MATERIAL BALANCE NOTES

Revision 3

Irven Rinard
Department of Chemical Engineering
City College of CUNY

and

Project ECSEL

October 1999

© 1999 Irven Rinard
## CONTENTS

### INTRODUCTION 1
- A. Types of Material Balance Problems
- B. Historical Perspective

### I. CONSERVATION OF MASS 5
- A. Control Volumes
- B. Holdup or Inventory
- C. Material Balance Basis
- D. Material Balances

### II. PROCESSES 13
- A. The Concept of a Process
- B. Basic Processing Functions
- C. Unit Operations
- D. Modes of Process Operations

### III. PROCESS MATERIAL BALANCES 21
- A. The Stream Summary
- B. Equipment Characterization

### IV. STEADY-STATE PROCESS MODELING 29
- A. Linear Input-Output Models
- B. Rigorous Models

### V. STEADY-STATE MATERIAL BALANCE CALCULATIONS 33
- A. Sequential Modular
- B. Simultaneous
- C. Design Specifications
- D. Optimization
- E. Ad Hoc Methods

### VI. RECYCLE STREAMS AND TEAR SETS 37
- A. The Node Incidence Matrix
- B. Enumeration of Tear Sets

### VII. SOLUTION OF LINEAR MATERIAL BALANCE MODELS 45
- A. Use of Linear Equation Solvers
- B. Reduction to the Tear Set Variables
- C. Design Specifications
VIII. SEQUENTIAL MODULAR SOLUTION OF NONLINEAR MATERIAL BALANCE MODELS
   A. Convergence by Direct Iteration
   B. Convergence Acceleration
   C. The Method of Wegstein

IX.  MIXING AND BLENDING PROBLEMS
   A. Mixing
   B. Blending

X.  PLANT DATA ANALYSIS AND RECONCILIATION
   A. Plant Data
   B. Data Reconciliation

XI. THE ELEMENTS OF DYNAMIC PROCESS MODELING
   A. Conservation of Mass for Dynamic Systems
   B. Surge and Mixing Tanks
   C. Gas Holders

XII. PROCESS SIMULATORS
   A. Steady State
   B. Dynamic

BIBLIOGRAPHY

APPENDICES
   A. Reaction Stoichiometry
   B. Evaluation of Equipment Model Parameters
   C. Complex Equipment Models
   D. Linear Material Balance by Spreadsheet - Example
   E. The Kremser Model of Gas Absorbers
INTRODUCTION

The material balance is the fundamental tool of chemical engineering. It is the basis for the analysis and design of chemical processes. So it goes without saying that chemical engineers must thoroughly master its use in the formulation and solution of chemical processing problems.

In chemical processing we deal with the transformation of raw materials of lower value into products of higher value and, in many, cases unwanted byproducts that must be disposed of. In addition many of these chemical compounds may be hazardous. The material balance is the chemical engineer's tool for keeping track of what is entering and leaving the process as well as what goes on internally. Without accurate material balances, it is impossible to design or operate a chemical plant safely and economically.

The purpose of these notes is to provide a guide to the use of material balances in chemical engineering. Why one might ask? Aren't there already enough books on the subject, books such as those by Felder and Rousseau, by Himmelblau, and by Reklaitis? To answer that question we need to look briefly at the history of the problem.

A. Types of Material Balance Problems

First let us look at the types of material balance problems that arise in chemical engineering. There are four basic types of problems:

(1) Flow sheet material balance models for continuous processes operating in the steady state,

(2) Mixing and blending material balances,

(3) Flow sheet material balances for non-steady state processes, either continuous or batch, and

(4) Process data analysis and reconciliation

A flow sheet is a schematic diagram of a process which shows at various levels of detail the equipment involved and how it is interconnected by the process piping (See, for instance Figures II-1 and II-2 in Chapter II). A flow sheet material balance shows the flow rates and compositions of all streams entering and leaving each item of equipment.

Most of the emphasis on material balance problems has been on continuous processes operating in the steady state. Again one might ask why. The reason is simple. Of the total tonnage of chemicals produced, the vast majority is produced using continuous steady-state processes. This includes oil refineries as well as chemical plants producing large tonnage products such as sulfuric acid, ethylene, and most of the other commodity chemicals, petrochemicals and
polymers. It has been found that the most economical and efficient way to produce such chemicals on a large scale is via the continuous process operating in the steady-state. This is the reason for the emphasis on this type of material balance problem.

Another class of material balance problems is those involving blending and mixing. A substantial number of the products produced by the chemical processing industries are blends or mixtures of various constituents or ingredients. Examples of blends are gasoline and animal feeds; of precise mixtures, prescription drugs and polymeric resins.

Dynamic material balance problems arise in the operation and control of continuous processes. Also, batch processes, by their very nature, are dynamic. In either case we must consider how the state of the process varies as a function of time. In addition to determining the flow rates and compositions of the interconnecting streams, we must also follow the changes in inventory within the process itself.

In the three types of problems just discussed, we are interested in predicting the performance of the process or equipment. Our models start by assuming that the law of conservation of mass is obeyed. A fourth type of problem, which encountered by engineers in the plant, starts with actual operating data, generally flow rates and compositions of various streams. The problem is to determine the actual performance of the plant from the available data.

This, in many ways, is a much more difficult problem than the first three. Why? Simple. The data may in error for one reason or another. A flow meter may be out of calibration or broken entirely. A composition measurement is not only subject to calibration errors but sampling errors as well. Thus the first thing one must do when dealing with plant data is to determine, if possible, whether or not it is accurate. If it is, then we can proceed to use it to analyze it to determine process performance. If not, we must try to determine what measurements are in error, by how much, and make the appropriate corrections to the data. This is known as data reconciliation and is possible only if we have redundant measurements.

B. Historical Perspective

The solution of material balance problems for continuous steady-state processes of any complexity used to be very difficult. By its nature, the problem is one of solving a large number of simultaneous algebraic equations, many of which are highly nonlinear. Before the availability of computers and the appropriate software, the solution of the material balance model for a chemical process typically took a team of chemical engineers using slide rules and adding machines days or weeks, if not months. And given the complexity of the problem, errors were common.

The methods used in those days to solve material balance problems days are best described as ad hoc. Typically an engineer started with the process specifications such as the production
rate and product quality and calculated backwards through the process. Intermediate specifi-
cations would be used as additional starting points for calculations. As will be seen later in these
notes, such an approach goes against the output-from-input structure of the process and can lead
to severe numerical instabilities.

The growing availability of digital computers in the late 1950's led to the development of
the first material balance programs such as IBM's GIFS, Dartmouth's PACER and Shell’s
CHEOPS. Almost every major oil and chemical company soon developed in-house programs of
which Monsanto's Flowtran is the best-known example. By the 1970's several companies
specializing in flow sheet programs had come into existence. Today companies such as
Simulation Sciences, Aspen Technology and Hyprotech provide third-generation versions of
steady-state flow sheet simulation programs that provide a wide range of capabilities and are
relatively easy to use compared to earlier versions.

Dynamic simulation is less advanced than steady-state simulation. This is due, in part, to
the lack of emphasis until recently on the dynamic aspects of chemical engineering operations.
This situation is changing rapidly due to demands for improved process control and for simulators
for training operating personnel. The companies mentioned in the previous paragraph have all
recently added dynamic simulators to their product lines. In addition several companies such as
ABB Simcon offer training simulators for the process industries.

C. Material Balance Methodology

There are two major steps involved in applying the principle of conservation of mass to
chemical processing problems. The first is the formulation of the problem; the second, its solu-
tion.

By formulation of the problem is meant determining the appropriate mathematical
description of the system based on the applicable principles of chemistry and physics. In the case
of material balances, the appropriate physical law is the conservation of mass. The resulting set of
equations is sometimes referred as a mathematical model of the system.

What a mathematical model means will be made clearer by the examples contained in these
notes. However, some general comments are in order. First, there may be a number of mathe-
matical models of varying levels of detail that can apply to the same system. Which we use
depends upon what aspects of the process we wish to study. This will also become clearer as we
proceed. Second, for many systems of practical interest, the number of equations involved in the
model can be quite large, on the order of several hundred or even several thousand.

Thus, the process engineer must have a clear of how to formulate the model to insure that
it is a correct and adequate representation of the process for the purposes for which it is intended.
This is the subject of Sections I - IV of these notes.

Today, using process simulation program such as PRO-II, ASPEN, and HYSIM, a single
engineer can solve significant flow sheeting problems in as little as a day or two and, moreover, do it much more accurately and in much more detail than was previously possible. The process engineer can now concentrate on the process model and the results rather than concocting a scheme to solve the model equations themselves. The simulation program will do that, at least most of the time. However, things do go wrong at times. Either the problem is very difficult for the simulator to solve or a mistake has been made in describing the process to the program. Thus, in order to fix what is wrong, the engineer does need to know something about how the simulation program attempts to solve the problem. This is the subject of Sections V, VIII, and IX of these notes. Steady-state simulation programs are described briefly in Section XII.

Simple material balance problems involving only a few variables can still be solved manually. However, it is generally more efficient to use a computer program such as a spreadsheet. Both approaches are discussed in Section VII.

In order to achieve high levels of mass and energy utilization efficiency, most processes involve the use of recycle. As will be seen, this creates recycle loops within the process which complicate the solution of material balances models for the process. A systematic procedure for identifying recycle loops is presented in Section VI.

An introduction to problems encountered in determining plant performance from plant is given in Section X.

There are two basic process operating modes that are of interest to chemical engineers, dynamic and steady state. All processes are dynamic in that some or all of the process variables change with time. Many processes are deliberately run dynamically; batch processes being the prime example. However, many large-scale processes such as oil refineries and petrochemical plants are run in what is called the continuous or steady state operation. The appropriate model for dynamic processes are differential equations with respect to time. In general, continuous processes operating in the steady state are modeled by algebraic equations. Dynamic process modeling is discussed briefly in Section XI and dynamic process simulators in Section XII.

Many topics in process modeling are not covered in these notes. The most serious omission is the companion to the material balance, namely, the energy balance. Also, little attention is paid to what are known as first-principle or rigorous equipment models. Such modeling is more properly covered in texts and courses on unit operations and chemical reaction engineering. However, a few of the simpler and more useful models are given in Appendix E.
I. CONSERVATION OF MASS

Revised October 2, 1999

The principle of conservation of mass is fundamental to all chemical engineering analysis. The basic idea is relatively easy to understand since it is fact of our everyday life.

