical pipe for a gas or liquid. The chemical substance is either a free element, a compound, or a mixture. The dimensions for quantity $\dot{m}$ are "mass per time".

The cross-sectional area is the 2-dimensional space formed by the perpendicular intersection of an imaginary plane with the flowing mass of the chemical substance. For a cylindrical pipe the cross-sectional area is a circle; for a rectangular channel it is a rectangle; and, for a conveyor belt it is the irregular area formed by the intersection of the flowing solid with the imaginary plane.

For example, for elemental copper (**Cu**) as a **solid** at 25˚C and 1 atm:

$\dot{m}$ = 125.0 grams per second,
or $\dot{m}$ = 125.0 g/s,
or $\dot{m}$ = 7500 grams per minute,
or $\dot{m}$ = 7500 g/min

For example, for compound water (**H_2O**) as a **liquid** at 75˚C and 1 atm:

$\dot{m}$ = 0.1250 kilogram per second,
or $\dot{m}$ = 0.1250 kg/s,
or $\dot{m}$ = 450.0 kilograms per hour,
or $\dot{m}$ = 450.0 kg/h

For example, for a mixture of air as a **gas** at 25˚C and 3 atm:

$\dot{m}$ = 0.2750 pound-mass per second,
or $\dot{m}$ = 0.2750 lb_m/s,
or $\dot{m}$ = 990.0 pound-mass per hour,
or $\dot{m}$ = 990.0 lb_m/h

where the symbols—**g/s**, **kg/h**, **lb_m/h**—are the commonly-used units for mass flow rate.

In these examples, a mass flow rate means that for every unit of time a specific amount of mass of a chemical substance passes through a cross-sectional area of the transporting medium. For the example of water, a flow rate of 0.1250 kg/s means that every second 0.1250 kg of water passes through a cross-sectional area.

Mathematically, the mass flow rate of a chemical substance ($\dot{m}$) is equal to the mass of that substance (**m**) divided by the time (**t**) for that mass to pass through a cross-sectional area of the transporting medium; that is, $\dot{m} = m / t$.

For a unit of time, the mass of chemical substance passing through the cross-sectional area is assumed to be uniform in temperature (**T**), pressure (**P**), composition (**comp**), and velocity (**u**). When these four quantities are not uniform, they are averaged over the unit of time.

When a cement truck pours its contents, the cement slurry (a mixture of solids and water) flows down the half-moon, delivery channel of the truck and exits from this channel into a construction form for a sidewalk or driveway. This slurry flows at a constant rate, as measured at the exit of the delivery channel. The mass flow rate at this exit position is associated with the cross-sectional area (a semi-circle) at that same position.

When you turn on the water faucet at the kitchen sink, the water flows at a constant rate, as measured at the exit of the faucet. The mass flow rate at this exit position is associated with the cross-sectional area (a circle) at that same position.

When you turn the cock valve of a compressed air line in a chemistry laboratory, the air flows at a constant rate, as measured at the exit of the cock valve. The mass flow rate at this exit position is associated with the cross-sectional area (a circle) at that same position.

The mass flow rate ($\dot{\mathbf{m}}$) and velocity ($\mathbf{u}$) of a chemical substance passing through a cross-sectional area are related by the following two equations:

$$\dot{\mathbf{m}} = \rho\, \mathbf{u}\, \mathbf{A} \qquad \textbf{continuity equation} \qquad \textbf{(A.19)}$$

$$\rho = \mathit{rho}[\, \mathbf{T}, \mathbf{P}, \mathbf{comp}\,] \qquad \textbf{(A.20)}$$

where $\dot{\mathbf{m}}$ is the mass flow rate of that substance in "mass / time",
ρ is the density of that substance in "mass / length^3",
$\mathbf{u}$ is the velocity of that substance in "length / time",
$\mathbf{A}$ is the cross-sectional area of flow in "length^2",
$\mathbf{T}$ is the temperature of that substance in "temperature",
$\mathbf{P}$ is the pressure of that substance in "force / length^2",
comp is the composition of that substance in mass or mole fractions,
rho[ ] is the density function for that chemical substance.

For a chemical substance that is a mixture, the mass flow rate of a component **j** in that mixture is expressed by the subscripted equation:

$$\dot{\mathbf{m}}_j = \dot{\mathbf{m}} \cdot \mathbf{w}_j$$

where $\dot{\mathbf{m}}_j$ is the mass flow rate of component **j** in "mass j / time",
$\dot{\mathbf{m}}$ is the mass flow rate of the mixture in "mass mix / time",
$\mathbf{w}_j$ is the mass fraction of component **j** in "mass j / mass mix".

Molar Flow, $\dot{\mathbf{n}} = \mathbf{n} / \mathbf{t}$, "mass-mole / time". LoQ

It is the rate at which the mass-moles of a chemical substance flow per unit of time past a cross-sectional area of the transporting medium, such as a conveyor belt for a solid, a square channel for a liquid, or a cylindrical pipe for a gas or liquid. The chemical substance is either a free element, a compound, or a mixture. The dimensions for quantity $\dot{\mathbf{n}}$ are "mass-mole per time".

The cross-sectional area is the 2-dimensional space formed by the perpendicular intersection of an imaginary plane with the flowing mass of the chemical substance. For a cylindrical pipe the cross-sectional area is a circle; for a rectangular channel it is a rectangle; and, for a conveyor belt it is the irregular area formed by the intersection of the flowing solid with the imaginary plane.

For example, for elemental copper (**Cu**) as a **solid** at 25˚C and 1 atm:
$\dot{\mathbf{n}}$ = 1.967 gram-moles per second,
or $\dot{\mathbf{n}}$ = 1.967 g-mol/s,
or $\dot{\mathbf{n}}$ = 118.0 gram-moles per minute,
or $\dot{\mathbf{n}}$ = 118.0 g-mol/min

For example, for compound water (**$\mathbf{H_2O}$**) as a **liquid** at 75˚C and 1 atm:
$\dot{\mathbf{n}}$ = 0.006 939 kilogram-mole per second,
or $\dot{\mathbf{n}}$ = 0.006 939 kg-mol/s,
or $\dot{\mathbf{n}}$ = 24.98 kilogram-moles per hour,
or $\dot{\mathbf{n}}$ = 24.98 kg-mol/h

For example, for a mixture of air as a **gas** at 25˚C and 3 atm:
$\dot{\mathbf{n}}$ = 0.009 494 pound-mole per second,
or $\dot{\mathbf{n}}$ = 0.009 494 lb-mol/s,
or $\dot{\mathbf{n}}$ = 34.18 pound-moles per hour,
or $\dot{\mathbf{n}}$ = 34.18 lb-mol/h

where the symbols—**g-mol/s** (or **mol/s**), **kg-mol/h**, **lb-mol/h**—are the commonly-used units for molar flow rate.

In these examples, a molar flow rate means that for every unit of time a specific amount of mass-moles (i.e., molecules) of a chemical substance passes through a cross-sectional area of the transporting medium. For the example of water, a flow rate of 24.98 kg-mol/h means that every hour 24.98 kg-mol of water pass through a cross-sectional area.

Mathematically, the molar flow rate of a chemical substance ($\dot{\mathbf{n}}$) is equal to the mass-moles of that substance ($\mathbf{n}$) divided by the time ($\mathbf{t}$) for that mass-moles to pass through a cross-sectional area of the transporting medium; that is, $\dot{\mathbf{n}} = \mathbf{n} / \mathbf{t}$.

For a unit of time, the mass-moles of chemical substance passing through the cross-sectional area are assumed to be uniform in temperature ($\mathbf{T}$), pressure ($\mathbf{P}$), composition (**comp**), and velocity ($\mathbf{u}$). When these four quantities are not uniform, they are averaged over the unit of time.

The molar flow rate ($\dot{\mathbf{n}}$) and mass flow rate ($\dot{\mathbf{m}}$) of a chemical substance passing through a cross-sectional area are related by the following equation:

$$\dot{\mathbf{n}} = \dot{\mathbf{m}} / \mathbf{M}$$

where $\dot{\mathbf{n}}$ is the molar flow rate of that substance in "mass-mole / time",
$\dot{\mathbf{m}}$ is the mass flow rate of that substance in "mass / time",

M is the molecular weight of that substance in "mass / mass-mole".

For a chemical substance that is a mixture, the molar flow rate of a component **j** in that mixture is expressed by the subscripted equation:

$$\dot{n}_j = \dot{n} \cdot x_j$$

where $\dot{n}_j$ is the molar flow rate of component **j** in "mass-mole j / time",
$\dot{n}$ is the molar flow rate of the mixture in "mass-mole mix / time",
x_j is the mole fraction of component **j** in "mass-mole j / mass-mole mix".

Volumetric Flow, $\dot{V} = V / t$, "length^3 / time". LoQ

It is the rate at which the volume of a chemical substance flows per unit of time past a cross-sectional area of the transporting medium, such as a conveyor belt for a solid, a square channel for a liquid, or a cylindrical pipe for a gas or liquid. The chemical substance is either a free element, a compound, or a mixture. The dimensions for quantity $\dot{V}$ are "length^3 per time".

The cross-sectional area is the 2-dimensional space formed by the perpendicular intersection of an imaginary plane with the flowing mass of the chemical substance. For a cylindrical pipe the cross-sectional area is a circle; for a rectangular channel it is a rectangle; and, for a conveyor belt it is the irregular area formed by the intersection of the flowing solid with the imaginary plane.

For example, for element copper (**Cu**) as a **solid** at 25˚C and 1 atm:

$\dot{V}$ = 14.01 cubic centimeters per second,
or $\dot{V}$ = 14.01 cm^3/s,
or $\dot{V}$ = 840.8 cubic centimeters per minute,
or $\dot{V}$ = 840.8 cm^3/min

For example, for compound water (**H_2O**) as a **liquid** at 75˚C and 1 atm:

$\dot{V}$ = 0.000 1288 cubic meter per second,
or $\dot{V}$ = 0.000 1288 m^3/s,
or $\dot{V}$ = 463.5 liters per hour,
or $\dot{V}$ = 463.5 L/h

For example, for a mixture of air as a **gas** at 25˚C and 3 atm:

$\dot{V}$ = 1.240 cubic feet per second,
or $\dot{V}$ = 1.240 ft^3/s,
or $\dot{V}$ = 4465 cubic feet per hour,
or $\dot{V}$ = 4465 ft^3/h

where the symbols—**cm^3/s**, **L/h**, **ft^3/h**—are the commonly-used units for volumetric flow rate.

In these examples, a volumetric flow rate means that for every unit of time a specific amount of volume of a chemical substance passes through a cross-sectional area of the transporting medium. For the example of water, a flow rate of 463.5 L/h means that every hour 463.5 L of water pass through a cross-sectional area.

Mathematically, the volumetric flow rate of a chemical substance ($\dot{\mathbf{V}}$) is equal to the volume of that substance ($\mathbf{V}$) divided by the time ($\mathbf{t}$) for that volume to pass through a cross-sectional area of the transporting medium; that is, $\dot{\mathbf{V}} = \mathbf{V} / \mathbf{t}$.

For a unit of time, the volume of chemical substance passing through the cross-sectional area is assumed to be uniform in temperature ($\mathbf{T}$), pressure ($\mathbf{P}$), composition ($\mathbf{comp}$), and velocity ($\mathbf{u}$). When these four quantities are not uniform, they are averaged over the unit of time.

The volumetric flow rate ($\dot{\mathbf{V}}$) and mass flow rate ($\dot{\mathbf{m}}$) of a chemical substance passing through a cross-sectional area are related by the following two equations:

$$\dot{\mathbf{V}} = \dot{\mathbf{m}} / \rho$$

$$\rho = \mathit{rho}[\ \mathbf{T}, \mathbf{P}, \mathbf{comp}\ ]$$

where			
	$\dot{\mathbf{V}}$	is	the volumetric flow rate of that substance in "length^3 / time",
	$\dot{\mathbf{m}}$	is	the mass flow rate of that substance in "mass / time",
	ρ	is	the density of that substance in "mass / length^3",
	$\mathbf{T}$	is	the temperature of that substance in "temperature",
	$\mathbf{P}$	is	the pressure of that substance in "force / length^2",
	$\mathbf{comp}$	is	the composition of that substance in mass or mole fractions,
	rho[ ]	is	the density function for that chemical substance.