Let us consider a simple example. Suppose we are required to prepare one kilogram of a solution of ethanol in water such that the solution will contain 40% ethanol by weight. So, we weigh out 400 grams of ethanol and 600 grams of water and mix the two together in a large beaker. If we weigh the resulting mixture (making appropriate allowance for the weight of the beaker), experience says it will weigh 1000 grams or one kilogram. And it will. This is a manifestation of the conservation of mass.

That, in the absence of nuclear reactions, mass is conserved is a fundamental law of nature.

This law is used throughout these notes and throughout all chemical engineering.

Suppose we happened to measure the volumes involved in making up our alcohol solution. Assuming that we do this at 20 C, we would find that we added 598.9 ml of water to 315.7 ml of ethanol to obtain 935.2 ml of solution. However, the sum of the volumes of the pure components is 914.6 ml. We conclude that volume is not conserved.

Let us take note of one other fact about our solution. If we were to separate it back into its pure components (something we could do, for instance, by azeotropic distillation) and did this with extreme care to avoid any inadvertent losses, we would obtain 400 gm of ethanol and 600 gm of water. Thus, in this case, not only was total mass conserved but the mass of each of the components was also.

This is not always true. Suppose that instead of adding ethanol and water, we added (carefully and slowly) sodium hydroxide to sulfuric acid. Suppose that the H$_2$SO$_4$ solution contains exactly 98.08 pounds of H$_2$SO$_4$ and that we add exactly 80.00 pounds of NaOH. A chemical reaction will take place as follows:

\[
\text{H}_2\text{SO}_4 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2 \text{H}_2\text{O}.
\]

Notice that the amount of H$_2$SO$_4$ in the original solution is 1.0 lb-mol and that the amount of NaOH added is exactly 2.0 lb-mols. What we are left with is 1.0 lb-mol of Na$_2$SO$_4$ or 142.05 lbs and 2.0 lb-mols of H$_2$O or 36.03 lbs. No individual component is conserved; the H$_2$SO$_4$ and the NaOH have disappeared and in their place we have Na$_2$SO$_4$ and H$_2$O. However, if we look at the atomic species H, O, S, and Na, we will find that these are all conserved. That is exactly what the reaction equation expresses.
Thus we have to be careful to identify the appropriate conserved species for the system we are analyzing. If no chemical reactions are involved, then each of the molecular species is conserved. If chemical reactions are involved, then only atomic species are conserved. There will be a mass balance for each of the conserved species. In the example above it does not make much difference since there are four conserved atomic species and four molecular species. But, if additional reactions take place involving, say, $Na_2S$ and $NaHSO_4$, then the number of molecular species exceeds the number of conserved atomic species. This will generally be the case.

A. Control Volumes

We apply the principle of the conservation of mass to systems to determine changes in the state of the system that result from adding or removing mass from the system or from chemical reactions taking place within the system. The system will generally be the volume contained within a precisely defined section of a piece of equipment. We refer to this precisely defined volume as a control volume.

It may be the entire volume of the equipment. This would be the case if the system is a cylinder containing a gas or gas mixture. Or it may be the volume associated with a particular phase of the material held within the system. For instance, a flash drum is used to allow a mixture of vapor and liquid to separate into separate vapor and liquid phases. The liquid phase will occupy part of the total volume of the drum; the vapor, the remainder of the volume. If we are interested only in what happens to the liquid phase, then we would specify the volume occupied by the liquid as our control volume.

Note that the control volume can change over the course of an operation. Suppose we are adding liquid to a tank that contains 100 Kg of water to start with and that we add another 50 Kg. The tank would originally contain 100 liters of water but would contain 150 liters after the addition. On the other hand, if our interest is in the entire contents of the tank - both the liquid and the vapor in the space above it - then we would take the volume of the tank itself as our control volume. This volume, of course, will not change.

B. Holdup or inventory

Another concept that we will need to make precise is that of holdup, also known as inventory or accumulation. Holdup refers to the amount of a conserved species contained within a control volume. We can refer to the total holdup as simply the total mass of material contained within the control volume. Or we can refer to the holdup of a particular component, sodium chloride say, which is contained within the control volume. Needless to say, the sum of the holdups of all of the individual components within the control volume must equal the total holdup.
C. Material Balance Basis

Whenever we apply the principle of conservation of mass to define a material balance, we will want to specify the basis for it. Generally, the basis is either the quantity of total mass or the mass of a particular component or conserved species for which the material balances will be defined. Or, for continuous processes, it might be the mass flow rate of a component or conserved species.

Quite often the basis will be set by the specification of the problem to be solved. For instance, if we are told that a tank contains 5,000 pounds of a particular mixture about which certain questions are to be answered, then a natural basis for the problem would the 5,000 pounds of the mixture. Or, if we are looking at a continuous process to make 10,000 Kg/hr of ethanol, a reasonable choice for a basis would be this production rate.

Some problems, however, do not have a naturally defined basis so we must choose one. For instance, if we are asked what is the mass ratio of NaOH to H₂SO₄ required to produce a neutral solution of NaCl in water, we would have to specify a basis for doing the calculations. We might choose 98.08 Kg of H₂SO₄ (1.0 Kg-mol) as a basis. Or we could chose 1.0 lb of H₂SO₄. Either is acceptable. One basis may make the calculations simpler than another, but in this day of personal computers the choice is less critical than it might have been years ago. Whatever the choice of basis, it is mandatory that all material balances are defined to be consistent with it.

D. Material Balances

We are now in a position to define material balances for some simple systems. (Note: Material balances are sometimes referred to as mass balances.) There are three basic situations for which we will want to do this:

1) A discrete process in which one or more steps are carried out over a finite but indefinite period of time.

An example of such a process is the dissolving of a specified quantity of salt in a quantity of water contained in a tank. We are only interested in the concentration in weight % of the salt in the water after it is completely dissolved and not how long it takes for the salt to dissolve.

2) A continuous process operating in the steady state.

By definition, continuous process operating in the steady state undergoes no changes in its internal state variables such as temperatures, pressures, compositions, and liquid levels. In addition, all the flow rates of all streams entering and leaving each item of equipment are constant. What this means from the standpoint of material balances is that there is no change in any of the holdups in the system.
3) Dynamic processes.

This is the general case in which both the holdups within equipment as well as the flow rates and compositions of the input and output streams can vary with time. This type of mass balance is discussed in more detail in Section XI.

Examples

a. Discrete process

Let us now consider the application of the principle of the conservation of mass to a discrete process. For each of the conserved species, it can be stated as follows:

\[
\text{Change in holdup} = \text{additions to the control volume} - \text{withdrawals from the control volume}
\]

Consider the following example:

We have a tank that initially holds 100 Kg of a solution containing 40% by weight of salt in water.

(1) We add 20 Kg of salt to the tank and allow it to dissolve.

What do we now have in the tank?

First we have to identify the conserved species. Since there are no chemical reactions involved, both salt and water are conserved species. Next we have to define the control volume. It seems natural to choose the salt solution in the tank. Our basis is the amount of solution originally contained in the tank.

Now we can define a material balance for each conserved species as follows:

**Water**

Initial holdup of water = \((1 - 0.4)(100) = 60\) Kg

Change in holdup of water = additions of water to the control volume - withdrawals of water from the control volume

Since no water is either added or withdrawn, the change in this holdup is zero. Therefore the holdup of water after the salt addition is still 60 Kg.

**Salt**

Initial holdup of salt = \((0.4)(100) = 40\) Kg
Change in holdup of salt = additions of salt to the control volume
- withdrawals of salt from the control volume

We add 20 Kg of salt and withdraw no salt. Therefore the change in the holdup of salt = +20 Kg and the holdup of salt after the addition is 40 + 20 = 60 Kg. A simple calculation shows that the concentration of salt in the tank is now 50 weight %.

(2) We withdraw 40 Kg of the solution now in the tank.

Since the solution in the tank is 50 weight % salt and 50 weight % water, in withdrawing 40 Kg of solution, we will withdraw 20 Kg of salt and 20 Kg of water. This will leave 60 - 20 = 40 Kg of each component in the tank. The composition has not changed from Step 1.

b. Continuous steady-state process

Let us consider a continuous mixer which has two input streams and, of course, one output stream (See Figure 6 for a diagram). Suppose the first input stream has a flow rate of 10000 lb/hr of a 40 wt. % solution of salt in water while the second input stream has a flow rate of 20000 lb/hr of a 70 wt. % solution of salt in water. What is the flow rate and composition of the output stream?

Since the system is now characterized in terms of rates of flow into the control volume (additions) and rates of flow out of the system (withdrawals), we need to restate the principle of conservation of mass as follows:

(I-2) \[
\text{Rate of change of holdup} = \frac{\text{rate of additions to the control volume}}{} - \frac{\text{rate of withdrawals from the control volume}}{}
\]

For a continuous system operating in the steady state, the holdup does not change with time. Therefore, the rate of change of holdup is zero and Eqn. I-2 becomes

(I-3) \[
\text{Rate of withdrawals from the control volume} = \frac{\text{Rate of additions to the control volume}}{}
\]

Let us apply this to the mixer problem. The control volume is the contents of the mixer (even though these do change) and the basis is the total rate of flow to the mixer. As in the previous example, the conserved species are salt and water.

Salt
Rate of withdrawal of salt = 
rate of additions of salt to the mixer

Rate of additions = (10000)(0.4) + (20000)(0.7) 
= 18000 lb/hr of salt

Water

Rate of withdrawal of water = 
rate of additions of water to the mixer

Rate of additions = (10000)(0.6) + (20000)(0.3) 
= 12000 lb/hr

Thus the stream leaving the mixer has a flow rate of 18000 lb/hr of salt and 12000 lb/hr of water, for a total of 30000 lb/hr. This is exactly the total flow rate of the mixer output we get by adding up the total flow rates to the mixer. Also, the composition of salt of the stream leaving the mixer =

\[(100)(18000)/(30000) = 60 \text{ wt } \%\].

c. Dynamic Process

Consider the surge tank shown in Figure I-1. Water flows into the tank with a flow rate \( F_{\text{in}} \) lb/hr. It flows out at a rate \( F_{\text{out}} \) lb/hr. The flow rates in and out can be adjusted by means of the valves in the inlet and outlet piping. The tank has the form of an upright cylinder that has a cross section area of \( S \) ft\(^2\). The liquid level in the tank is \( z \) ft.

We know from experience that if the flow rates in and out are not exactly equal, the level in the tank will change with time. If the inlet flow rate exceeds the outlet flow rate, then the level will rise and vice versa. Now, the purpose of a surge tank is to absorb changes in the inlet flow rate while maintaining a relatively constant outlet flow rate. (The reservoirs that supply water to a town or city are surge tanks where the inlet flow is the run-off from rainstorms and the outlet flow \( F_{\text{out}} \) is the daily consumption by the town or city.) Thus, a question that designers of surge tanks must ask is, given an estimate of the variations of inlet and outlet flow rates as functions of time, how
big must the surge tank be so that it never runs dry (town loses its water supply) or never overflows (area surrounding the reservoir is flooded). In general this is a complex design problem but let us look at a simple example to at least illustrate the concept.

Suppose that under normal conditions the level in the tank is to be half the height of the tank. If the flow rate into the tank becomes zero for a period of time (no rain), how long will it take for the tank to run dry if the outlet flow rate is maintained at its usual value? Specifically, suppose that the cross section area of the tank is 10 ft$^2$ and its height is 10 ft and the normal outlet flow rate is 12,480 lb/hr.

First, let us take the volume of liquid in the tank as the control volume. The holdup of water in the control volume will be

$$\text{Holdup} = Sz \rho,$$

where $\rho$ is the density of water (62.4 lb/ft$^3$).

Consider an interval of time $\Delta t$. Suppose that over that time interval the inlet and outlet flow rates are constant but not necessarily equal. Then, by the conservation of mass the change in the holdup will be given by

$$(I-1) \quad \text{Holdup}\big|_{t=t} - \text{Holdup}\big|_{t=0} = F_{in} \Delta t - F_{out} \Delta t$$

Now, if we divide both sides of the mass balance equation (Eqn. I-1) by $\Delta t$ and take the limit as $\Delta t \to 0$, we get the differential form of the mass balance, to wit,

$$(I-2) \quad d[Sz \rho]/dt = F_{in} - F_{out}$$

If we assume that $\rho$ is constant (a reasonable assumption if the temperature is also reasonably constant), then our mass balance equation becomes

$$(I-3) \quad dz/dt = (F_{in} - F_{out})/Sz \rho$$

For our problem $F_{in} = 0$ and $F_{out} = 12,480$ lb/hr, both constant. We can calculate $dz/dt$, that is

$$dz/dt = (0 - 12480)/(10)(62.4) = -20 \text{ ft/hr}.$$  

Since the nominal level is 5.0 ft (half the tank height of 10ft), it will take 0.25 hour or 15 minutes for the tank to run dry.

Further examples of the application of the principle of conservation of mass, particularly for reacting systems, will be found in the subsequent sections of these notes.
A. The Concept of a Process
Processes are the main concern of chemical engineers. A process is a system that converts feedstocks of lower intrinsic value to products of higher value. For instance, the block diagram of a process to manufacture ammonia from natural gas is shown in Figure II-1. This process has several sections, each one of which carries out a specific task and is, in effect, a mini-process. Natural gas, steam and air are fed to the Reformer Section that converts these feeds into a mixture of H₂, CO₂, and H₂O. The overall chemical reactions involved are:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3 \text{H}_2 \\
\text{CH}_4 + \text{O}_2 & \rightarrow \text{CO} + 2 \text{H}_2 \\
\text{CH}_4 + 2 \text{O}_2 & \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}.
\end{align*}
\]

Since H₂ is the desired raw material from which to make ammonia, this gas mixture is sent to the CO Shift Section where additional steam is added to improve conversion by the water gas shift reaction:

\[
\text{CH}_4 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow 2 \text{CO} + 3 \text{H}_2.
\]
CO + H₂O $\rightarrow$ H₂ + CO₂.

The CO₂ and H₂O present in the gas mixture leaving the CO Shift Section are removed in the CO₂ Removal Section. The gas mixture leaving the CO₂ Removal Section contains primarily a 3/1 mixture of H₂ and N₂ (the N₂ coming from the air fed to the Reformer Section). It also contains small amounts of CO (the water gas shift reaction is equilibrium limited) as well as argon from the air feed to the Reformer Section.

The CO must be removed from this mixture because it will deactivate the catalyst used in the ammonia converter. This is done in the Methanation Section via the reaction

CO + 3 H₂ $\rightarrow$ CH₄ + H₂O.

The gas mixture leaving the Methanation Section contains a 3/1 mixture of H₂ and N₂ and trace amounts of CH₄ and Ar. This is sent to the NH₃ Synthesis Loop where the ammonia is made via the well-known reaction

N₂ + 3 H₂ $\rightarrow$ 2 NH₃.

So far each section of the process has been considered as a black box. Let us look at the Ammonia Synthesis Loop in more detail. A process flow diagram (PFD) is shown in Fig. II-2.

The ammonia synthesis reaction is equilibrium limited to the point where it must be run at rather high pressures (3000 PSIA or 20 mPa) in order to achieve a reasonable conversion of Syn Gas to ammonia across the Converter. Since the front end of the process is best run at much lower pressures, a Feed Compressor is needed to compress the Syn Gas to the operating pressure of the Synthesis Loop.

Due to the unfavorable reaction equilibrium, only part of the Syn Gas is converted to ammonia on a single pass through the Converter. Since the unconverted Syn Gas is valuable, the majority of it is recycled back to the Converter. Due to pressure drop through the Synthesis Loop equipment, a Recycle Compressor is required to make up this pressure drop. The recycled Syn Gas is mixed with fresh Syn Gas to provide the feed to the Synthesis Converter.

The effluent from the Synthesis Converter contains product ammonia as well as unreacted Syn Gas. These must be separated. At the pressure of the synthesis loop ammonia can be condensed at reasonable temperatures. This is done in the Ammonia Condenser where the Syn Gas is cooled to approximately ambient temperature using cooling water (CW). The liquid ammonia is then
Fig. II-2. Ammonia Synthesis Loop Process Flow Diagram

separated from the cycle gas in the Ammonia Knockout (KO) Drum. The liquid ammonia is removed from the bottom of the drum and the cycle gas leaves the top.

Some of the cycle gas must be purged from the Synthesis Loop. Otherwise, the argon that enters the loop in the Syn Gas has no way to leave and will build up in concentration. This will reduce the rate of the ammonia synthesis reaction to an unacceptable level. To prevent this from happening, a small amount of the cycle gas must be purged, the amount being determined by the amount of argon in the feed and its acceptable level in the Synthesis Converter feed (generally about 10 mol %).

This description of the Ammonia Synthesis Loop covers only the most important aspects. Modern ammonia plants are much more complex due to attention paid to maximizing the amount of ammonia produced per mol of Syn Gas fed to the loop. However, the process shown in Figure II-2 is typical of many chemical processes.
B. Basic Processing Functions

Several basic processing activities are required by the Ammonia Synthesis Loop in order to convert the hydrogen and nitrogen to ammonia product. These activities are common to almost all chemical processes; the functionality of each can be considered independently of any specific process.

There are five of these processing activities that are of major interest in chemical engineering:

1. Chemical Reaction
2. Mixing
3. Separation
4. Materials Transfer (Fluid flow)
5. Energy (Heat) Transfer

Of these the first three are involved in the process material balance. The last two are necessary adjuncts to operation of chemical processes. Material must be transported from one piece of equipment to another. For the large number of chemical plants processing only liquids and vapors, this involves fluid flow. Also, streams must be heated to or cooled to specified temperatures as dictated by the needs of the process. For example, reactors in general are operated at temperatures higher than those that are acceptable for most separation operations. Thus, streams must be heated to reaction temperature and then cooled back down for subsequent processing.

1. Chemical Reaction

What distinguishes the chemical process industries from almost all others is the use of chemical reactions to convert less valuable raw materials to more valuable products. In other words, chemical reaction is the heart and soul of almost all processes.

In the Ammonia Synthesis Loop example, R-1, the Synthesis Converter is where the ammonia synthesis reaction takes place.

2. Mixing

Many chemical reactions involve two or more reactants. In order for these reactants to react, these must be brought into contact at the molecular level, i.e., mixed, before the desired reactions can proceed properly.

Mixing is also required if several substances are to be blended to create a product mixture with the desired properties.
For our example process, mixing of fresh synthesis gas and recycled synthesis gas takes place in the Feed Mixer, M-1, before being sent to the Synthesis Converter.

3. **Separation**

In an ideal chemical process, exactly the right amounts of reactants would be mixed and reacted completely to the desired product. Unfortunately, this is seldom the case. Many reactions cannot be carried to completion for various reasons. Seldom do the reactants react only to the desired product. Unwanted byproducts are formed in addition to the target product. Finally, the reactants are seldom 100% pure, again for many reasons.

The result is that the material leaving the reactor is a mixture containing the desired product, by-products, unreacted raw materials, and impurities. It may also contain other components deliberately introduced for one reason or another. The use of a homogeneous catalyst is just one example of this.

This mixture must be separated into its various constituents. The product must be separated from almost everything else and brought to an acceptable level of purity such that it can be sold. The reactants, being valuable, must be recovered and recycled back to the reactor. The impurities and by-products must be separated out for disposal in a suitable manner.

Thus, the activity of separation is fundamental to the operation of almost any process. Some separation systems are relatively simple. Others constitute the major part of the process. As will be seen, separation takes on many forms.

Separation of ammonia from cycle gas takes place in the Ammonia KO Drum, F-1. The cycle gas leaving the Ammonia Condenser, E-1, contains droplets of liquid ammonia. This mixture enters the middle of the KO Drum. The vapor, being less dense, flows upward while the liquid ammonia falls to the bottom of the drum.

4. **Materials Transfer**

The Ammonia Synthesis Loop (Figure II-2) consists of several items of equipment, each of which has material flowing in and material flowing out. These flows take place through process piping connecting the various items of equipment. If the pressure in the upstream item of equipment is sufficiently higher than that in the downstream item, then material will flow from the upstream equipment to that downstream without the need for any additional equipment. This pressure difference is necessary to overcome the friction due to fluid flow through the piping. As a result, the pressure will decrease in the direction of flow through the process.

Thus, as synthesis gas flows from the inlet to the reactor (Stream 3) through the reactor, condenser and knockout drum, the pressure decreases significantly. In order to be able to recycle the unreacted hydrogen and nitrogen back to the reactor, some means is required to increase the
pressure of this stream back to that of the reactor inlet. Hence the presence of the compressor in the recycle loop.