The volumetric flow rate ($\dot{\mathbf{V}}$) and velocity ($\mathbf{u}$) of a chemical substance passing through a cross-sectional area are related by the following two equations:

$$\dot{\mathbf{V}} = \mathbf{u}\ \mathbf{A} \qquad \textbf{continuity equation} \qquad \textbf{(A.19)}$$

where			
	$\dot{\mathbf{V}}$	is	the volumetric flow rate of that substance in "length^3 / time",
	$\mathbf{u}$	is	the velocity of that substance in "length / time",
	$\mathbf{A}$	is	the cross-sectional area of flow in "length^2",

Mass Velocity, $\dot{G} = \dot{m} / A$, "mass / time·length^2". LoQ

It is the mass flow rate of a chemical substance divided by the cross-sectional area of the transporting medium, such as a conveyor belt for a solid, a square channel for a liquid, or a cylindrical pipe for a gas or liquid. The chemical substance is either a free element, a compound, or a mixture. The dimensions for quantity $\dot{G}$ are "mass per time·length^2".

Mathematically, the mass velocity of a chemical substance ($\dot{G}$) is equal to the mass flow rate of that substance ($\dot{m}$) divided by the cross-sectional area (A) of the transporting medium; that is, $\dot{G} = \dot{m} / A$.

Molar Flux, $\dot{N} = \dot{n} / A$, "mass-mole / time·length^2". LoQ

It is the molar flow rate of a chemical substance divided by the cross-sectional area of the transporting medium, such as a conveyor belt for a solid, a square channel for a liquid, or a cylindrical pipe for a gas or liquid. The chemical substance is either a free element, a compound, or a mixture. The dimensions for quantity $\dot{N}$ are "mass-mole per time·length^2".

Mathematically, the molar flux of a chemical substance ($\dot{N}$) is equal to the molar flow rate of that substance ($\dot{n}$) divided by the cross-sectional area (A) of the transporting medium; that is, $\dot{N} = \dot{n} / A$.

Introduction

As a chemical engineer, you need to master the intellectual skill of converting units between the meter-kilogram-second (**mks**), foot-pound-second (**fps**), and centimeter-gram-second (**cgs**) systems of units. We assume you know how to do units conversion. Click here if you need a refresher on the matter. This appendix presents a general procedure that you can review. This procedure can be applied to simple as well as complex conversion problems. The following four examples illustrate units conversion:

1. Convert 1500 g to lb_m :

$$\begin{aligned} m &= 1500\ \text{g}\left\langle \frac{1\ \text{lb}_\text{m}}{453.592\ \text{g}} \right\rangle \\ &= 3.30694\ \text{lb}_\text{m} \quad = \quad 3.3\ \text{lb}_\text{m} \\ &\cong \frac{2}{5}\times\frac{10^{+3}}{10^{+2}} \quad \cong \quad 4.0\ \text{lb}_\text{m} \qquad\qquad \text{a mental check} \end{aligned}$$

2. Convert 32.54 ft/min to m/s:

$$\begin{aligned} u &= 32.54\ \frac{\text{ft}}{\text{min}}\left\langle \frac{1\ \text{m}}{3.2808\ \text{ft}}\cdot\frac{1\ \text{min}}{60\ \text{s}} \right\rangle \\ &= 0.165305\,\frac{\text{m}}{\text{s}} \quad = \quad 0.1653\,\frac{\text{m}}{\text{s}} \\ &\cong \frac{3}{3\cdot 6}\times\frac{10^{+1}}{10^{+1}} \quad \cong \quad 0.1667\,\frac{\text{m}}{\text{s}} \qquad\qquad \text{a mental check} \end{aligned}$$

3. Convert 3 weeks to milliseconds:

$$\begin{aligned} t &= 3\ \text{wk}\left\langle \frac{7\ \text{d}}{1\ \text{wk}}\cdot\frac{24\ \text{h}}{1\ \text{d}}\cdot\frac{60\ \text{min}}{1\ \text{h}}\cdot\frac{60\ \text{s}}{1\ \text{min}}\cdot\frac{1\ \text{ms}}{10^{-3}\ \text{s}} \right\rangle \\ &= 1.8144\times 10^{+9}\ \text{ms} \\ &\cong 3\cdot 7\cdot 2\cdot 6\cdot 6\times\frac{10^{+1+1+1}}{10^{-3}} \quad \cong \quad 1.5\times 10^{+9}\ \text{ms} \qquad\qquad \text{a mental check} \end{aligned}$$

4. Convert expression for Reynolds Number (Re) to unitless:

$$\begin{aligned} \text{Re} &= \left(2.067\ \text{in}\cdot\frac{0.048\ \text{ft}}{\text{s}}\cdot\frac{0.805\ \text{g}}{\text{cm}^3}\cdot\frac{\text{m s}}{4.3\times 10^{-4}\ \text{kg}} \right)\left\langle \frac{1\ \text{kg}}{10^{+3}\ \text{g}}\cdot\frac{1\ \text{ft}}{12\ \text{in}}\cdot\frac{3.2808\ \text{ft}}{1\ \text{m}}\cdot\frac{28\,317\ \text{cm}^3}{1\ \text{ft}^3} \right\rangle \\ &= 1437.99 \quad = \quad 1400 \\ &\cong \frac{2\cdot 5\cdot 8\cdot 3\cdot 3}{4\cdot 1}\times\frac{10^{2-1+4}}{10^{-4+3+1}} \quad \cong \quad 1.8\times 10^{+3} \qquad\qquad \text{a mental check} \end{aligned}$$

These four problems exemplify the knowledge required to do units conversion, calculate the answer, account for precision, and approximate the answer to check the calculated result. For the conversion process, you have a starting point (a "Given") and an ending point (a "Find") as illustrated for the above four examples in the example units problems below. Your goal is to create a dimensional equation that goes from the “Given” to the “Find” using the **units conversion algorithm** outlined in the remainder of this appendix.

Example Units Problems

Starting Point

Given	Find
symbol, name	as
value(s) and units	new units

Some Examples

Given	Find
m, mass	as
1500 g	lb_m

Given	Find
u, velocity	as
32.54 ft/min	m/s

Given	Find
t, time	as
3 wk	ms

Given	Find
Re, Reynolds Number	as
$\dfrac{2.067\ \text{in} \cdot \dfrac{0.048\ \text{ft}}{\text{s}} \cdot \dfrac{0.805\ \text{g}}{\text{cm}^3}}{4.3\times10^{-4}\ \dfrac{\text{kg}}{\text{m s}}}$	unitless

Ending Point

A dimensional equation: (the Given) < series of conversion factors > = answer

Units Conversion Algorithm

1. Begin the dimensional equation. Write the “Given” as a product of factors as follows:

$$\frac{\#\,\text{num\_unit}}{\text{dem\_unit}}\cdot\frac{\#\,\text{num\_unit}}{\text{dem\_unit}}\cdot\quad\cdots\quad\cdot\frac{\text{num\_unit}}{\#\,\text{dem\_unit}}\cdot\frac{\text{num\_unit}}{\#\,\text{dem\_unit}}\cdot\quad\cdots$$

2. Select a unit in the “Given” that belongs to a specific unit class, such as length, time, or mass. Call it the current state.

3.
```
If   the “Find” is not unitless   then
    identify a unit in the “Find” with the same unit class as the current state.
else
    identify a unit in the “Given” with the same unit class as the current state.
endif.
```

   Call this identify unit the goal state.

4. Select an appropriate equivalence (≡) that relates the "current state" unit to the "goal state" unit. Use **Table** “**gotche**” in Chapter 3 of this *CinChE* manual or www.onlineconversion.com. E.G.,

Current State: kg
Goal State: oz

Equivalences	**Selection**
1 kg ≡ 1000 g 1 kg ≡ 2.20462 b_m 1 kg ≡ 35.27396 oz	1 kg ≡ 35.27396 oz

Current State: lb_m
Goal State: g

Equivalences	**Selection**
1 kg ≡ 1000 g 1 kg ≡ 2.20462 lb_m 1 kg ≡ 35.27396 oz	2.20462 lb_m ≡ 1000 g

5. Generate a conversion factor from the equivalence relationship as follows:

Equivalence: current ≡ goal Conversion factor: $\left\langle \frac{\text{goal}}{\text{current}} \right\rangle$

For example, $\left\langle \frac{35.27396\ \text{oz}}{1\ \text{kg}} \right\rangle$ or $\left\langle \frac{1000\ \text{g}}{2.20462\ \text{lb}_m} \right\rangle$

6. Place the conversion factor as the next product term in the dimensional equation, but invert it only if the “current state” unit appears in the denominator of the dimensional equation.

For example, $$1500\ \text{lb}_\text{m} \left\langle \frac{1000\ \text{g}}{2.20462\ \text{lb}_\text{m}} \right\rangle$$

For example, $$\frac{1}{1500\ \text{lb}_\text{m}} \left\langle \frac{2.20462\ \text{lb}_\text{m}}{1000\ \text{g}} \right\rangle$$

7. Raise the conversion factor to a power, if necessary.

For example, $$\left\langle \frac{1^3\ \text{m}^3}{3.2808^3\ \text{ft}^3} \right\rangle$$

8. Place a SI prefix conversion factor as the next product term, if necessary.

For example, $$1500\ \text{kg} \left\langle \frac{1\ \text{lb}_\text{m}}{453.592\ \text{g}} \cdot \frac{10^3\ \text{g}}{\text{kg}} \right\rangle$$

9. Cancel those units in the numerators and denominators that match.

10. Continue Steps 2 to 9 until the remaining units in the dimensional equation are the "Find" units.

11. Do the calculation using a calculator and record the answer using 6 significant digits.

For example, $$\begin{aligned} \text{m} &= 1500\ \text{kg} \left\langle \frac{1\ \text{lb}_\text{m}}{453.592\ \text{g}} \cdot \frac{10^3\ \text{g}}{\text{kg}} \right\rangle \\ &= 3306.94\ \text{lb}_\text{m} \end{aligned}$$

12. Account for precision and report the final answer.

For example, $$\begin{aligned} \text{m} &= 1500\ \text{kg} \left\langle \frac{1\ \text{lb}_\text{m}}{453.592\ \text{g}} \cdot \frac{10^3\ \text{g}}{\text{kg}} \right\rangle \\ &= 3306.94\ \text{lb}_\text{m} \quad = \quad 3300\ \text{lb}_\text{m} \end{aligned}$$

13. Approximate the answer using scientific notation, as a mental check on the calculated result.

For example, $$\frac{1.5}{4.5} \times \frac{10^{+3+3}}{10^{+2}} \quad \cong \quad 3333\ \text{lb}_\text{m}$$

Introduction

Much of your engineering career will be spent solving systems of equations. Consequently, this chapter will review for you the important concepts concerning equations that you will have to draw on. The sections which follow will review the differences between equations and equivalence relationships, define the concept of dimensional homogeneity, and review several properties of algebraic equations as well as several aspects of summation notation.