C. Unit Operations

One of the major contributions to the practice of chemical engineering is the concept of the unit operations. This concept was developed by Arthur D. Little and Warren K. Lewis in the early 1900's. Prior to its development, chemical engineering was, to a large extent, practiced along the lines of specific process technologies. For instance, if distillation was required in the manufacture of acetic acid, it became a problem in acetic acid distillation. The fact that a similar distillation might be required for the manufacture of, say, acetaldehyde was largely ignored. What Little and Lewis did was to show that the principles of distillation (as well as many other processing operations) were the same regardless of the materials being processed. So, if one knew how to design distillation columns, one could do so for acetic acid, acetaldehyde, or any other mixture of reasonable volatility with equal facility. The same proved to be true of other operations such as heat transfer by two-fluid heat exchangers, gas compression, liquid pumping, gas absorption, liquid-liquid extraction, fluid mixing, and many other operations common to the chemical industry.

The case for chemical reactors is less clear. Each reaction system tends to be somewhat unique in terms of its reaction conditions (temperature, pressure, type of catalyst, feed composition, residence time, heat effects, and equilibrium limitations). Thus, each reaction system must be approached on its own merits with regard to the choice of reactor type and design. However, the field of chemical reaction engineering has undergone substantial development over the past few decades, the result being that much of what is required for the choice and design of reactors is subject to a rational and quantitative approach.

D. Modes of Process Operation

As mentioned previously, there are several modes of process operation. The one that has been most widely studied by chemical engineers is that of the steady-state operation of continuous processes. The reasons have also been discussed. In this mode of operation we assume that the process is subject to such good control that as feed materials flow into the process as constant flow rates, the necessary reactions, separations, and other operations all take place at conditions that do not vary with time. The amount of material in each item of equipment (its inventory) does not vary with time; pressures and liquid levels are constant. Nor do temperatures, compositions, and flow rates at each point in the process vary with time. From the standpoint of the casual observer, nothing is happening. However, finished product is flowing out of the other end of the process into the product storage tanks.

The next most common mode of process operation is known as batch operation. Here, every processing operation is carried out in a discrete step. Reactants are pumped into a reactor,
mixed, and heated up to reaction temperature. After a suitable length of time, the reactor turned off by cooling it down. It now contains a mixture of products, by-products, and unreacted reactants. These are pumped out of the reactor to the first of the various separation steps, possibly a batch distillation or a filtration if one of the products or byproducts is a solid. Each batch step has a beginning, a time duration, and an end. (Most activities around the home are batch in nature - cooking, washing clothes, etc.).

A third mode is cyclic operation. From the standpoint of flows in and out of both the process and individual items of equipment, operation is continuous. However, in one or more items of equipment, operating conditions vary in time in a cyclical manner. A typical example is reactor whose catalyst deactivates fairly rapidly with time due to, say, coke formation on the catalyst. To recover the catalyst activity, it must be regenerated by being taken out of reaction operation. The coke is removed either by stripping by blowing an inert gas over the catalyst or, in the more difficult cases, by burning the coke off with dilute oxygen in an inert gas carrier.

Two characteristics of cyclical operation become apparent. First off, if the process is to be operated continuously but it one or more items of equipment must be taken off line for regeneration of one sort or another, we must have at least two of such items available in parallel. One is on line while another is being regenerated. The second characteristic is the is that operation conditions in the cyclically operated equipment must vary with time. If catalyst activity decrease with time, then something must be done to maintain the productivity of the reactor. Usually this is achieved by raising the reactor temperature. Thus, a freshly regenerated reactor will start off at a relatively low temperature; the temperature will be raised during the cycle; and the reactor will be taken off line when no further benefit is to be obtained by raising the temperature any further. (The catalyst may melt, for instance.)
III. PROCESS MATERIAL BALANCES

Revised October 10, 1999
Material balances result from the application of the law of conservation of mass to individual items of equipment and to entire plants (or subsections thereof). When the mass conservation equations are combined with enough other equations (energy balances, equilibrium relationships, reaction kinetics, etc.) for an individual item of equipment (such as a reactor or a distillation column), the result is a mathematical model of the performance of that equipment item. The model can be dynamic or steady state, depending upon how it is formulated.

For the present let us confine our attention to steady-state models. Such equipment models are generally nonlinear and must be solved by iterative procedures, usually with the help of a computer. However, if we make enough simplifying assumptions, linear models will result. While these will not be as accurate as the more rigorous nonlinear models, they are a good starting point for many applications, one which is pursued in subsequent sections of these notes.

Individual models can be combined to represent the performance of an entire chemical plant or sections thereof. For instance, one might start by modeling the performance of the reaction section. When this is in hand, one can then add other parts of the plant such as the separation and purification sections. As will be seen, if we limit ourselves to simple, linear equipment models, then the overall process or flowsheet model will also be linear. This we can solve using a spreadsheet for instance. Not only that, we can solve rather large flowsheet models with a relatively modest amount of effort. This is one motivation for using linear models.

If the equipment models are nonlinear, we almost always require the use of a computer. Indeed, there are special-purpose programs that have been developed just for solving process flowsheet models. These programs are generally known as steady-state process simulators or flowsheeting programs.

A. The Stream Summary

Before discussing equipment characterization in detail, it is necessary to consider the characterization of the streams entering and leaving each item of equipment. While there is no unique way of doing this, the following characterization is typical. Each stream is represented by a vector of various quantities. If there are nc components of significance in the stream, then the first nc entries in the vector will be

\[ f_{i,n} \] - the molar flow rate of the component \( i \) in stream \( n \).

Additional quantities that may be included in this vector are:

\[ F_n \] - the total molar flow rate of stream \( n \),

\[ T_n \] - the temperature of stream \( n \),
\( P_n \) - the pressure of stream \( n \),

\( R_n = V/F \), (the mols of stream \( n \) that are vapor)/(the total mols of stream \( n \)) \([V/F = 0, \text{ stream is liquid; } V/F = 1, \text{ stream is vapor; } 0 < V/F < 1, \text{ stream is a two-phase mixture of liquid and vapor}])

\( \rho_n \) - mass density of stream \( n \),

\( M_{w_n} \) - average molecular weight of stream \( n \),

\( W_n \) - the total mass flow rate of stream \( n \),

\( H_n \) - the total enthalpy of stream \( n \),

\( S_n \) - the total entropy of stream \( n \), and

\( G_n \) - the total free energy of stream \( n \).

Not all of these quantities have to be included in the stream vector for all problems. Only the \( f_{i,n} \) are needed for linear material balance calculations. However, most process simulation programs include all of the variables listed above in the stream characterization vector as well as mol fractions and weight fractions of the individual components. Since the total mass balance around each item of equipment is easy to check, we will include \( W_n \) in the stream vector (and will need \( M_{w_n} \) to calculate it from \( F_n \)).

A typical summary is shown in the Table III-1 below. It is for the Ammonia Synthesis Loop whose PID was presented in Fig. II-1 of the previous chapter. It was computed using the EXCEL spreadsheet program based on the linear material solution technique developed in Chapter VII. The details of the spreadsheet solution are given in Appendix D.

**B. Equipment Characterization**

1. **Reactors**

The reactor is the heart of almost any chemical process. A simple reactor is shown schematically in Fig. III-1. The input or feed stream \( ST_{in} \) contains the reactants along any inerts, feed impurities, and diluents (all of which have usually been premixed in a mixer). One or more chemical reactions take place in the reactor and the reaction products, any remaining unreacted reactants, and the inerts, diluents, and feed impurities leave in the reactor output or effluent stream \( ST_{out} \).

<table>
<thead>
<tr>
<th>Stream Summary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp</td>
</tr>
</tbody>
</table>

-22-
<table>
<thead>
<tr>
<th>Lb-mol/hr</th>
<th>H2</th>
<th>N2</th>
<th>Argon</th>
<th>Ammonia</th>
<th>Total mol/hr</th>
<th>Mol percent</th>
<th>Average MW</th>
<th>Total lb/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>750.00</td>
<td>2894.03</td>
<td>2193.37</td>
<td>2191.18</td>
<td>2.19</td>
<td>47.15</td>
<td>2144.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>250.00</td>
<td>934.20</td>
<td>700.65</td>
<td>699.25</td>
<td>1.40</td>
<td>15.05</td>
<td>684.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.00</td>
<td>425.95</td>
<td>425.95</td>
<td>425.10</td>
<td>0.85</td>
<td>9.15</td>
<td>415.95</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.00</td>
<td>4.62</td>
<td>471.72</td>
<td>4.72</td>
<td>467.00</td>
<td>0.10</td>
<td>4.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1010.00</td>
<td>4258.79</td>
<td>3791.69</td>
<td>3320.25</td>
<td>471.45</td>
<td>71.45</td>
<td>3248.79</td>
<td></td>
</tr>
</tbody>
</table>

Table III-1. Stream Summary for Ammonia Synthesis Loop

There are many ways of characterizing reactors. In general, what we want to know is the extent of reaction $\Delta_i$ for each component $i$. We define the extent of reaction of component $i$ as the mols of $i$ that are made or used up in the reactor. For a continuous steady-state reaction, the extent of reaction is really a rate, namely, the mols of $i$ formed or consumed per unit time.

\[ f_{out, i} = f_{in, i} + \Delta_i \]

Figure III-1. Reactor

The extent of reaction can be determined in various ways. Regardless of how determined, the $\Delta_i$ must satisfy the reaction stoichiometry. Let us consider a simple example. Let us suppose that methane (CH4) is being oxidized using air to a mixture of CO and CO2 according to the following chemistry:

1) \[ \text{CH}_4 + \frac{3}{2} \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2\text{O} \]

2) \[ \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \]
This reaction system involves two reactions. There are five components involved the reactions as well as one inert - the nitrogen that comes with the air. (Let us assume that for present purposes, the small amount of argon also present in the air can be lumped with the nitrogen.)

Let \( r_j \) = the rate of the jth reaction in, say, lb-mol/hr and

\[ a_{i,j} = \text{the mols of component i that are formed or consumed by one mol of reaction j.} \]
\[ a_{i,j} \text{ is known as the stoichiometric coefficient of component i with respect to reaction j.} \]

Then if there are \( nr \) reactions in the system,

\[
(III - 1) \quad \Delta_i = \sum_{j=1}^{nr} a_{i,j} r_j
\]

For the CH\(_4\) oxidation reactions, the stoichiometric coefficient matrix is:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>CH(_4)</th>
<th>O(_2)</th>
<th>CO</th>
<th>CO(_2)</th>
<th>H(_2)O</th>
<th>N(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
<td>-3/2</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>-2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

Note that the stoichiometric coefficients for reactants are negative; those for products, positive.

Let us suppose that \( r_1 = 20 \text{ lb-mol/hr} \) and \( r_2 = 10 \text{ lb-mol/hr} \).

Then

\[ \Delta_{CH_4} = (-1)(20) + (-1)(10) = -30 \text{ lb-mol/hr} \]
\[ \Delta_{O_2} = (-3/2)(20) + (-2)(10) = -50 \text{ lb-mol/hr} \]
\[ \Delta_{CO} = (1)(20) + (0)(10) = 20 \text{ lb-mol/hr} \]
\[ \Delta_{CO_2} = (0)(20) + (1)(10) = 10 \text{ lb-mol/hr} \]
\[ \Delta_{H_2O} = (2)(20) + (2)(10) = 60 \text{ lb-mol/hr} \]
\[ \Delta_{N_2} = (0)(20) + (0)(10) = 0 \text{ lb-mol/hr} \]

Note: For a reactor to operate at these reaction rates, the feed will have to contain at least 30 lb-mol/hr of CH\(_4\) and 50 lb-mol/hr of O\(_2\). If this is not the case, the reactant that is in short supply is termed the limiting reactant. For instance, suppose that the feed contains 60 lb-mol/hr of O\(_2\) but only 15 lb-mol/hr of CH\(_4\). CH\(_4\) will then the limiting reactant. The best we can expect to do is 50% of the assumed reaction rates.
Often, the overall reactor performance is characterized in terms of *conversion* and *selectivity*. We pick a key component, usually either the more valuable reactant or the limiting reactant.

We define the *conversion* $C_k$ with respect to the key component $k$ as follows:

$$C_k = \frac{\text{Mols of key component converted by all reactions}}{\text{Total mols of key component in the reactor feed}}$$

For our reaction system above, suppose we feed 50 mols/hr of CH$_4$ to the reactor. The conversion of CH$_4$ is then

$$C_{\text{CH}_4} = \frac{30}{50} = 0.6 \text{ or } 60\%$$

We define the *selectivity* $S_{k,j}$ of the key component with respect to the $j$th reaction as follows:

$$S_{k,j} = \frac{\text{Mols of key component converted by reaction } j}{\text{Mols of key component converted by all reactions}}$$

For our reaction system above, the selectivity of CH$_4$ to CO (Reaction 1) is

$$S_{\text{CH}_4,1} = \frac{20}{30} = 0.667 \text{ or } 66.7\%,$$

and the selectivity to CO$_2$ (Reaction 2) is

$$S_{\text{CH}_4,2} = \frac{10}{30} = 0.333 \text{ or } 33.3\%.$$ 

Note that the selectivities over all reactions must sum to unity, i.e.,

$$(III - 2) \quad \sum_{j=1}^{nr} S_{j,k} = 1$$

One should be aware that there are other definitions of selectivity that are used in the literature. However, the one given above is the most commonly used and the only one that has the property expressed in Eqn. III-2.

Let $f_{k,in}$ = the feed rate of the key component to the reactor.

Then,

$$(III-3) \quad r_j = C_k \ S_{k,j} \ f_{k,in}, \quad j = 1, \ldots, nr.$$
The extents of reaction $i$ can be calculated using Eqn. II-1.

2. Separators

to any chemical process. A simple separator is shown in Figure III-2. It has one input stream, $\text{ST}_{\text{in}}$, and two output streams, $\text{ST}_{\text{1out}}$ and $\text{ST}_{\text{2out}}$. This separator can be used to represent flash drums, simple distillation columns and other separators that do not require a mass separating agent.

More complex separators are shown in Figure III-3. Separator A is typical of gas absorbers and liquid-liquid extractors where $\text{ST}_{\text{1in}}$ is the input stream which is to be separated and $\text{ST}_{\text{2in}}$ is the lean mass separating agent. $\text{ST}_{\text{1out}}$ corresponds to $\text{ST}_{\text{1in}}$ from which the components of interest have been removed. $\text{ST}_{\text{2out}}$ is a mass separating agent enriched with the components of interest that were to be separated from $\text{ST}_{\text{1in}}$.

Separator B is typical of a complex distillation column with side stream ($\text{ST}_{\text{2out}}$) as well as the distillate or overhead ($\text{ST}_{\text{2out}}$) and the bottoms ($\text{ST}_{\text{3out}}$).

There are two indices of how well a separator does its job. The first is the fraction of a given component that is recovered from a specified feed stream. The second is the purity of one or more output streams from the separator.

The fractional recovery is important from an economic point of view. Purity specifications have to be met in order to satisfy the feed purity requirements of down-stream equipment or, if the output stream is a final product, the sales purity specifications.
Simple separators can be characterized at the simplest level in terms of a separation coefficient. This is defined in Chapter IV. Evaluation of equipment model parameters such as the separation coefficient is covered in Appendix B. Complex separators can be characterized using the basic material balance models as is described in Appendix C.

3. Mixers

A mixer is a device that brings together two or more input streams of different compositions and produces an

\[ f_{out,i} = \sum_{j=1}^{nin} f_{in,i,j} \]

Fig. III-3. Complex Separators

Fig. III-4. Mixer
output stream that is a uniform mixture of the input streams. A typical mixer is shown in Figure III-4. As will be seen in the next chapter, characterization of mixers from the standpoint of conservation of mass is quite straightforward.

4. Flow Splitters

A flow splitter divides a stream into two or more output streams, each having the composition of the feed stream. The sum of all of the stream flow rates leaving the splitter must equal the flow rate of the feed stream. A simple flow splitter is shown in Figure III-5.

![Flow Splitter Diagram]

\[
\begin{align*}
    f_{out\,i,1} &= P \, f_{in\,i} \\
    f_{out\,i,2} &= (1 - P) \, f_{in\,i}
\end{align*}
\]

*Figure III-5. Flow Splitter*
A. Unit Models -- General Considerations

Material balance calculations begin with the characterization of the individual unit operations by mathematical models. These are known as unit models or process blocks.

Consider the generalized process block shown in Figure IV-1. Here, \( \text{in1} \) and \( \text{in2} \) are the numbers or names of the input streams to the process block and \( \text{out1} \) and \( \text{out2} \) are the numbers or names of the output streams. A block can have more or less than the two input streams shown; the same is true of output streams.

Also, the quantities \( P_1, P_2, \ldots, P_m \) are a vector of parameters required to characterize the process block. For instance, if the block represents an isothermal flash, two parameters, namely the flash pressure and temperature, would have to be specified as part of the characterization of the block.

A process unit operation block can now be characterized as follows:

Let \( X_n \) = the stream characterization vector for stream \( n \).

Then

(IV-1a) \[ X_{\text{out1}} = G_{J,1}[X_{\text{in1}}, X_{\text{in2}}, \ldots, X_{\text{inn}}, P_1, P_2, \ldots, P_m] \]

(IV-1b) \[ X_{\text{out2}} = G_{J,2}[X_{\text{in1}}, X_{\text{in2}}, \ldots, X_{\text{inn}}, P_1, P_2, \ldots, P_m] \]

. . .

(IV-1c) \[ X_{\text{outn}} = G_{J,n}[X_{\text{in1}}, X_{\text{in2}}, \ldots, X_{\text{inn}}, P_1, P_2, \ldots, P_m] \]
In general, these models are nonlinear and difficult to solve without using a computer.

A. Linear Input-Output Models

For many purposes such as preliminary material balance calculations for scoping out a design, simple linear unit models are perfectly adequate. These allow the material balance to be done by manual calculations (or by a spreadsheet program). This direct participation in the calculations at the early stages is recommended since in general the engineer will develop more insight into the workings of the process than if the calculations are done at one remove by a process simulation program.

Four simple models are all that are needed in order to do linear material balances. Actually only two are needed. The remaining two are special cases of the others.

1. Mixer (MIX)

In this model two or more streams are added together to produce a single output stream that is a mixture of all the input streams (See Figure III-4).

A mass balance on the ith component gives the equation describing the mixer, i.e.,

\[ f_{out,i} = \sum_{j=1}^{n} f_{in,i,j} \]

Note that no parameters are required to characterize a mixer. This is not the case for any of the other equipment models.

2. Reactor (REACT)

A Reactor takes a feed stream, and by chemical reactions, converts some into other components (See Figure III-1).

A mass balance on the ith component again gives the performance equation for the reactor, i.e.,

\[ f_{i, out} = f_{i, in} + i \]

where \( i \) = the extent of reaction of component \( i \), i.e., the net number of mols of component \( i \) produced by reaction.

Note: \( i \) will be negative for reactants, positive for products.
Note also that REACT is a special case of MIX where \(i\), can be considered the flow rate of component \(i\) in the second input stream to MIX.

The procedure for evaluating the \(\Delta_i\) given conversion and selectivity information is discussed in Section II. Or the \(\Delta_i\) may be given as constant values based on a specified production rate and the reaction stoichiometry. If a mathematical model for the reaction kinetics is available and the reactor type has been chosen, the \(\Delta_i\) can be estimated from a separate reactor calculation.

### 3. Separator (SEPAR)

A Separator is used to model process units in which each component in the feed is separated into two output streams (See Figure III-2).

The mass balance equations describing the performance of the Separator for the \(i\)th component are:

\[
\begin{align*}
(\text{IV-4a}) \quad f_{i,\text{out}1} &= s_i f_{i,\text{in}} \\
(\text{IV-4b}) \quad f_{i,\text{out}2} &= (1 - s_i) f_{i,\text{in}}
\end{align*}
\]

where \(s_i\) = the separation coefficient for component \(i\).

Note that conservation of mass dictates that \(0 \leq s_i \leq 1\).

As with the \(\Delta_i\) for REACT, the \(s_i\) for SEPAR must be known or estimated by other means. For conceptual design material balances for which the separation equipment generally has not yet been selected, let alone designed, one will generally assume reasonable values, say 99% recovery of one key component in the overhead (ST\(_{1\text{out}}\)) and a similar recovery of the other key component in the bottoms (ST\(_{2\text{out}}\)).

Complex separators, such as those shown in Figure III-3, can be modeled by a combination of the models for MIX and SEPAR.

### 4. Flow Splitter (SPLIT)

In many processes, a stream is split into two smaller streams, each having the same composition as the input stream (See Figure III-5).

The governing equation for the Stream Splitter is an overall or total mass balance, i.e.,
The same relationship holds for each component. So,

\[(IV-6a) \quad f_{i,\text{out1}} = S \ f_{i,\text{in}} \quad \text{and} \quad (IV-6b) \quad f_{i,\text{out2}} = (1 - S) \ f_{i,\text{in}}\]

Note that SPLIT is a special case of SEPAR for which \(s_i = S\) for all \(i\). Also, \(0 \leq S \leq 1\). A flow splitter having more than two output streams can be written along similar lines.