C.1 Algebraic Equations

In Appendix B you were introduced to dimensional equations, but you are probably familiar with other types of equations such as algebraic equations and differential equations. As you progress through your education as a chemical engineer, differential equations will be of great importance and usefulness to you, but for the immediate future your work in this course will focus on algebraic equations. What exactly, then, is an algebraic equation? Webster's Ninth Collegiate Dictionary defines an equation as a "**formal statement of the equality of mathematical or logical expressions**." For the purposes of this course, we will concentrate on equations which express the equality of mathematical expressions. **A mathematical equation can then be thought of as a statement which expresses the equality of a mathematical expression on the left-hand side of the equation to a mathematical expression on the right-hand side of the equation**. Below are several examples of equations:

$$\begin{aligned} 3 &= 3 \\ y &= 3 \\ a^2 &= b^2 + c^2 \\ x - y &= z + x - 2 \\ x_1 + x_2 + x_3 &= 2 \\ 2 + 3 &= T \\ TF &= 1.8\ TC + 32 \end{aligned}$$

Notice that in the equations above, the "=" symbol is used to indicate equality of a mathematical expression on the left-hand side of the equation to a mathematical expression on the right-hand side of the equation. Also notice that all but the first equation above contain symbols which represent numbers. **An equation which contains symbols that represent numbers is known as an algebraic equation.**

Since equations express the equality of two mathematical expressions, those expressions must be equal in every aspect including the net units of both mathematical expressions. Therefore, in order **for an equation to be valid the equation must exhibit dimensional homogeneity**; that is, the units on the right side of the equation must be identical to those on the left side of the equation. This fact separates equations from equivalence relations where the units on the right side of the relation differ from those on the left side.

	Valid Equation	Invalid Equation	Equivalence Relation
(1)	$L\ (\text{ft}) = 6\ \text{ft} - 3\ \text{ft}$	$L\ (\text{ft}) = 6\ \text{ft} - 3\ \text{in}$	$1\ \text{ft} \equiv 12\ \text{inches}$
(2)	$m\ (\text{g}) = 25\ \text{g} + 15\ \text{g}$	$m\ (\text{g}) = 25\ \text{g} + 15\ \text{lb}_m$	$1000\ \text{g} \equiv 2.20462\ \text{lb}_m$
(3)	$F\ (\frac{\text{kg m}}{\text{s}^2}) = 100\ \text{kg} \cdot 9.8\ \frac{\text{m}}{\text{s}^2}$	$F\ (\frac{\text{kg m}}{\text{s}^2}) = 100\ \text{kg} \cdot 32.174\ \frac{\text{ft}}{\text{s}^2}$	$1\ \text{lb}_f \equiv 4.4482\ \text{N}$

Three important points should be made about the valid equations above. First, in order to add or subtract two terms in a mathematical expression, the terms must have the same units (see Lines 1 and 2 above). Second, terms with different units can be multiplied and/or divided (e.g., 100 kg · 9.8 m/s^2 in Line 3 above). Third, while the three valid equations above all exhibit dimensional homogeneity and the invalid equations do not, it is possible for an equation to exhibit dimensional homogeneity and not be valid. For instance, the equation

$$6\ \text{ft} = 3\ \text{ft}$$

exhibits dimensional homogeneity but is obviously not valid. Thus, for an equation to be valid, dimensional homogeneity is necessary, but is not sufficient.

C.2 Linear Equations

A special subset of algebraic equations is linear equations. **A linear equation is an equation in which each of its terms has only one unknown variable and the power on that variable is one**. Thus, any term whose unknown variable has a power other than one, like 2 or ½, makes the equation non-linear. Also, any term that has an unknown variable times or divide by an unknown variable, X*Y or X/Y, makes the equation non-linear. Because you will spend considerable time working with linear equations, some additional information specific to linear equations is contained in Section C.2.1 to C.2.6.

C.2.1 A System of Linear Equations

A simple system of linear equations might be:

$$\begin{array}{ccccccccc} x_1 & + & x_2 & + & x_3 & = & 2 & \qquad & \text{C.2.1.1} \\ 2x_1 & + & & & x_3 & = & 1 & & \text{C.2.1.2} \\ x_1 & + & 2x_2 & & & = & 5 & & \text{C.2.1.3} \\ 6x_1 & + & & & 3x_3 & = & 3 & & \text{C.2.1.4} \\ 4x_1 & + & 6x_2 & + & 2x_3 & = & 14 & & \text{C.2.1.5} \end{array}$$

where x_1, x_2, and x_3 are the unknown variables.

C.2.2 Matrix Notation

Any system of linear equations can be represented in the general matrix form:

$$\mathbf{A}\,\mathbf{x} = \mathbf{b} \qquad \text{C.2.2.1}$$

where, if "m" is the number of equations contained in the system and "n" is the number of unknowns in the system, **A** is a "m x n" matrix whose elements are the coefficients of the unknown variables in the equations, **x** is a "n x 1" vector whose elements are the unknown variables of the system, and **b** is "m x 1" vector whose elements are the constant terms of the system's equations. Expressing the example system of linear equations contained in Equations C.2.1.1 to C.2.1.5 in the form of Equation C.2.2.1 yields:

$$\begin{bmatrix} 1 & 1 & 1 \\ 2 & 0 & 1 \\ 1 & 2 & 0 \\ 6 & 0 & 3 \\ 4 & 6 & 2 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} 2 \\ 1 \\ 5 \\ 3 \\ 14 \end{bmatrix} \qquad \text{C.2.2.2}$$

where

$$\mathbf{A} = \begin{bmatrix} 1 & 1 & 1 \\ 2 & 0 & 1 \\ 1 & 2 & 0 \\ 6 & 0 & 3 \\ 4 & 6 & 2 \end{bmatrix} \quad \text{, a “5 x 3” matrix,} \qquad \text{C.2.2.3}$$

$$\mathbf{x} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} \quad \text{, a “3 x 1” vector,} \qquad \text{C.2.2.4}$$

and

$$\mathbf{b} = \begin{bmatrix} 2 \\ 1 \\ 5 \\ 3 \\ 14 \end{bmatrix} \quad \text{, a “5 x 1” vector.} \qquad \text{C.2.2.5}$$

C.2.3 Other Forms of Matrix Notation

Two other forms of matrix notation are necessary in determining the solution to a system of linear equations. They are the augmented matrix and the transpose of a matrix. An augmented matrix is formed by adding an additional column containing the elements of the **b** vector to the **A** matrix. Thus, the augmented matrix formed from Equation C.2.2.2, denoted [**A**|**b**], would be:

$$[\mathbf{A}|\mathbf{b}] = \left[\begin{array}{ccc|c} 1 & 1 & 1 & 2 \\ 2 & 0 & 1 & 1 \\ 1 & 2 & 0 & 5 \\ 6 & 0 & 3 & 3 \\ 4 & 6 & 2 & 14 \end{array}\right] \qquad \text{C.2.3.1}$$

The transpose of any matrix **E** is formed by exchanging the rows of **E** with the columns of **E**, and is denoted $\mathbf{E}^T$. Thus, the transpose of the **A** matrix in Equation C.2.2.2 would be:

$$\mathbf{A}^T = \begin{bmatrix} 1 & 2 & 1 & 6 & 4 \\ 1 & 0 & 2 & 0 & 6 \\ 1 & 1 & 0 & 3 & 2 \end{bmatrix}. \qquad \text{C.2.3.2}$$

The diagonal of any matrix **D** is those elements labeled $d_{1,1}$, $d_{2,2}$, $d_{3,3}$, etc. in the following example of a "3x5" matrix:

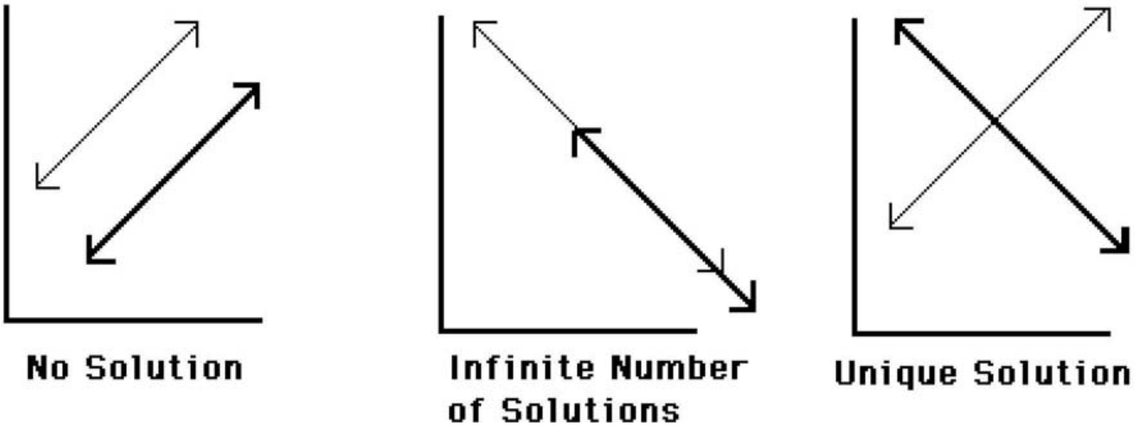
$$\mathbf{D} = \begin{bmatrix} d_{1,1} & d_{1,2} & d_{1,3} & d_{1,4} & d_{1,5} \\ d_{2,1} & d_{2,2} & d_{2,3} & d_{2,4} & d_{2,5} \\ d_{3,1} & d_{3,2} & d_{3,3} & d_{3,4} & d_{3,5} \end{bmatrix}. \qquad \text{C.2.3.3}$$

In the index notation of "*i, j*" like "3, 2", the first number is the row position and the second number is the column position. For the **A** matrix in Equation C.2.2.3, the diagonal is (1 0 0), while the diagonal for matrix $\mathbf{A}^T$ above is also (1 0 0).

C.2.4 Types of Solutions

The solution to any system of linear equations will fall into one of three categories—no solution exists, an infinite number of solutions exist, or a unique solution exists. For example, if a system of linear equations contains only two unknowns, no solution exists when the equations of the system are parallel to each other. An infinite number of solutions would exist if the equations in the system are coincidental to each other. Finally, a unique solution exists when each of the system's equations intersects in a single point. A graphical representation of each of the solution types for the special case of a system of linear equations that consists of two equations and two unknowns is shown in Figure C.1.

Figure C.1. Solution Types for a System of Linear Equations Consisting of Two Equations in Two Unknowns



C.2.5 Linear Independence

Section C.2.4 stated that a system of linear equations must fall into one of three solution categories: no solution exists, an infinite number of solutions exist, or a unique solution exists. A system of linear equations will fall into this last solution category only if the number of linearly independent equations in the system is equal to the number of unknowns in the system; that is,if “m” = “n” of the **A** matrix. In order for an equation to be linearly independent of the other equations in the system, two conditions must be met. First, the equation in question cannot be a multiple of any other equation in the system. Second, this equation cannot be a linear combination of the other equations in the system.

C.2.6 Determining Linear Dependence By Inspection

Usually in a small system of equations, the linear independence or dependence of the individual equations can be determined by inspection. For instance, it can readily be seen that Equation C.2.1.4 has been formed by multiplying Equation C.2.1.2 by 3. Equation C.2.1.5 can be formed by doubling Equations C.2.1.1 and C.2.1.3 and then adding the results. Thus, only Equations C.2.1.1, C.2.1.2, and C.2.1.3 are linearly independent of each other. The formal relationship for linear independence is that the Rank(**A**) must equal the Rank(**Ab**), where the “rank” indicates the number of linear independent equations. Software tools like Excel®, Matlab®, Mathematica®, and MathCAD® contain procedures to determine the rank of any matrix.

C.3 Properties of Algebraic Equations

When working with algebraic equations involving real numbers, several properties for the addition and multiplication of real numbers are important. These properties are the commutative, associative, and distributive properties along with the additive and multiplicative identities and inverses. Although you have probably utilized these properties numerous times since you first encountered them in high school algebra class, they are listed below to refresh your memory.