The major difference between SEPAR and SPLIT is that the \(s_i\) are dictated by physical considerations such as relative volatilities and how the equipment is operated. However, \(S\) is can be assigned any value between 0 and 1.

**B. Rigorous Models**

The models described in the previous have two advantages. They are both simple and linear. Thus they are well suited to calculating the material balances for entire processes. However, beyond conserving mass, these models are not very realistic. Their model parameters must be known from other sources. This is discussed in Appendix B.

This presents a problem in doing accurate flowsheet material balances. In order to get the model parameters for the linear material balance calculations, we must do separate rigorous calculations for the individual items of equipment. To do this we must know the feed streams to each item of equipment for which we must do the flowsheet material balances. Thus we have a situation in which we must assume values of all of the parameters, do the flowsheet material balances using the linear models, then evaluate the parameters from the rigorous models for the individual items of equipment. If the assumed and calculated values of the parameters do not agree within some reasonable tolerance, we must repeat the procedure. Indeed, we may have to do it many times. Clearly, there should be a better way.

The better way is to use rigorous equipment models directly in the flowsheet material balance calculations. Since most rigorous models are nonlinear and difficult to solve in their own, this approach is not amenable to hand calculations. It is possible with a spreadsheet but considerable effort, skill, and time are required.

The way that has been adopted for doing rigorous flowsheet calculations is to use a steady-state flowsheet simulation program. Solution of the flowsheet materials using rigorous equipment models is discussed in the next section. A brief introduction to commercially available programs is given in Section X.

**V. STEADY-STATE MATERIAL BALANCE CALCULATIONS**
There are a number of techniques that have been developed for the solution of steady-state flowsheet performance equations. In general, this is an exercise in the numerical solution of a set of algebraic (generally nonlinear) equations for which there are many algorithms and computer codes available. One approach is to write out all the equations, specify enough parameters so that the number of unknown variables equals the number of equations, and use the equation solver of choice. Indeed, this is the approach taken in many of the texts on material and energy balances. There is nothing wrong with it. However, it tends to obscure the underlying physical significance of the problem, particularly where recycles are involved. Instead we will look at some of the techniques that have been developed specifically for solving the flowsheeting problem.

A. Sequential Modular

One technique for solving the material balances for an entire process (although not the only one) is called Sequential Modular. In this technique the material balances for a entire process are solved one module (process block) at a time.

Let us first consider the process shown schematically in Figure V-1. There are three process operations or process blocks. The exact nature of each is not important at the moment. However, it is assumed that block equations (Eqns. IV-1a, IV-1b, ..., IV-1c) can be solved for each block in the process. In other words, if all of the input stream vectors and the parameter vector are known, then the output stream vectors for the block can be computed via a well defined procedure. (For the linear models of Eqns. IV-2 through IV-6, the computations are simple and direct. For the nonlinear models used in more realistic block characterizations, the computational procedure may require a trial-and-error or iterative algorithm.)

So, the ground rule for direct sequential modular material balance calculations (a.k.a. process simulation), the output streams can be calculated if the input streams and the block parameters are known.  

*Figure V-1. Sequential Process Flow Diagram*
Thus, in the three-block process shown, one can start by calculating Block A to determine Streams 3 and 4. Then Block B can be calculated to give Streams 5 and 6. Finally Block C can be calculated to give Streams 7 and 8.

Now let us consider a second process, one with recycle, as shown in Figure V-2. If the calculations are to be started at Block A, there is a problem. Stream 2 is not known since it is an output stream from Block B that has not been calculated yet. Suppose we decide to start with Block B instead. Again there is a problem; Streams 3 and 4 are unknown. A similar problem occurs if we attempt to start with Block C.

So how can we possibly calculate this process? Only by agreeing to guess values for the unknown input streams to each block in the process. Suppose now we start with Block A. Stream 2 must be guessed. To calculate Block B another stream, Stream 4, must be guessed. Block 5 can be calculated without having to guess any further streams.

Once all the blocks have been calculated, we will have computed values for all the streams we originally guessed. If the computed values agree with the guessed values within some acceptable tolerance, then the material balance for the process has been solved. If not, the whole procedure has to be repeated with new guesses. One strategy is to use the previously computed values for the next round of guesses.

This technique for solving the overall flow sheet material balance problem is known as the sequential modular approach. We calculate each unit operations block or module in the process sequence, providing initial guesses of unknown recycle streams where necessary. New values of the guessed (or tear) streams are produced as a result of each pass through the process sequence calculations. Methods for doing so are discussed in Section VII of these notes. When the differences between successive guessed values become sufficiently small, the procedure is considered to be converged. The conditions under which it converges are Section VIII. We will see that because of the conservation of mass, convergence is guaranteed for linear flowsheet models and strongly favored for nonlinear models.

The large majority of commercially available steady-state process simulators use the sequential modular approach.
B. Simultaneous

The sequential modular approach can generally be made to converge, even for difficult problems. However, it tends to be inefficient. Made of the unit operations models have internal iterative procedures just to solve for their output streams as functions of their input streams and operating parameters. Embed these iterative calculations within the sequential modular flowsheet calculations and one has a massive loops-within-loops calculation with the potential to be very inefficient. So, why not solve all of the equations simultaneously?

As we will see, this procedure is straightforward if all of the equations are linear. If they are not, an appropriate algorithm such as Newton-Raphson must be employed to solve large sets of nonlinear equations. This approach has been taken in several simulators developed in academia. SPEEDUP, developed at Imperial College, and ASCEND, developed at Carnegie-Mellon, are two of the more advanced of this type of simulator. SPEEDUP is currently available commercially through Aspen Technology, Inc.

It is not the intent of these notes to go into the pros and cons of the simultaneous approach versus the sequential modular. Suffice it to say that neither approach is without its drawbacks and difficulties. We note, however, that the sequential modular approach has been much widely used in commercial simulators than the simultaneous. And it tends to be fairly robust for reasons that are discussed in Section VIII.

C. Design Specifications

The calculations discussed so far are, in process control terminology, for processes operated in open loop. All the input streams and block model parameters are specified and all of the block output streams are then calculated. We have no way of knowing beforehand what the values of the output stream vectors will be.

Usually, the specification of the performance that the process must achieve will involve selected variables in the output stream vectors. The production rate, i.e., the flow rate of the product stream must meet the capacity specification. This stream must also meet the product purity specifications. The composition of streams being discharged to the environmental must meet emission specifications. Many other specifications such as reactor temperature and pH, flash drum vapor flow rates, and fractional recoveries in separators must be met. This can only be done by adjusting feed stream flow rates and block model operating parameters. In some process simulators, these are known as design specifications. In fact, they have the form of feedback control loops.

There are many techniques for incorporating design specifications into the flowsheet calculations. All commercially available flowsheet simulators provide the means to do so. In sequential modular simulators, the design specifications are handled as control loops around the open loop simulation, which adjust selected parameters to satisfy the design specifications. One
of the advantages of simulators using the simultaneous approach is that the design specifications can be added directly to the other equations being solved.

D. Optimization

Quite often one is not just interested in a solution to a flowsheet material balance problem but one that is best in some sense, usually economic. Finding such a solution by adjusting selected input and block model parameters is known as optimization. Most commercially available simulators have optimization capability. Many spreadsheets also have some optimization capability such as a linear programming solver.

Optimization is beyond the scope of these notes. We will, however, look at a specific type of optimization that arises in blending problems. The optimization technique we will use is linear programming.

E. Ad Hoc Methods

We term the computational method employed as ad hoc when one attempts to solve a flowsheet material balance by starting with design specifications and working backwards through the various block models and even the entire process. For flowsheets of any complexity, this a difficult approach since flowsheet calculations tend to be quite stable and well-behaved if one calculates block output streams from block input streams but notoriously unstable if one attempts to do the reverse.

Another characteristic of ad hoc methods is the use of overall material balances around two or more items of equipment, either on a component or total flow rate basis. The use of overall material balances is to be avoided. Use component material balances around individual items of equipment. This is the rule followed in Section IV of these notes.

For simple flowsheets, particularly when one is just interested in the input-output structure, ad hoc methods can be used to estimate raw material requirements based on reactor selectivities and separator efficiencies. The problem is that each material balance solution is a special case. Change the form of a design specification and the entire procedure must be revised.

One is advised to use the linear material balance approach, at least initially, since it is straightforward in its application to almost any problem. If the calculations are done using a spreadsheet, then adjusting inputs and parameters to meet design specifications can be done by trial-and-error if there are not too many. The inclusion of design specs is discussed in Section VII-C.

VI. RECYCLE STREAMS AND TEAR SETS
In the previous section, the sequential modular method of solving process material balance was described, the first step of which was to choose a set of streams which, if their values are known, allow us to calculate the process material balance unit by unit. It is presumed that for each unit the input streams and operating parameters are known and that the unit calculations involve calculating the output streams from that unit. If the process contains no recycle streams, then the choice is obvious, namely, the input streams to the process that originate from outside the process. These are often referred to as the feed streams to the process. For example, in Fig. VI-1, there is only one such stream, namely, Stream 1.

Figure VI-1. Process Flow Diagram for Example #1.

However, if the process contains recycle streams, the choice of a set of streams with which to start the calculations is not so simple. Just knowing the feed streams is not sufficient. Referring again to Fig. VI-1, suppose we want to start the unit calculation sequence with the mixer M-1. Stream 1 is a feed stream and is presumed known. But we also need to know Streams 3 and 8. But Stream 3 is an output stream from the separator S-1 while Stream 8 is an output of S-3. At the outset these are not known. What to do? We could, as previously described, guess values for these two streams. Then we could calculate M-1, getting a value for Stream 2 as a result. This would then allow us to calculate S-1 getting Streams 3 and 4 as a result. Next we would like to calculate M-2 but we do not know Stream 6. Proceeding as we did for M-1, we could guess Stream 6 and thereby calculate S-2 and S-3 in turn as well as the remaining streams for the process. Does this complete out material balance calculations? The answer probably is no. Unless we were very clever (or very lucky), the values we guessed for Streams 3, 8 and 6 will differ from those we subsequently calculated. If any of these differ by more than an acceptable amount, we will have to guess new values of these streams and repeat the calculations. This procedure will have to be repeated as many times as is necessary to achieve an acceptable agreement between the guessed and calculated values of the three streams.