Commutative Properties: $a + b = b + a$ $\qquad ab = ba$

Associative Properties: $a + (b + c) = (a + b) + c$ $\qquad a\,(bc) = (ab)\,c$

Distributive Properties: $a\,(b + c) = ab + ac$ $\qquad (a + b)\,c = ac + bc$

Identities: $a + 0 = a$ $\qquad a \cdot 1 = a$
$0 + a = a$ $\qquad 1 \cdot a = a$

Inverses: $a + (-a) = 0$ $\qquad a\left(\frac{1}{a}\right) = 1 \text{ if } a \neq 0$
$(-a) + a = 0$ $\qquad \left(\frac{1}{a}\right) a = 1 \text{ if } a \neq 0$

C.4 Valid Transformations of Equations

There are three general types of transformation operations that may be performed to an individual equation without affecting the solution to the equation. These transformations are:

1) adding or subtracting the same term from both sides of the equation;

2) multiplying or dividing both sides of the equation by the same non-zero term.

   It is very important that any symbolic algebraic term used to transform an equation in this fashion be non-zero under all circumstances to ensure that extraneous roots are not introduced into the solution to the equation.

3) multiplying any term in the equation by some form of the multiplicative identity 1.

Each of these transformations are demonstrated below on the equation $\frac{3}{5}\,x - 2 = 1$, which has a solution $x = 5$.

$$\frac{3}{5}\,x - 2 = 1 \quad ==> \quad \frac{3}{5}\,x - 2 + 2 = 1 + 2 \quad ==> \quad \frac{3}{5}\,x = 3$$

$$\frac{3}{5}\,x - 2 = 1 \quad ==> \quad \frac{3}{5}\,x - 2 - 1 = 1 - 1 \quad ==> \quad \frac{3}{5}\,x - 3 = 0$$

$$\frac{3}{5}\,x - 2 = 1 \quad ==> \quad 5 \cdot \left(\frac{3}{5}\,x - 2\right) = 5 \cdot 1 \quad ==> \quad 3\,x - 10 = 5$$

$$\frac{3}{5}\,x - 2 = 1 \quad ==> \quad \frac{3}{5}\,x - \frac{5}{5}\cdot 2 = \frac{5}{5}\cdot 1 \quad ==> \quad \frac{3}{5}\,x - \frac{10}{5} = \frac{5}{5}$$

C.5 Valid Transformations of a System of Linear Equations

There are three general types of transformations that may be performed on a system of linear equations without affecting the solution to the set of equations. These transformations are:

1) interchanging the position of two equations;

2) multiplying or dividing both sides of the equation by the same non-zero constant;

3) replacing any equation by adding that equation to a constant times any other equation.

   Note: This operation is the same as solving an equation for a single variable and then substituting that equation into a second equation.

The following example will demonstrate each of the above methods. Consider the system of linear equations whose solution is $x = 2$ and $y = -3$:

$$\begin{aligned} 2x + 3y &= -5 \\ x - 2y &= 8. \end{aligned}$$

Method 1

$$\begin{aligned} 2x + 3y &= -5 \\ x - 2y &= 8 \end{aligned} \quad ==> \quad \begin{aligned} x - 2y &= 8 \\ 2x + 3y &= -5 \end{aligned}$$

Note that $x = 2$ and $y = -3$ still satisfy the second set of equations.

Method 2

$$\begin{aligned} 2x + 3y &= -5 \\ x - 2y &= 8 \end{aligned} \quad ==> \quad \begin{aligned} 2x + 3y &= -5 \\ 4(x - 2y &= 8) \end{aligned} \quad ==> \quad \begin{aligned} 2x + 3y &= -5 \\ 4x - 8y &= 32 \end{aligned}$$

Note that $x = 2$ and $y = -3$ still satisfy the second and third sets of equations.

Method 3

$$\begin{aligned} 2x + 3y &= -5 \\ \underline{+4(x - 2y} &\underline{= 8)} \end{aligned} \quad ==> \quad \begin{aligned} 6x - 5y &= 27 \\ x - 2y &= 8 \end{aligned}$$

Note that $x = 2$ and $y = -3$ still satisfies the second set of equations.

Thus, each of the above operations produced a new system of equations without changing the solution to the system of equations. Therefore, these transformations can be applied to a system of equations in the process of finding the solution to the system of equations without changing the solution to the system.

<u>Gaussian Elimination</u> is a numerical technique that uses the above three transformations to find the solution for the unknown variables. Consider the following example of three linear equations in three unknown variables:

SOLVE X, Y, Z **IN**

$$\begin{array}{lrcrcrcr}
\text{Eq. 1:} & X & + & 2\,Y & + & 4\,Z & = & 10 \\
\text{Eq. 2:} & 8\,X & + & 4\,Y & + & 2\,Z & = & 20 \\
\text{Eq. 3:} & 4\,X & + & 6\,Y & + & 10\,Z & = & 20
\end{array}$$

END

The objective of the Gaussian Elimination technique is to transform the augment coefficient matrix (*Ab*) so that only zeros appear below the diagonal, as illustrated below for the example:

$$Ab = \left[\begin{array}{ccc|c} 1 & 2 & 4 & 10 \\ 8 & 4 & 2 & 20 \\ 4 & 6 & 10 & 20 \end{array}\right] \xrightarrow[\textit{transformation}]{} \left[\begin{array}{ccc|c} \# & \# & \# & \# \\ 0 & \# & \# & \# \\ 0 & 0 & \# & \# \end{array}\right]$$

where # represents a number.

The transformation process on the example is depicted next:

$$Ab = \left[\begin{array}{ccc|c} 1 & 2 & 4 & 10 \\ 8 & 4 & 2 & 20 \\ 4 & 6 & 10 & 20 \end{array}\right] \xrightarrow[\substack{\text{Row 2 = 8 * Row 1 - Row 2} \\ \text{Row 3 = 4 * Row 1 - Row 3}}]{\text{Step 1}} \left[\begin{array}{ccc|c} 1 & 2 & 4 & 10 \\ 0 & 12 & 30 & 60 \\ 0 & 2 & 6 & 20 \end{array}\right]$$

$$Ab = \left[\begin{array}{ccc|c} 1 & 2 & 4 & 10 \\ 0 & 12 & 30 & 60 \\ 0 & 2 & 6 & 20 \end{array}\right] \xrightarrow[\text{Row 3} = \frac{\text{Row 2}}{6} - \text{Row 3}]{\text{Step 2}} \left[\begin{array}{ccc|c} 1 & 2 & 4 & 10 \\ 0 & 12 & 30 & 60 \\ 0 & 0 & -1 & -10 \end{array}\right]$$

The transformed augmented coefficient matrix with zeros below its diagonal can now be rewritten in equation form:

$$\begin{array}{lrcrcrcr}
\text{Eq. 1:} & X & + & 2\,Y & + & 4\,Z & = & 10 \\
\text{Eq. 2:} & & & 12\,Y & + & 30\,Z & = & 60 \\
\text{Eq. 3:} & & & & & Z & = & 10
\end{array}$$

Using a process of back substitution, the final solution for the linear equation set is:

$$\begin{array}{lccccr}
\text{Eq. 3:} & Z & = & 10 & = & 10 \\
\text{Eq. 2:} & Y & = & 60/\,12 \;-\; (30\,Z)\,/\,12 & = & -20 \\
\text{Eq. 1:} & X & = & 10 \;-\; 2\,Y \;-\; 4\,Z & = & 10
\end{array}$$

Since Gaussian Elimination is a tedious technique to do manually, computer programs like Matlab®, Mathematica®, E-Z Solve®, and Excel® have built-in operations to automate this technique.

C.6 Transforming an Equation to a Different System of Units

Sometimes you will be given an equation in one set of units, and you will need to transform it to a second set of units in order to solve a particular system of equations. For instance, let's say you were given the following equation which relates two physical quantities X and Y:

$$\underset{\frac{\text{in}}{\text{s}}}{\underset{\uparrow}{Y}} = \underset{\frac{\text{in}}{\text{s}}}{\underset{\uparrow}{2}} + 3\,\underset{\frac{\text{in}}{\text{s}}}{\underset{\uparrow}{X}} + \underset{\frac{\text{s}}{\text{in}}}{\underset{\uparrow}{5}}\,\underset{\frac{\text{in}^2}{\text{s}^2}}{\underset{\uparrow}{X^2}}$$

where the net units on each term are in/s, but all of the other equations you are working with have units of cm/s. In the original equation above, the constant “3” is unitless. Thus, for the above equation to be useful to you, you must convert this equation to a new equation whose net units are cm/s. The process for performing this conversion is the following:

1) for each variable in the original equation write a dimension equation (DE) that equates the original variable and its primed variable using appropriate conversion factors;

2) substitute each dimensional equation (DE’s) resulting from Steps 1 into the original equation for its original variable;

3) perform the algebra necessary to make the coefficient of the left-hand side of the new or primed equation be unitless one.

4) drop the primes from the variables in the new equation and note that this equation is different from the original equation, because the units of the variables are different and the constants in the equation have changed.

This process is demonstrated in the example which follows.

Original Equation ==> $Y = 2 + 3\,X + 5\,X^2$ where Y and X have units of in/s.

Need to convert original equation to a new or primed equation with net units of cm/s.

Primed Equation ==> $Y' = \# + \#\,X' + \#\,(X')^2$ where Y' and X' have units of cm/s, and the first constant “#” has units of cm/s, the second constant “#” is unitless, and the third constant “#” has units of “s/cm”.

Formulation of DE’s ==> $Y = Y'\left\langle \dfrac{1\ \text{in}}{2.54\ \text{cm}} \right\rangle$ where Y' has units of cm/s, and

Y has units of in/s.

==> $X = X'\left\langle \frac{1\text{ in}}{2.54\text{ cm}} \right\rangle$ where X' has units of cm/s, and X has units of in/s.

Using these dimensional equations, substitute for the variables in the original equation in order to produce the new or primed equation.

Primed Equation ==>

$$\underbrace{Y'\left\langle \frac{1\,\text{in}}{2.54\,\text{cm}} \right\rangle}_{\frac{\text{in}}{\text{s}}} = \underbrace{2}_{\frac{\text{in}}{\text{s}}} + 3\,\underbrace{X'\left\langle \frac{1\,\text{in}}{2.54\,\text{cm}} \right\rangle}_{\frac{\text{in}}{\text{s}}} + \underbrace{5}_{\frac{\text{s}}{\text{in}}}\,\underbrace{\left(X'\left\langle \frac{1\,\text{in}}{2.54\,\text{cm}} \right\rangle \right)^2}_{\frac{\text{in}^2}{\text{s}^2}}$$

where Y' and X' have units of cm/s, and the constant "2" has units of in/s, the constant "3" is unitless, and the constant "5" has units of "s/in". Note that the net units of each term is in/s.

Multiplying both sides of the above equation by "(2.54 cm)" yields the following:

Transformed Equation ==> $Y'\cdot(1\text{ in}) = 2\cdot(2.54\text{ cm}) + 3\,X'\cdot(1\text{ in}) + 5\,(X')^2\cdot\left(\frac{1\text{ in}^2}{2.54\text{ cm}}\right)$.

At this point all the terms in the above equation have units of $\frac{\text{cm in}}{\text{s}}$. Dividing both sides of the equation by "(1 in)" produces the desired transformed equation of

$$Y' = 5.08 + 3\,X' + 1.9685\,(X')^2$$

New Equation ==> $Y = 5.08 + 3\,X + 1.9685\,X^2$

In this new equation without the primes, the new variables of Y and X have units of cm/s. Note that all the terms in this new equation have net units of cm/s, and the constant "5.08" has units of cm/s, the constant "3" is unitless, and the constant "1.9685" has units of "s/cm".

Once you have completed an equation transformation, you should check both equations to see if they give the correct answers. For example, if X = 1 in/s, then X' = 2.54 cm/s. Thus,

Original Equation ==> $Y = 2 + 3\,(1) + 5\,(1)^2 = 10$ in/s and $Y' = 25.4$ cm/s.

New Equation ==> $Y' = 5.08 + 3\,(2.54) + 1.9685\,(2.54)^2 = 25.39$ cm/s. **OK!**

C.7 Exponential and Logarithmic Relationships

Below you will find a listing of the transcendental equations for exponential and logarithmic relationships with which you will need to be familiar.