But this is not the subject of this section of these notes. Our topic is more limited, namely, how to chose the a set of streams and the associated sequence of unit models to begin the
calculations. Now we could do this by just starting at the upstream end of the process and guessing as many streams as we need to get the calculations started. But, as we will see, this may require guessing more streams than are absolutely necessary which, in turn, may cause the calculations to be more difficult or inefficient than would otherwise be the case. So, what is presented in this section is a simple technique for determining all sets of streams that minimize the number to be guessed. Further, this technique will show us what the recycle structure of the process is, something that is important not only for the calculations but also for the behavior and operability of the process.

The procedure of choosing streams to guess is called tearing or cutting. The process flow diagram can be considered as a directed graph where each process block is a node and the nodes are connected by streams, each of which has direction from one node toward another. The terminology "cutting" or "tearing" comes from graph theory (See Mah [1990] for more details).

The question is, for a given process graph or diagram, what and how many streams have to be cut or torn so that the process can be calculated sequentially? Each set of streams which allow this to be done is called a cut or tear set. For each choice of sequence, there will be a tear set. For some choices the tear set will be smaller than for others. Those tear sets which require the fewest number of streams to be torn are called minimal tear sets.

There are several ways to determine the minimal tears sets for a process graph. The first is by determining the tear set for each possible choice of sequence and then selecting the minimal tear sets from among all the tear sets. This is what we did above. However, since the number of sequences for N process units is N!, this method becomes impractical for processes having more than a few process units.

A second method one which much less time-consuming, is based on the node-incidence matrix. The method proceeds in four steps. The first step is to construct the matrix. The second is to determine all of the closed cycles within the graph that the matrix represents. The third is to identify the minimal tear sets and the fourth is to list the computational sequences corresponding to each minimal tear set.

A. Construction of the Node Incidence Matrix

The node-incidence matrix contains a row for each process block and a column for each process stream that connects two process blocks. Feed streams to the process from the outside and product streams to the outside are not included.

As an example, let us construct the node-incidence matrix for the process shown in Figure VI-1. For each stream, enter a 0 in the row for the process block from which the stream comes. Enter a 1 in the row for the process block at which the stream terminates. (Some authors use -1 instead of 0. Since no numerical computations are involved, the basis for choice is clarity.)
The node-incidence matrix for our example is:

<table>
<thead>
<tr>
<th>Block</th>
<th>Streams:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 3 4 5 6 7 8</td>
</tr>
<tr>
<td>M-1</td>
<td>0 1 0 0 0 0 0</td>
</tr>
<tr>
<td>S-1</td>
<td>1 0 0 0 0 0 0</td>
</tr>
<tr>
<td>M-2</td>
<td>1 0 0 0 0 0 0</td>
</tr>
<tr>
<td>S-2</td>
<td>1 0 0 0 0 0 0</td>
</tr>
<tr>
<td>S-3</td>
<td>1 0 0 0 0 0 0</td>
</tr>
</tbody>
</table>

Note that Streams 1 and 9 have not been included in the node-incidence matrix. Since these two streams either enter or leave the process flow diagram, they cannot be part of recycle loop. For a stream to be a candidate for a recycle loop, it must both originate and terminate within the process flow diagram.

B. Determination of all Closed Cycles

In the second step, each cyclical path through the graph is determined. First, determine all the cycles formed by pairs of streams (2-loops). Start with the first stream, in this case Stream 2. It originates at M-1, as indicated by the 0, and terminates at S-1, as indicated by the 1. Now, try to find a stream originating at S-1 that terminates at M-1. In this case there is one, Stream 3. Repeat the procedure for each stream, ignoring duplicate cycles. Two 2-loopss are found, namely (2,3) and (5,6).

Next, repeat the process, this time looking for three-stream cycles (3-loops). There are none. Proceed to look for four-stream cycles (4-loops). Again, there are none. Go on to look for 5-loops. Here, there is one, namely (2,4,5,7,8). This terminates our search since there can be no cycles having more than five streams since there are only five nodes (blocks) in the process graph.

C. Identification of all Minimal Tear Sets

In the third step, examine all the cycles from Step B to identify those sets of streams that qualify as tear sets. A tear set is a set of streams such that at least one member of this set is also a member of at least one cycle (or loop). Those tear sets that contain the smallest number of streams are the minimal tear sets.

For our example, there are three loops, namely, (2,3), (5,6) and (2,4,5,7,8). There are many candidate tear sets. The set [2,5] is a tear set in that either Stream 2 or Stream 5 is a member of all three loops. So are the sets [2,6] and [3,5]. There are no more tear sets of only two streams. It makes no sense to look for tear sets containing three streams (such as [3,6,7] for instance) since we are only interested in minimal tears sets. So, the question remains are there any tear sets containing only one stream? The answer is clearly no. So, as a result we have identified three minimal tear sets.
D. Listing of Computational Sequences

If we are to calculate the process material balance based on guessed values for a given minimal tear set, we must determine what computational sequences can be used, i.e., what sequences allow us to compute a given process block for which all of the input streams are known. This means that each input stream must be (1) an external feed stream to the process, (2) a tear stream for which a guessed value has been made, or (3) the output stream from a process block that has already been calculated.

A computational sequence for the tear set [2,5] is [S-1, S-2, S-3, M-1, M-2]. There are others, all of which are minor variations on this one. For instance we could calculate S-2 before S-1. We must always calculate S-3 before we can calculate M-1 but we can calculate M-2 any time after we have calculated S-1 and S-2. The question is whether or not one sequence is better than the others. The answer in general is no unless the initial guess of one or more tear streams happens to be zero. If the input streams to a process block are all zero, then the calculations for that block are meaningless and must be bypassed until a later iteration has produced a non-zero value for at least one input stream.

We can similarly determine the computational sequences for the other minimal tear sets. The final question to be considered concerns the choice tear set. Is one better than another? If we have some basis for making reasonable guesses of some recycle streams but not others, then we should chose the tear for which we can make the best guesses. Otherwise, there is not much of a basis for choosing one over another.

After all this, one might ask why do we need to construct a node-incidence matrix? Why can’t we just identify the various cycles by inspection of the process flow diagram? The answer is that, in principle, one can. However, for more complex processes involving more process blocks and streams than the simple examples contained herein, determining all the cycles is more difficult and it is easy to overlook some. The use of the node-incidence matrix makes the procedure somewhat more straightforward, but does not guarantee a complete enumeration either. (There are computer algorithms for doing this which, of course, can be expected to identify all the cycles and the minimal tear sets.) But, for anything but the simplest processes, use of the node-incidence matrix is recommended.

For most processes, there is a rule of thumb that will allow one to identify at least one minimal tear set within going through the entire node-incidence procedure. Choose as a tear set those streams that are the outputs of all mixers that have one or more recycle streams as inputs. For Example #1, these would be Streams 2 and 5 which are one of the three minimal tear sets we identified using the node-incidence method.

E. Further Examples
Let us look at two further examples, each of which will tell us something more about the recycle structure of processes. Example #2 (shown in Fig. VI-2) looks to be very similar to Example #1 but is distinctly different in one important respect. Note that Stream #8 recycles back to mixer M-2 rather than mixer M-1. We can determine all the cycles by inspection. They are (2,3), (5,6) [the same as in Example #1] and (5,7,8). Now, however, there are only two minimal tear sets, namely, [2,5] and [3,5]. The important difference between this example and the previous one is in the structure of the loops. In Example #1 both 2-loops contained streams which were common to the 5-loop, namely, Streams 2 and 5. However, in Example #2, this is not the case. The 2-loop (2,3) can be torn by either Stream 2 or Stream 3 alone while both the 2-loop (5,6) and the 3-loop (5,7,8) can be torn by Stream 5 alone. Put another way, as is obvious from the diagram, there are two separate recycle structures in Example #2. This is not the case for Example #1. In Example #2 we can solve the sequence [M-1,S-1] as though the rest of the process is not there. Then, having a value for Stream 4, we can solve the sequence [M-2,S-2, S-3] as a separate problem. Indeed, this is exactly how a process flowsheeting program such as ASPEN would do it. The same is not true of Example #1; the entire sequence must be solved simultaneously. Thus, we must be careful to look for separate subproblems so as to minimize the computational work involved.

Our third example (Fig. VI-3) is a four-tray gas absorber that is to be solved as a process flow sheet problem. (There are more efficient specialized algorithms for gas absorbers, but the purpose of this example is to illustrate the recycle structure of multi-stage countercurrent separators.)
Figure VI-3. Example #3

The node-incidence matrix is:

<table>
<thead>
<tr>
<th>Block</th>
<th>Streams:</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>0 1</td>
<td>0</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-2</td>
<td>1 0 0 1</td>
<td></td>
<td></td>
<td>0</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-3</td>
<td>1 0 0 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>S-4</td>
<td>1 0 0 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The cycles are:
2-loops: (3,4), (5,6), and (7,8)
3-loops: (3,5,6,4) and (5,7,8,6)
4-loops: (3,5,7,8,6,4)

There are many minimal tear sets: [3,5,7], [4,6,8], [3,6,8], [4,6,8], and [3,5,8]. The computational sequence for [3,5,7] is [S-4, S-3, S-2, S-1] (top down) while that for [4,6,8] is [S-1, S-2, S-3, S-4] (bottom up). The computational sequences for the other tear sets are mixed.

The important point to be made here is that multi-staged separator is highly recycled if we look at it from the standpoint of a process consisting of a number of separation stages arranged in a countercurrent sequence. Looked at from the standpoint of a single piece of equipment, the recycle structure does not show. It is internal to that piece of equipment. If we use one of the many algorithms for solving the steady-state problem for distillation or gas absorption, then the internal recycle structure does not enter into the solution of a process flow sheet for which the separator is merely one process block. But the internal recycle structure does have important consequences, particularly when it comes to the dynamics of both the separator and the process.
VII. SOLUTION OF LINEAR MATERIAL BALANCE MODELS

Revised October 11, 1999

In this section we consider the solution of steady-state process material balances when the equations are linear. First we look at the solution of performance material balances, i.e., those for which the parameters for each equipment model and the external input streams to the process are all specified. In the terminology of the control engineer, this is the solution of the open-loop problem.

It is often the case however, that we want some internal stream variable, say the mol fraction of a given component or a total flow rate, to achieve a specified value. This is known as a design specification, or design spec for short. In the terminology of the control engineer, this is the solution of the closed-loop or control problem.

Achieving a design spec is accomplished by varying either one of the model parameters or the flow rate of one of the external input streams. The problem that arises from adding a design spec to a process material balance may or may not be linear. Fortunately, the most commonly imposed design specs generally lead to linear problems. Even if this is not the case, clever use of a spreadsheet can still allow us to solve a material balance with a limited number design specs in an efficient manner.