Exponential Relationships:

(i) $a^m = a \cdot a \cdot a \ldots$ to m factors

(ii) $a^m \cdot a^n = a^{(m+n)}$

(iii) $a^m \cdot a^n \cdot a^p = a^{(m+n+p)}$

(iv) $\frac{a^m}{a^n} = a^{(m-n)}$ if $m > n$

$= a^{-(m-n)}$ if $n > m$

(v) $(a^m)^n = a^{(mn)}$

(vi) $a^0 = 1$

(vii) $a^{-n} = \frac{1}{a^n}$

(viii) $(ab)^m = a^m b^m$

(ix) $\left(\frac{a^m}{a^n}\right)^x = \frac{a^{mx}}{a^{nx}}$

(x) $a^{m/n} = \sqrt[n]{a^m}$

Logarithmic Relationships:

(i) $a^{\log_a x} = x$ for every $x > 0$

(ii) $\log_a a = 1$

(iii) $\log_a 1 = 0$

(iv) $\log_a (uw) = \log_a u + \log_a w$

(v) $\log_a \frac{u}{w} = \log_a u - \log_a w$

(vi) $\log_a (u^c) = c \log_a u$
for every real number c

Note: When no base (i.e., a) is indicated, the base is assumed to be 10.

Change of Base Equations:

(i) $\log_b u = \dfrac{\log_a u}{\log_a b}$

(ii) $\log_b a = \dfrac{1}{\log_a b}$

(iii) $\ln x = \log_e x$ for every $x > 0$

(iv) $\ln x = 2.30259 \log x$

Natural Logarithm Relationships:

(i) $e^{\ln x} = x$ for every $x > 0$

(ii) $\ln e = 1$

(iii) $\ln 1 = 0$

(iv) $\ln (uw) = \ln u + \ln w$

(v) $\ln \dfrac{u}{w} = \log_a u - \log_a w$

(vi) $\ln (u^c) = c \log_a u$ for every real number c

Units:

(i) The exponent of any exponential term must be dimensionless (i.e., unitless). In the following example equation,

$$\dot{m} = 4.2 \cdot e^{-\frac{2}{t}}$$

the quantity of "$\dot{m}$ "has units of *g/s* and the quantity of "*t*" has units of time in *s*. Thus, the constant "4.2" has units of *g/s*, while constant "2" must have units of *s*, in order for the exponent to be unitless. Any exponential, like $e^{-\frac{2}{t}}$, is always unitless.

(ii) The argument in any logarithmic term must be dimensionless (i.e., unitless). In the following example equation,

$$u = 3.4 \cdot \log_{10}(6.8/h)$$

the quantity of "*u*" has units of *cm/s* and the quantity of "*h*" has units of *ft*. Thus, the constant "3.4" has units of *cm/s*, while constant "6.8" must have units of *ft*, in order for the logarithmic argument to be unitless. Any logarithm, like $\log_{10}(6.8/h)$, is always unitless.

C.8 Summation Notation

Because the general equations for the material and energy balances can be concisely expressed using summation notation, some of the fundamental summation theorems are represented below for your reference.

(i) $\displaystyle\sum_{k=1}^{n} a_k = a_1 + a_2 + \ldots + a_n$

(ii) $\displaystyle\sum_{k=1}^{n} c = n \cdot c$ where "c" is a constant.

(iii) $\displaystyle\sum_{k=1}^{n} (a_k + b_k) = \sum_{k=1}^{n} a_k + \sum_{k=1}^{n} b_k$

(iv) $\displaystyle\sum_{k=1}^{n} (a_k - b_k) = \sum_{k=1}^{n} a_k - \sum_{k=1}^{n} b_k$

(v) $\displaystyle\sum_{k=1}^{n} c \cdot a_k = c \sum_{k=1}^{n} a_k$ where "c" is a constant.

(vi) $\displaystyle\sum_{j=1}^{m} \sum_{k=1}^{n} a_{j,k} = (a_{1,1} + a_{1,2} + \ldots + a_{1,n}) + (a_{2,1} + a_{2,2} + \ldots + a_{2,n}) + \ldots + (a_{m,1} + a_{m,2} + \ldots + a_{m,n})$

(vii) $\displaystyle\sum_{j=1}^{m} \sum_{k=1}^{n} a_{j,k} = \sum_{j=1}^{m} \left(\sum_{k=1}^{n} a_{j,k} \right)$

(viii) $\displaystyle\sum_{j=1}^{m} \sum_{k=1}^{n} (a_{j,k} + b_{j,k}) = \sum_{j=1}^{m} \sum_{k=1}^{n} a_{j,k} + \sum_{j=1}^{m} \sum_{k=1}^{n} b_{j,k}$

(ix) $\displaystyle\sum_{j=1}^{m} \sum_{k=1}^{n} c \cdot a_{j,k} = c \sum_{j=1}^{m} \sum_{k=1}^{n} a_{j,k}$ where "c" is a constant.

(x) $\displaystyle\sum_{j=1}^{m} \sum_{k=1}^{n} a_j b_k = \left(\sum_{j=1}^{m} a_j \right) \left(\sum_{k=1}^{n} b_j \right)$

Conservation of Mass (non-reacting mixture)

$$m = \sum_{j=1}^{NC} m_j = m_1 + m_2 + \cdots\cdots + m_{NC}$$

a first principle

$$1.0 = \sum_{j=1}^{NC} \frac{m_j}{m} = \frac{m_1}{m} + \frac{m_2}{m} + \cdots\cdots + \frac{m_{NC}}{m}$$

$$1.0 = \sum_{j=1}^{NC} w_j$$

NC is the number of chemical components in the mixture.

Conservation of Moles (non-reacting mixture)

$$n = \sum_{j=1}^{NC} n_j = n_1 + n_2 + \cdots\cdots + n_{NC}$$

a first principle

$$1.0 = \sum_{j=1}^{NC} \frac{n_j}{n} = \frac{n_1}{n} + \frac{n_2}{n} + \cdots\cdots + \frac{n_{NC}}{n}$$

$$1.0 = \sum_{j=1}^{NC} x_j$$

Total Volume of a Mixture (constant T & P & non-reacting mixture)

$$V = V_1 + V_2 + \cdots\cdots + V_{NC} + \Delta V_{mix}$$

a first principle

$$V = \sum_{j=1}^{NC} V_j + \Delta V_{mix}$$

where $V_j = V[T, P]$ I.E., pure j at T and P of mixture.

$$1.0 = \frac{V_1}{V} + \frac{V_2}{V} + \cdots\cdots + \frac{V_{NC}}{V} + \frac{\Delta V_{mix}}{V}$$

$$1.0 = \sum_{j=1}^{NC} \frac{V_j}{V} + \frac{\Delta V_{mix}}{V}$$

$$1.0 = \sum_{j=1}^{NC} y_j + \frac{\Delta V_{mix}}{V}$$

for real mixtures

$$1.0 = \sum_{j=1}^{NC} y_j$$

for ideal mixtures, since $\Delta V_{mix} = 0$.

Click here to view a presentation about the volume-of-mixing effect.

Introduction

In a problem-based learning (PBL) environment, the problems are the vehicles that drive the learning process. Students practice just-in-time learning to master whatever content is needed to help them solve the problem. These activities of content comprehension and problem solving are often challenging, particularly when fifteen, twenty, or more equations are required to model the phenomena in the problem. When freshmen or sophomore majors are taking their first course in chemical engineer, they usually have little or no experience with problem-based learning. Early in this first course, students need structure and coaching to help them make the adjustment from a traditional lecture-based experience to a problem-based learning approach.

The six example problems in the table below are designed to provide the structure and coaching that students need as they adjust to the problem-learning environment. The first four problems on material balances can serve as the first two-week project for a four-member team, as outlined in the Preface of this *CinChE* manual. The fifth problem can be added for a five-member team. The sixth problem addresses how to complete the material balances for a recycle system containing a chemical reactor.

Problem	Material Balance Problem Description	Page #
P1.A1	Semi-Continuous Process for Drying of Moist Air with Calcium Chloride	E-02
P1.A2	Semi-Batch Process for Converting Strawberry and Sugar into a Jam	E-11
P1.A3	Continuous Process for Removing Urea from Blood with an Artificial Kidney	E-20
P1.A4	Batch Process for Converting Ethane to Acetylene by a Chemical Reaction	E-27
P1.A5	Safety Precaution for Determining Human Expiration Time in Pure Nitrogen	E-36
sixth	Recycle Process for Producing Ethylene Oxide from Ethylene in a Reactor	E-41

Before examining the above six problems, you may want to click here and review some drill and practice problems that use the problem-solving methodology defined in Chapter 4 of this *CinChE* manual.

In this appendix, solution templates are provided for the first five problems (P1.A1 to P1.A5). For each template, the instructor has worked out the problem solution on engineering paper, scanned that solution into an Adobe ".pdf" file, and used the Acrobat program to blank out parts of the problem solution. Associated with each solution template is a coaching document that helps guide students through the application of the problem solving methodology to produce the conceptual model, mathematical model, mathematical algorithm, numerical solution, and heuristic observations. This coaching document also serves to illustrate the documentation standards for the problem solution. A coaching document basically is a copy of the solution template that is annotated with PDF popup notes. Yellow notes provide direction, explanation, and/or cite appropriate pages in the *CinChE* manual that the students are to review. Each red note provides a question to ponder, and its answer is provided in the adjacent green note. While viewing a "coaching" document, proceed from left-to-right and top-to-bottom in the Acrobat Reader window. You can access a coaching document through a web link that is provided on the first page of a solution template.

Problem Solution Variability

The application of the steps in the problem-solving methodology, found in Chapter 4 of the *CinChE* manual, could produce variability in the problem solution; that is, the conceptual model, mathematical model, mathematical algorithm, numerical solution, and the heuristic observations. Therefore, no two solutions to a specific problem statement will be exactly alike in their documentation. Click here to examine six example scenarios that demonstrate the kinds of variability one might encounter when comparing one problem solution to another problem solution for the same problem statement.

Click here to print this solution template. Click here to view its coaching notes.

Problem P1.A1

1 of 9

Problem Statement {Problem 4.20 in F&R, 3rd Edition, but modified}

Your three-year old sibling has an asthmatic condition, and you mother is concerned about the humidity level in your sibling's bedroom. Your mother is very proud that you are majoring in chemical engineering and asks you to find a way to reduce the humidity level. Your professor recently completed an experiment in the laboratory using calcium chloride as a desiccant and suggests that you solve the following problem to develop some background before tackling your sibling's problem.

Dry calcium chloride pellets in the amount of 3.40 kg are packed in a cylindrical Plexiglas column. Moist air with 4.0 mole percent water vapor at ambient conditions is feed into the bottom of the column. At 5.0 hours of operation, the pellets have adsorbed 97.0 percent on a molar basis of the water and none of the oxygen and nitrogen in the air mixture. At the end of five hours, the pellets have a mass of 3.54 kg. What are the molar flow (mol/h) of the feed gas and the mole fractions of oxygen, nitrogen, and water vapor in the product gas? How many parts per million (ppm) of water vapor exist in the product gas? What would be the diameter and height in inches of the column for a gas velocity of 0.062 m/s?

In the first 10 hours of conducting the desiccant experiment, your professor observed that the composition of the water vapor in the product gas remained constant at the value calculated in the above problem. However, it began to increase after 10 hours of operation. Why would the composition of the water vapor continue to increase? What will the mole fraction of water vapor in the product gas eventually be if the process continues to run? How much water will have been absorbed by the pellets?

Model Assumptions

1. process
2. column contains dry $CaCl_2$ and dry air just before $t_i = 0$. dry air has of oxygen and nitrogen on a molar basis.
3. oxygen and nitrogen achieve steady state at $t_i = 0$, when the moist air in Stream F starts flowing.
4. no chemical
5. ambient conditions are
6. material within the system boundary is at
7. velocity applies to the stream
8. feed and product streams behave
9. height of column is determined by the dihydrate form of calcium chloride:

   The dihydrate density is , as given by http://en.wikipedia.org/wiki/Calcium_chloride, 12/31/07.

Click here to print this solution template. Click here to view its coaching notes.

Problem P1.A2

1 of 9

Problem Statement {Problem 4.9 in F&R, 3rd Edition, but modified }

Every year near the end of June, your grandpa picks his strawberries and makes his famous jam. After thirty years of making this jam, your grandpa has found that on average the strawberries contain about 15 weight percent solids and the rest is pure water. After crushing the strawberries, he mixes them with sugar in a mass ratio of 45:55 at ambient conditions. He places the mixture in a stainless steel boiler and evaporates most of the water, leaving one-third water by mass remaining in the boiler pot. Since your grandpa is very proud that you are majoring in chemical engineering, he asks you to answer some questions about making strawberry jam. How many pounds of strawberries are needed to make a pound of jam, and what are the mass fractions of solids and sugar in that jam? Based on evaporating the water at 1.0 atm, how much heat must be added to the boiler pot? When the jam is poured into a glass jar that is 3.0 inches in diameter and 6.0 inches high, what percentage of the height does it fill?

For a metric ton of jam, what amount of strawberries is needed? What is the cost to produce this metric ton, based on industrial electricity prices as reported by the U.S. Energy Information Administration?

Model Assumptions

1. process

2. no

3. ambient conditions are and

4. temperature within the system boundary increase from to , the boiling point of water at 1 atm

5. some water within the system vaporizes at atm, and the vapor leaves in stream

6. the final solution cools to and atm, before it is poured into a glass jar

7. density of final solution at and 1 atm is that of dissolved in liquid water

8. the composition of the is the combined mass fractions of

9. density of solution as a function of composition is given at http://www.cyberlaboratory.com in the "Library" option, 1/2/2008.

10. industrial electricty price is \$/kWh in 2006, as given by the U.S. Energy Info. Admin. Also, 1 Wh ≡ 3600 J

Click here to print this solution template. **Click here** to view its coaching notes.

Problem P1.A3

1 of 7

Problem Statement {Problem 4.23 in F&R, 3rd Edition, but modified}

Your aunt visits a dialysis center to have waste materials removed from her blood. She described her dialysis process to you and asked you to answer some questions about it. Blood from one of her arteries flows on the insides of a bundle of hollow cellulose acetate fibers of an artificial kidney. A dialyzing solution of water and dissolved salts flows on the outside of the fibers counter current to the blood flow. Waste materials (urea, water, and other metabolites) in the blood pass through the fiber walls into the dialyzing solution. The purified blood is returned to one of her veins. Some data for her dialysis are as follows:

	Arterial (entering)	**Venous (exiting)**
Flow rate:	200.0 mL/min	195.0 mL/min
Urea Concentration:	1.90 mg/mL	1.75 mg/mL

At what mass rates are urea and water being removed from her blood, and what is their volumetric flow rate? When the dialyzing solution enters at a rate 1500 mL/min, what is the concentration of urea in the exiting solution (dialysate)? What is the volumetric flow rate of the dialysate?

Your aunt's doctor wants to reduce her urea level from 2.7 mg/mL to 1.1 mg/mL. If the average rate of urea removal is that calculated in the above problem, how long must your aunt be on dialysis for a total blood volume of 5.0 liters.

Model Assumptions

1. at state
2. no
3. temperature of streams A, V, F + D is °F; that is, °c average human body temperature
4. pressure of streams A, V, F, + D is atm
5. blood is , , and other material
6. dialysate is , , and salts
7. and only pass through acetate fibers
8. density of is kg/L from wikipedia, 1/4/08
9. streams F, W, + D are and essential
10. density of streams F, W, + D is that of pure at °c and 1 atm

Click here to print this solution template. Click here to view its coaching notes.

Problem P1.A4

1 of 9

Problem Statement

{Problem 4.44 in F&R, 2nd Edition, but modified}

Acetylene is an industrial gas that is use for oxyacetylene gas welding and cutting of metal materials. One way to produce acetylene is to fill a reaction vessel completely with 150 moles of ethane at 25°C and 1.0 atm. The following dehydrogenation reaction occurs isothermally after closing the reactor:

$$C_2H_6 \rightarrow C_2H_2 + 2\,H_2$$

to produce acetylene and hydrogen. While heat is supplied to the reactor, eighty percent of the ethane is consumed by this endothermic reaction. What are the total moles, molecular weight, mole ratio of hydrogen to acetylene, and mass of acetylene in the final product? What is the final composition and final gauge pressure (mm Hg) in the reactor for the given conversion of ethane?

In the above problem, suppose the amount of the acetylene was specified instead of the ethylene amount charged to the reactor. Starting with the original mathematical model, what is the mathematical algorithm where an acetylene amount of 240 g-mol is specified? Why is this mathematical algorithm more complex and what caused the complexity? Without using this second mathematical algorithm, determine the amount of ethane charged to the reactor and the product composition to produce 240 g-mol of acetylene?

Model Assumptions

1. process
2. volume of the reactor does not
3. ethane, acetylene, and hydrogen are at 25°C and 1 atm. The normal (at 1 atm) boiling temperatures of the components are:

   $T_{NBP,ET} =$ °C, $T_{NBP,AC} =$ °C, $T_{NBP,H2} =$ °C
4. the gas in the batch reactor behaves as an
5. barometer reads atm as the barometric pressure, P_b

Click here to print this solution template. Click here to view its coaching notes.

Problem P1.A5

1 of 5

Problem Statement

A substitute problem based on gas absorption exists for **P1.A5**. If your instructor assigns it, **click here** to access it.

Toxic exposure control and personal protective equipment are important safety considerations when working as a chemical engineer. The second and third paragraphs present a modified version of Problem 3 from the booklet entitled *Safety, Health, and Loss Prevention in Chemical Processes*. As background information, Problem 3 is available in the **Assignments** section of the Blackboard CHEG 200 course, or click here to view it.

Normally, a person inhales about 30 L/min of air at 500 mL/inhalation (or about 1 breath per second). You are asked by your project supervisor to clean the inside of 500-gallon tank that normally contains air when empty. Unbeknownst to you and your project supervisor, the maintenance crew filled this tank with nitrogen earlier in the day to eliminate a fire potential, but they forgot to post on the tank its contents. When the average composition of oxygen in your lungs drops below 11 volume percent, you will lose consciousness. You may recover if you get into fresh air before the average composition drops below 6.0 volume percent. Below this lower oxygen composition, you will die. If you were to enter the tank that is completely filled with nitrogen, how many breaths will you take before losing consciousness? How much time do you have before expiring?

Given this potential hazardous situation, should you use an air-purifying respirator or an air-supplying respirator to clean the nitrogen-filled tank and why?

Model Assumptions

1. ______ process, but ______ state
2. consider only ______ and ______ in the lung. ignore smaller quantities of other constituents like CO_2 and ______ vapor.
3. consider only the ______ balance, since O_2 is being depleted in the lung.
4. total ______ intake equals total ______ outtake, ______
5. exhaled gas is at the same temperature, pressure, and ______ as that of the lung.
6. inhaled gas is at ___ °C and ___ atm, and its O_2 composition is ______ when the worker enters the pure nitrogen environment
7. density of O_2 inhaled, exhaled, and within the lung is ______.
8. worker takes one breath every ______, based on inhaling about 30 L/min

CHEG 200
Hanyak

Reactor with Recycle

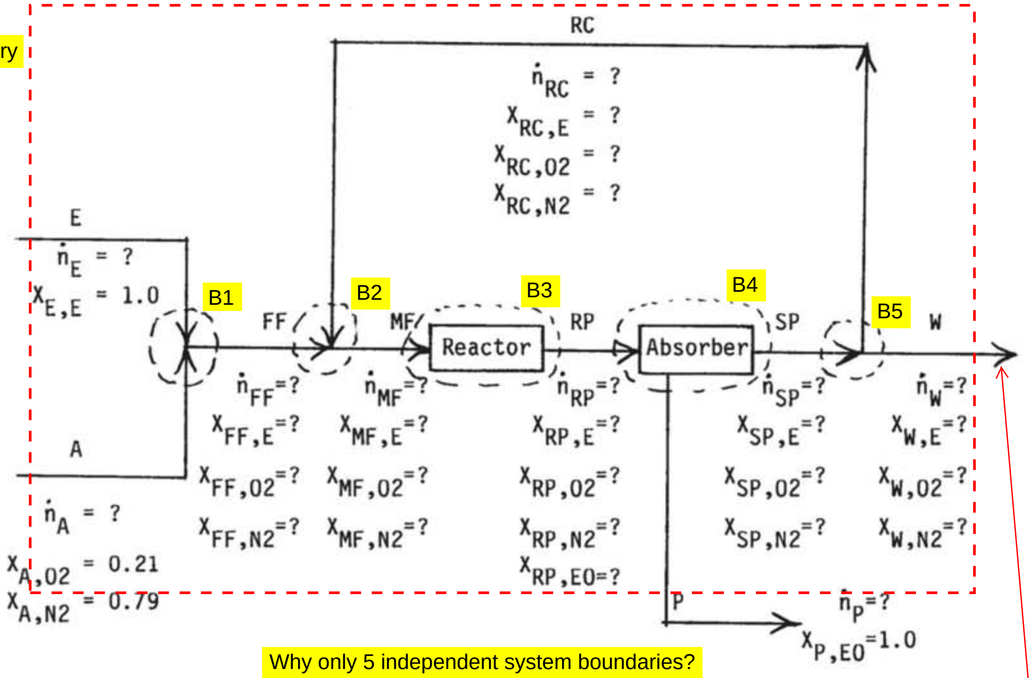
7/29/91
1 of 7

Problem Statement

Let us consider the recycle operation depicted below for the production of ethylene oxide. The ethylene/air ratio in the fresh feed is 1:10 and the conversion of ethylene to ethylene oxide on a once-through basis is 55 percent. What will be the improvement in the overall conversion if 65 percent of the gases leaving the absorber are recycled to the reactor? Also, what is the selectivity and yield and the composition of the exiting gases W?

Diagram

temperatures and pressures were not listed in the diagram, since they are not needed in the solution



Why only 5 independent system boundaries?
That is, B1, B2, B3, B4, and B5; not B6.

purge stream

Why? No N_2 buildup in the recycle stream

F&R, 3rd Edition
Page 138

Assumptions

1. steady state and continuous process
2. reaction only in reactor
3. air contains 21 mol% O_2 & 79 mol% N_2
4. ideal separation in absorber
5. Basis: $\dot{n}_E$ = 10 mol/hr

Additional Data

Rxn I : $2\ C_2H_4 + O_2 \rightarrow 2\ C_2H_4O$

When writing balances and independent mixture equations for each process unit, assume you know the flow rates of the incoming streams. The goal is to get a proper set of equations for a process unit, in order to calculate the outgoing flow rates, such that the DOF equals the number of flow rates in the incoming streams.

Math. Model

Ethylene-Air Mix:

see Page 5-6

① TM: $\underline{\dot{n}_E} + \dot{n}_A - \dot{n}_{FF} = 0$

② E: $\underline{\dot{n}_E} - \dot{n}_{FF,E} = 0$

③ O_2: $0.21\,\dot{n}_A - \dot{n}_{FF,O2} = 0$

④ N_2: $0.79\,\dot{n}_A - \dot{n}_{FF,N2} = 0$

⑤ $\dot{n}_A/\underline{\dot{n}_E} = 10$

vars = 6
eqns = $\underline{5}$
1

no mix FF equation, why?

Feed Mixer:

see Page 5-6

⑥ TM: $\dot{n}_{FF} + \dot{n}_{RC} - \dot{n}_{MF} = 0$

⑦ E: $\dot{n}_{FF,E} + \dot{n}_{RC,E} - \dot{n}_{MF,E} = 0$

⑧ O_2: $\dot{n}_{FF,O2} + \dot{n}_{RC,O2} - \dot{n}_{MF,O2} = 0$

⑨ N_2: $\dot{n}_{FF,N2} + \dot{n}_{RC,N2} - \dot{n}_{MF,N2} = 0$

vars = 12
eqns = $\underline{4}$
8

no mix MF equation, why?

Recycle, Not Indep. $\dot{n}_{RC} = \dot{n}_{RC,E} + \dot{n}_{RC,O2} + \dot{n}_{RC,N2}$

why? see Equation 25.

Reactor:

see Page 5-6

⑩ TM: $\dot{n}_{MF} - \dot{n}_{RP} - \dot{R}_I = 0$

⑪ E: $\dot{n}_{MF,E} - \dot{n}_{RP,E} - 2\dot{R}_I = 0$

⑫ O_2: $\dot{n}_{MF,O2} - \dot{n}_{RP,O2} - \dot{R}_I = 0$

⑬ N_2: $\dot{n}_{MF,N2} - \dot{n}_{RP,N2} = 0$

⑭ EO: $-\dot{n}_{RP,EO} + 2\dot{R}_I = 0$

vars = 10
eqns = $\underline{6}$
4

no mix RP equation, why?

⑮ $$\frac{\dot{n}_{MF,E} - \dot{n}_{RP,E}}{\dot{n}_{MF,E}} = 0.55 \longrightarrow \boxed{\dot{n}_{RP,E} = 0.45\,\dot{n}_{MF,E}}$$

single-pass conversion of E. see F&R, 3rd Ed., page 135.

or $n_{MF,E} - n_{RP,E} = 0.55\, n_{MF,E}$ with dots

ENTHALPY REFERENCE STATES

WHY ARE THEY ARBITRARY?

by

Dr. Michael E. Hanyak, Jr.
Full Professor

Bucknell University
Chemical Engineering Department
Lewisburg, PA 17837

A. Differential Energy Balance: (heat-of-formation method)

$$\underbrace{\sum_{i=1}^{ni} \dot{n}_i \hat{H}_i - \sum_{i=ni+1}^{nt} \dot{n}_i \hat{H}_i}_{\text{TEC}} \pm \dot{Q} \pm \dot{W}_S = \frac{d\left(n\hat{U}\right)_{sys}}{dt} \qquad \textbf{(7.1d)}$$

Pink Crib Sheet

Blue Crib Sheet

Total Enthalpy Change

$$\text{TEC} = \sum_{i=1}^{NI} n_i \hat{H}_i - \sum_{i=NI+1}^{NT} n_i \hat{H}_i = ?$$

$$\hat{H}_i = \sum_{j=1}^{NC} x_{i,j} \left[\sum_{k=1}^{NE} a_{j,k} \hat{H}_k^{T^\circ_j,P^\circ_j,Ph^\circ_k} + (\Delta\hat{H}^\circ_f)_j^{T^\circ_j,P^\circ_j,Ph^\circ_j} + \left(\hat{H}_j^{T_i,P_i,Ph_i} - \hat{H}_j^{T^\circ_j,P^\circ_j,Ph^\circ_j}\right)\right] + \Delta\hat{H}_{mix,i}^{T_i,P_i,\bar{x}_i}$$

reference enthalpy for a pure element.

heat of formation for a pure compound.

$$\text{TEC} = \sum_{i=1}^{NI} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left[\sum_{k=1}^{NE} a_{j,k} \hat{H}_k^{T^\circ_j,P^\circ_j,Ph^\circ_k} + (\Delta\hat{H}^\circ_f)_j^{T^\circ_j,P^\circ_j,Ph^\circ_j} + \left(\hat{H}_j^{T_i,P_i,Ph_i} - \hat{H}_j^{T^\circ_j,P^\circ_j,Ph^\circ_j}\right)\right] + \Delta\hat{H}_{mix,i}^{T_i,P_i,\bar{x}_i} \right\} -$$

$$\sum_{i=NI+1}^{NT} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left[\sum_{k=1}^{NE} a_{j,k} \hat{H}_k^{T^\circ_j,P^\circ_j,Ph^\circ_k} + (\Delta\hat{H}^\circ_f)_j^{T^\circ_j,P^\circ_j,Ph^\circ_j} + \left(\hat{H}_j^{T_i,P_i,Ph_i} - \hat{H}_j^{T^\circ_j,P^\circ_j,Ph^\circ_j}\right)\right] + \Delta\hat{H}_{mix,i}^{T_i,P_i,\bar{x}_i} \right\}$$

In general,

$$\sum_{i=1}^{NI} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left[\sum_{k=1}^{NE} A_{j,k} + B_j + C_j \right] + D_i \right\} =$$

$$\sum_{i=1}^{NI} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left[\sum_{k=1}^{NE} A_{j,k} \right] \right\} + \sum_{i=1}^{NI} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left[B_j + C_j \right] + D_i \right\}$$

Then, the total enthalpy change becomes:

$$\text{TEC} = \boxed{\underbrace{\sum_{i=1}^{NI} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left[\sum_{k=1}^{NE} a_{j,k} \hat{H}_k^{T^\circ_j,P^\circ_j,Ph^\circ_k} \right] \right\} - \sum_{i=NI+1}^{NT} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left[\sum_{k=1}^{NE} a_{j,k} \hat{H}_k^{T^\circ_j,P^\circ_j,Ph^\circ_k} \right] \right\}}_{\textbf{TREC}\text{ - Total Reference Enthalpy Change}}} +$$

$$\sum_{i=1}^{NI} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left[(\Delta\hat{H}^\circ_f)_j^{T^\circ_j,P^\circ_j,Ph^\circ_j} + \left(\hat{H}_j^{T_i,P_i,Ph_i} - \hat{H}_j^{T^\circ_j,P^\circ_j,Ph^\circ_j}\right] + \Delta\hat{H}_{mix,i}^{T_i,P_i,\bar{x}_i} \right\} -$$

$$\sum_{i=NI+1}^{NT} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left[(\Delta\hat{H}^\circ_f)_j^{T^\circ_j,P^\circ_j,Ph^\circ_j} + \left(\hat{H}_j^{T_i,P_i,Ph_i} - \hat{H}_j^{T^\circ_j,P^\circ_j,Ph^\circ_j}\right)\right] + \Delta\hat{H}_{mix,i}^{T_i,P_i,\bar{x}_i} \right\}$$

In general,

$$\sum_{i=1}^{NI} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left[\sum_{k=1}^{NE} A_{j,k} \right] \right\} = \sum_{k=1}^{NE} \left\{ \sum_{i=1}^{NI} \left[\sum_{j=1}^{NC} n_i x_{i,j} A_{j,k} \right] \right\}$$

Then, the total reference enthalpy change becomes:

$$\text{TREC} = \sum_{k=1}^{NE} \left\{ \sum_{i=1}^{NI} \left[\sum_{j=1}^{NC} \underbrace{n_i x_{i,j}}_{n_{i,j}} a_{j,k} \hat{H}_k^{T_j^\circ, P_j^\circ, Ph_k^\circ} \right] \right\} - \sum_{k=1}^{NE} \left\{ \sum_{i=NI+1}^{NT} \left[\sum_{j=1}^{NC} \underbrace{n_i x_{i,j}}_{n_{i,j}} a_{j,k} \hat{H}_k^{T_j^\circ, P_j^\circ, Ph_k^\circ} \right] \right\}$$

$$= \sum_{k=1}^{NE} \boxed{\underbrace{\left\{ \sum_{i=1}^{NI} \left[\sum_{j=1}^{NC} n_{i,j} a_{j,k} \right] - \sum_{i=NI+1}^{NT} \left[\sum_{j=1}^{NC} n_{i,j} a_{j,k} \right] \right\}}_{\text{Atom Balance for the k-th element = zero}}} \hat{H}_k^{T_j^\circ, P_j^\circ, Ph_k^\circ}$$

for steady-state operation, see Eq. 5.6d

Therefore, for a steady-state system, the total enthalpy change is:

Pink Crib Sheet

$$\begin{aligned} \text{TEC} = {} & \sum_{i=1}^{NI} n_i \left\{ \underbrace{\sum_{j=1}^{NC} x_{i,j} \left[(\Delta \hat{H}_f^\circ)_j^{T_j^\circ, P_j^\circ, Ph_j^\circ} + \left(\hat{H}_j^{T_i, P_i, Ph_i} - \hat{H}_j^{T_j^\circ, P_j^\circ, Ph_j^\circ} \right) \right]}_{H_i} + \Delta \hat{H}_{mix,i}^{T_i, P_i, \bar{x}_i} \right\} - \\ & \sum_{i=NI+1}^{NT} n_i \underbrace{\left\{ \sum_{j=1}^{NC} x_{i,j} \left[(\Delta \hat{H}_f^\circ)_j^{T_j^\circ, P_j^\circ, Ph_j^\circ} + \left(\hat{H}_j^{T_i, P_i, Ph_i} - \hat{H}_j^{T_j^\circ, P_j^\circ, Ph_j^\circ} \right) \right] + \Delta \hat{H}_{mix,i}^{T_i, P_i, \bar{x}_i} \right\}}_{\hat{H}_i} \end{aligned}$$

and it is independent of the values selected for $\hat{H}_k^{T_j^\circ, P_j^\circ, Ph_j^\circ}$.

The total enthalpy change can also be written to contain the standard heats of reaction. The TEC above can be arranged as follows:

$$\begin{aligned} \text{TEC} = {} & \sum_{j=1}^{NC} \boxed{\left[\sum_{i=1}^{NI} n_{i,j} - \sum_{i=NI+1}^{NT} n_{i,j} \right]} (\Delta \hat{H}_f^\circ)_j^{T_j^\circ, P_j^\circ, Ph_j^\circ} + \\ & \sum_{i=1}^{NI} n_i \left[\sum_{j=1}^{NC} x_{i,j} \left(\hat{H}_j^{T_i, P_i, Ph_i} - \hat{H}_j^{T_j^\circ, P_j^\circ, Ph_j^\circ} \right) + \Delta \hat{H}_{mix,i}^{T_i, P_i, \bar{x}_i} \right] - \\ & \sum_{i=NI+1}^{NT} n_i \left[\sum_{j=1}^{NC} x_{i,j} \left(\hat{H}_j^{T_i, P_i, Ph_i} - \hat{H}_j^{T_j^\circ, P_j^\circ, Ph_j^\circ} \right) + \Delta \hat{H}_{mix,i}^{T_i, P_i, \bar{x}_i} \right] \end{aligned}$$

use component balances and substitute for this difference.

$$\text{TEC} = \sum_{i=1}^{NI} n_i \hat{H}_i^{T_i,P_i,Ph_i} - \sum_{i=NI+1}^{NT} n_i \hat{H}_i^{T_i,P_i,Ph_i} - \underbrace{\sum_{j=1}^{NC} \sum_{\ell=1}^{NR} \nu_{\ell,j} \dot{R}_\ell (\Delta \hat{H}_f^\circ)_j^{T_j^\circ,P_j^\circ,Ph_j^\circ}}_{\sum_{\ell=1}^{NR} \dot{R}_\ell \underbrace{\sum_{j=1}^{NC} \nu_{\ell,j} (\Delta \hat{H}_f^\circ)_j^{T_j^\circ,P_j^\circ,Ph_j^\circ}}_{\text{standard heat of reaction}}}$$

For no rxn, $\dot{R}_\ell = 0$.

When no chemical reactions occur, the total enthalpy change becomes:

$$\text{TEC} = \sum_{i=1}^{NI} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left[\hat{H}_j^{T_j^\circ,P_j^\circ,Ph_j^\circ} + \left(\hat{H}_j^{T_i,P_i,Ph_i} - \hat{H}_j^{T_j^\circ,P_j^\circ,Ph_j^\circ}\right)\right] + \Delta \hat{H}_{mix,i}^{T_i,P_i,\bar{x}_i} \right\} -$$

$$\sum_{i=NI+1}^{NT} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left[\hat{H}_j^{T_j^\circ,P_j^\circ,Ph_j^\circ} + \left(\hat{H}_j^{T_i,P_i,Ph_i} - \hat{H}_j^{T_j^\circ,P_j^\circ,Ph_j^\circ}\right)\right] + \Delta \hat{H}_{mix,i}^{T_i,P_i,\bar{x}_i} \right\}$$

$$\text{TEC} = \underbrace{\sum_{i=1}^{NI} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \hat{H}_j^{T_j^\circ,P_j^\circ,Ph_j^\circ} \right\} - \sum_{i=NI+1}^{NT} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \hat{H}_j^{T{=}_j^\circ,P_j^\circ,Ph_j^\circ} \right\}}_{\text{TREC - Total Reference Enthalpy Change}} +$$

$$\sum_{i=1}^{NI} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left(\hat{H}_j^{T_i,P_i,Ph_i} - \hat{H}_j^{T_j^\circ,P_j^\circ,Ph_j^\circ}\right) + \Delta \hat{H}_{mix,i}^{T_i,P_i,\bar{x}_i} \right\} -$$

$$\sum_{i=NI+1}^{NT} n_i \left\{ \sum_{j=1}^{NC} x_{i,j} \left(\hat{H}_j^{T_i,P_i,Ph_i} - \hat{H}_j^{T_j^\circ,P_j^\circ,Ph_j^\circ}\right) + \Delta \hat{H}_{mix,i}^{T_i,P_i,\bar{x}_i} \right\}$$

The total reference enthalpy change becomes:

$$\text{TREC} = \sum_{j=1}^{NC} \underbrace{\left\{ \sum_{i=1}^{NI} n_{i,j} - \sum_{i=NI+1}^{NT} n_{i,j} \right\}}_{\text{Mole Balance for the j-th component equals zero for steady-state operation}} \hat{H}_j^{T_j^\circ,P_j^\circ,Ph_j^\circ}$$

Chapter 0 – Preface

Bloom, B. S. (1956). *Taxonomy of Educational Objectives, Handbook I: The Cognitive Domain*. David McKay, NY.

Felder, R. M. and Rousseau, R.W. (2005). *Elementary Principles of Chemical Processes*, 3rd Update Ed. John Wiley & Sons, Inc., New York, NY. ISBN 978-0-471-68757-3.

Hanyak, M. E. (2002). "Managing Your Time". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. and Raymond, T. M. (2009). "Teaching Material and Energy Balances to First-Year Students using Cooperative Team-Based Projects and Labs". *Proceedings of the 2009 American Society for Engineering Education Annual Conference*, Austin, TX, June 14-17.

Himmelblau, D. M. and Riggs, J. B. (2004). *Basic Principles and Calculations in Chemical Engineering*, 7th Ed. Prentice Hall, Upper Saddle River, NJ. ISBN 978-0-13-140634-6.

Johnson, D. W., Johnson, R. T., and Smith, K. A. (1998). *Active Learning: Cooperation in the College Classroom*. Interaction Book Co., Edina, MN. ISBN 0-0939603-14-4.

Murphy, R. M. (2007). *Introduction to Chemical Processes: Principles, Analysis, Synthesis*. McGraw-Hill Companies, Inc., New York, NY. ISBN 978-0-07-284960-8.

Oguzie, D. N. (2007). *e-LEAPS – An Interactive Web Application to Support Learning Engineering and Problem Solving*, M.S. Thesis. Dr. Michael E. Hanyak, Jr. (advisor), Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Prince, M. J. (2004). "Does Active Learning Work? A Review of the Research". *Journal of Engineering Education*, 93(3), pp. 223-231.

Prince, M. J. and Felder, R. M. (2006). "Inductive Teaching and Learning Methods: Definitions, Comparisons, and Research Bases". *Journal of Engineering Education*, 95(2), pp. 123-128.

Chapter 1 – A Problem-Solving Methodology

Halpern, D. F. (1989). *Thought and Knowledge: An Introduction to Critical Thinking*, Second Edition. Lawrence Erlbaum Associates, Inc., Hillsdale, NJ.

Miller, G. (1956): "The Magical Number Seven, Plus or Minus Two: Some Limits on Our Capacity for Processing Information", *Psychological Review*, Vol. 63 pp. 81-97.

Polya, G. (1945). *How to Solve It: A New Aspect of Mathematical Method*. Doubleday, New York, NY.

Polya, G. (1957). *How to Solve It: A New Aspect of Mathematical Method*, Second Edition. Doubleday, Garden City, NY.

Chapter 2 – First Principles in Chemical Engineering

Hanyak, M. E. (2006). "Styrene Monomer Interactive Demo". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2012). *Chemical Process Simulation and the AspenTech HYSYS Software*, Version 7.3. Self-published by Michael E. Hanyak, Jr., Chemical Engineering Department, Bucknell University, Lewisburg, PA. Available the Summer of 2012.

Koretsky, M. D. (2004). *Engineering and Chemical Thermodynamics*. John Wiley & Sons, Inc., New York, NY. ISBN 0-471-38586-7.

Chapter 3 – Fundamental Quantities in Chemical Engineering

AIChE. (2010). "Access the AIChE eLibrary". American Institute of Chemical Engineers, New York, NY.

Felder, R. M. and Rousseau, R.W. (2005). *Elementary Principles of Chemical Processes*, 3rd Update Ed. John Wiley & Sons, Inc., New York, NY. ISBN 978-0-471-68757-3.

Hanyak, M. E. (2007). "Fundamental Quantities and Relationships in Chemical Engineering", Table "gotche". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2008). "eLEAPS Script for the Ideal Gas Law, the Simplest Equation of State" and "eLEAPS How To" Explanation Document". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2010a). "Equations of State and Their Comparison to the NIST Data for the Pure Substance of Carbon Dioxide". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2010b). "Pressure-Enthalpy, Pressure-Internal-Energy, and Pressure-Temperature Diagrams for Pure Carbon Dioxide". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2011a). "Graphical Representations and Tabular Data for Water". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2011b). "Tutorial on Sketching Property Diagrams". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Lemmon, E. W., McLinden, M. O., and Friend, D. G. (2008). "Thermophysical Properties of Fluid Systems" in the NIST Chemistry WebBook, NIST Standard Reference Database Number 69. Editors: P.J. Linstrom and W.G. Mallard, National Institute of Standards Technology, Gaithersburg MD.

Online Conversions. (1997-2010). "Welcome to OnlineConversions.com". Robert Fogt, BlueSparks Network.

Chapter 4 – Problem-Solving Strategy

Felder, R. M. and Rousseau, R.W. (2005). *Elementary Principles of Chemical Processes*, 3rd Update Ed. John Wiley & Sons, Inc., New York, NY. ISBN 978-0-471-68757-3.

Hanyak, M. E. (2006). "What is the Meaning of the Extent of Reaction?". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2007). "Examples of Chemical Process Types". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2008). "eLEAPS Script for the Interactive Demo of the Math Algorithm Development" and "eLEAPS How To" Explanation Document". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Chapter 5 – Material Balance Problems

Felder, R. M. and Rousseau, R.W. (2005). *Elementary Principles of Chemical Processes*, 3rd Update Ed. John Wiley & Sons, Inc., New York, NY. ISBN 978-0-471-68757-3.

Hanyak, M. E. (2006). "What is the Meaning of the Extent of Reaction?". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2007a). "Examples of Chemical Process Types". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2007b). "Semi-Batch Reactor Example". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2008). "eLEAPS Script for a Continuous Reactor and the Production of Styrene Monomer" and "eLEAPS How To" Explanation Document". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2010a). "Application Advise for the Problem-Solving Methodology". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2010b). "Excess Air = Excess Oxygen". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2010c). "Scaling – An Important Technique". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Chapter 6 – Phase Equilibrium Problems

Barrie, P. J. (2008). "Java Script Programs for Solving Cubic Equations of State". Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, England.

EPI Suite. (2011). "Exposure Assessment Tools and Models". U.S. Environmental Protection Agency, Washington, DC.

Felder, R. M. and Rousseau, R.W. (2005). *Elementary Principles of Chemical Processes*, 3rd Update Ed. John Wiley & Sons, Inc., New York, NY. ISBN 978-0-471-68757-3.

Hanyak, M. E. (2008a). "eLEAPS Script for the Benzene-Styrene Distillation Column" and "eLEAPS How To" Explanation Document". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2008b). "Environmental Equilibrium Transport Problem". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2010). "Isothermal Flash Vaporization". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2011). "Ideal Gas Mixture: Amagat's Law and Dalton's Law". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Koretsky, M. D. (2004). *The ThermoSolver Software*. John Wiley & Sons, Inc., New York, NY.

Chapter 7 – Energy Balance Problems

Felder, R. M. and Rousseau, R.W. (2005). *Elementary Principles of Chemical Processes*, 3rd Update Ed. John Wiley & Sons, Inc., New York, NY. ISBN 978-0-471-68757-3.

Hanyak, M. E. (1986). "Enthalpy Reference States—Why are They Arbitrary?". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2007a). "Energy Balance with Chemical Reactions in a Problem", Pink Crib Sheet. Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2007b). "Energy Balance with No Chemical Reactions in a Problem", Blue Crib Sheet. Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2008). "eLEAPS Script for the Energy Balance and the Adiabatic Flame Temperature" and "eLEAPS How To" Explanation Document". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2010a). "Excess Air = Excess Oxygen". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2010b). "Pressure-Enthalpy, Pressure-Internal-Energy, and Pressure-Temperature Diagrams for Pure Carbon Dioxide". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2011a). "Arbitrary Component Reference States for the Heat-of-Reaction Method without Reaction". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2011b). "Kinetic Energy, Potenital Energy, and Specific Enthalpy Changes". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2011c). "Mixing Two Streams: Enthalpy Reference States for the Pure Components are Arbitrary". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2011d). "Pure-Compound Enthalpy Change". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2011e). "Strategy to Determine the Phase of a Chemical Mixture". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2011f). "Tutorial on Sketching Property Diagrams". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2011g). "What do you do when the ΔH_{mix} (heat of mixing) is not negligible?". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2011h). "Why is the Heat-of-Formation Method a Better Strategy?". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2011i). "Why Two Heats of Formation for a Pure Compound?". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Appendices

AIChE. (1979a). "*Letter Symbols for Chemical Engineering*". American Institute of Chemical Engineers, New York, NY.

AIChE. (1979b). "*SI for AIChE: A Guide for the Implementation of the International System of Units by the Chemical Engineering Profession*". American Institute of Chemical Engineers, New York, NY.

Brown, A. M. and Hanyak, M. E. (1998). "Volume Change of Mixing: An Investigation". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (1991a). "Some Drill and Practice Problems". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (1991b). "Units Conversion Primer—Methods and Techniques". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2008a). "Batch Process for Converting Ethane to Acetylene by a Chemical Reaction". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2008b). "Continuous Process for Removing Urea from Blood with an Artificial Kidney". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2008c). "Safety Precaution for Determining Human Expiration Time in Pure Nitrogen". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2008d). "Semi-Batch Process for Converting Strawberry and Sugar into a Jam". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2008e). "Semi-Continuous Process for Drying of Moist Air with Calcium Chloride". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Hanyak, M. E. (2010). "Application Advice for the Problem-Solving Methodology". Chemical Engineering Department, Bucknell University, Lewisburg, PA.

Online Conversions. (1997-2010). "Welcome to OnlineConversions.com". Robert Fogt, BlueSparks Network.

Physical Measurement Laboratory. (1998). "*The NIST Reference on Constants, Units, and Uncertainity*". United States National Institute of Standards and Technology (NIST), Gaithersburg, MD.