A. Use of Linear Equation Solvers

The material balance for any process can be modeled, albeit at very simple level, by the unit models MIX, REACT, SEPAR, and SPLIT. Further, if the model parameters are specified, each model is linear so that the overall system of equations will be linear also. Since the methods for solving sets of linear algebraic equations, even large sets, are well developed, the use of these four models to perform process material balances has obvious advantages. The disadvantage is that the engineer must evaluate all of the parameter sets before being able to do the material balance. This is not a serious problem once the engineer has some idea of what performance is expected of each process unit.

The simple form of these equations confers another advantage. Each equation for the ith component involves only the ith component. Thus, once the parameters for the ith component are known, its material balance can be solved independently of all the other components. This reduces the material balance problem in NS streams and NC components from one large NS x NC set of equations to NC sets, each of dimension NS. For instance if a process has 6 components and 21 streams, we have only to solve 21 equations 6 times rather than 6 x 21 = 126 equations at one time.

B. Reduction to the Tear Set Variables
A further reduction in the size of the problem can be accomplished by exploiting the structure of the process as follows:

a. Enumerate the tear sets for the flowsheet. Choose a minimal tear set that is convenient. A minimal tear set that includes all the reactor feed streams is generally a good choice.

b. Write out all the equations for a typical component, using the appropriate model for each process unit. Each equation will have the form:

\[(VII-1a)\quad f_{i,\text{out}} = \alpha_{i,1} f_{i,\text{in1}} + \alpha_{i,2} f_{i,\text{in2}}\]

\[(VII-1b)\quad f_{i,\text{out2}} = \alpha_{i,3} f_{i,\text{in1}} + \alpha_{i,4} f_{i,\text{in2}}\]

Note: A reactor is really a Stream Add where the component flows in the second stream are the \(\alpha_i\) and \(\alpha_{i,2} = 1\).

For each component there will be one equation that is the output of a block. Some of these streams are outputs from the process, i.e., are inputs to other blocks. The equations for these streams can be set aside until the last step.

c. Substitute for all of the non-cut set stream variables. Of the remaining equations, there will be one for each of the cut set streams which its \(f_{i,n}\) appears on the left-hand side of the = sign. Start with this set of equations, as many as there are cut set streams. Substitute from the remaining equations for all of the non-cut set flow rates. Continue back substituting until all of the flow rate variables which are neither cut set or input variables have been eliminated.

d. Solve the remaining equations for the tear set variables one component at a time. If there are only one or two tear, this can be done analytically. If there are more, it can be done numerically by Gaussian elimination or by using a linear equation solver. (Most of the flowsheets we will encounter will have only a few streams in their minimal tear sets.)

e. Compute all of the other stream flow rates by direct of the process sequence that corresponds to the cut set. The process output streams that were set aside in Step b should also be evaluated at this point.

Suggestions for avoiding pitfalls and mistakes.

1. Convert all problem data to molar quantities before doing anything else. Remember:

\[(VII-2)\quad F_{\text{mix}} = W_{\text{mix}} / MW_{\text{avg}}\]

where \(W_{\text{mix}}\) = the flow rate of a mixture in lb/hr (kg/hr)

-46-
\[ F_{\text{mix}} = \text{the flow rate of that mixture in lb-mol/hr} \]
\[ = \text{the flow rate of that mixture in kg-mol/hr} \]

and \[ MW_{\text{avg}} = \text{the average molecular weight of the stream.} \]

(VII-3) \[ MW_{\text{avg}} = \sum y_i \cdot MW_i \]

where \[ y_i = \text{the mol fraction of component } i, \text{ and} \]
\[ MW_i = \text{the molecular weight of component } i. \]

2. Do all material balance calculations in mols (unless, perhaps, the system is a single non-reacting component).

3. In writing out the equations in Step b and doing the reduction to cut set variables in Step c, do not substitute numbers for the parameters (coefficients in the equations). Do this in Step d. It is easier to check for mistakes and you can reuse the equations for all the components without having to repeat Steps b and c.

Example

The ammonia loop shown in Figure 2 will be used as an example. There is only a single recycle loop so let us choose Stream 3 as the tear stream. Since we are only interested in the material balance in this example, items of equipment which do not affect either the flowrate or composition of their output streams can be ignored. This includes the Feed Compressor C-1, the Recycle Compressor C-2, and the Ammonia Condenser E-1. Their output streams, ST2, ST10, and ST5 can be dropped from the stream list.

The process is specified as follows:

(1) The Synthesis Gas feed (ST1) provides 750 lb-mol/hr of H2, 250 of N2, and 10 of Argon.

(2) The Synthesis Converter R-1 operates at 25% conversion per pass of the N2 in its feed (ST3).

(3) The Ammonia Condenser condenses 99% of the NH3 in Synthesis Converter effluent (ST4) which is removed as liquid in the Ammonia KO Drum F-1. The other gases are slightly soluble in the liquid ammonia resulting in a 0.1% removal of H2 and 0.2% of both N2 and Argon.

(4) 5% of Stream 6 is purged.

We can write the linear material balance equations for the Synthesis Loop as follows:
Feed Mixer M-1

(E-1) \( f_{i,3} = f_{i,1} + f_{i,9} \)

Synthesis Converter R-1

(E-2) \( f_{i,4} = f_{i,3} + \Delta_i \)

Ammonia KO Drum F-1

(E-3) \( f_{i,6} = s_i f_{i,4} \)
\( f_{i,7} = (1 - s_i)f_{i,4} \)

Argon Purge

(E-4) \( f_{i,8} = P f_{i,6} \)
(E-5) \( f_{i,9} = (1 - P)f_{i,6} \)

The Synthesis Converter performance is given in terms of the conversion of \( N_2, C_{N_2} \). Thus

(E-6) \( \Delta_{N_2} = - C_{N_2} f_{N_2,3} \)

We can now solve for \( f_{N_2,3} \) by back-substituting Eqns. E-5, E-3, E-2, and E-6 into Eqn. E-1 as follows:

(E-7) \( f_{N_2,3} = f_{N_2,1} + (1 - P)f_{N_2,6} \)
\( = f_{N_2,1} + (1 - P)S_{N_2}f_{N_2,4} \)
\( = f_{N_2,1} + (1 - P)S_{N_2}(f_{N_2,3} + \Delta_i) \)
\( = f_{N_2,1} + (1 - P)S_{N_2}(1 - C_{N_2})f_{N_2,3} \)

Solving for \( f_{N_2,3} \) gives

(E-8) \( f_{N_2,3} = f_{N_2,1}/[1 - (1 - P)S_{N_2}(1 - C_{N_2})] \)

We can now calculate \( \Delta_{N_2} \) from Eqn. E-6. Knowing \( N_2 \), we can, by the reaction stoichiometry, calculate the other extents of reaction as follows:

(E-9) \( \Delta_{H_2} = 3 \Delta_{N_2} \),

-48-
\[ \Delta_{\text{NH}_3} = -2 \Delta_{\text{N}_2}, \text{ and, of course,} \\
\Delta_{\text{Ar}} = 0. \]

Knowing the extents of reaction for the non-key components, we can now solve for their component molar flow rates in the tear stream, again by back substitution. This gives

(E-10) \[ f_{i,3} = [f_{i,1} + (1 - P)s_i\Delta_i]/[1 - (1 - P)s_i], i \neq \text{N}_2. \]

Once the tear stream component flow rates are known, the flow rates for the remaining streams can be calculated directly starting with the Synthesis Converter. These calculations can be done by spreadsheet as shown in the following summary:

<table>
<thead>
<tr>
<th>Stream</th>
<th>Summary:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp</td>
<td>ST1</td>
</tr>
<tr>
<td>lb-mol/hr:</td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>750.00</td>
</tr>
<tr>
<td>N2</td>
<td>250.00</td>
</tr>
<tr>
<td>Ar</td>
<td>10.00</td>
</tr>
<tr>
<td>NH3</td>
<td>4.15</td>
</tr>
<tr>
<td>Total mol/hr</td>
<td>1010.00</td>
</tr>
<tr>
<td>MWavg</td>
<td>8.83</td>
</tr>
<tr>
<td>Total lb/hr</td>
<td>8914.98</td>
</tr>
</tbody>
</table>

We note in passing that this stream summary was produced using a spreadsheet and imported directly into this document. The details are given in the appendix. Also, the stream summary shown in Chapter III was produced using the same spreadsheet program. The only differences are that it includes more information and that the purge fraction was adjusted so that the Argon concentration in the reactor feed would be 10%. This is an example of a design specification, the subject of the next section.

C. Incorporation of Design Specifications

A performance material balance such that given in the example above allows us to calculate the component molar flow rates \( f_{i,j} \) of all of the output streams from all of the equipment blocks. However, we may want one or more of the stream variables to meet a performance (or design) specification.

For instance, if we look at Stream 3 in the stream summary above, we can calculate that the mol fraction of argon in the stream is approximately 5.9%. On the other hand, if we look at the purge stream, we see that we are losing 99.06 mol/hr of hydrogen. Since this amounts to
13.2% of the hydrogen fed to the synthesis loop, it represents a substantial yield loss. Suppose we can operate the loop with up to 10% argon in the reactor feed. This means that we can reduce the purge fraction from its nominal value of 5%, thereby reducing the amount of valuable hydrogen that is lost in the purge. The question is how to determine the purge fraction that will just meet the design spec of 10% argon in the reactor feed.

The most typical material balance design specs are:

1) Total flow rate of a stream

\[ F_j = \sum_{i=1}^{nc} f_{ij} = \Phi_{Fj} \]

where \( \Phi_{Fj} \) = the value for the flow rate design spec for the \( j \)th stream.

2) Mol fraction of a component in a stream

\[ f_{i,j} / F_j = \Phi_{Mij} \]

where \( \Phi_{Mij} \) = the value for the mol fraction design spec for the \( i \)th component in the \( j \)th stream, and

3) Molar ratio of component a to component b

\[ f_{a,j} / f_{b,j} = \Phi_{Rabj} \]

To meet a design spec we must have a process parameter available which can be varied. Typical parameters are

1) Purge fraction
2) Flow split fraction
3) Total fresh feed flow rate, i.e., the flow rate of stream which originates outside battery limits (OSBL).
4) Reactor conversion, or
5) A separator recovery parameter.

Let us now consider a simple example that leads to a linear solution for a design spec. Consider the hypothetical process to make methanol (MeOH) via the partial oxidation of methane (CH4). The proposed process is shown in Figure VII-1.
Fresh CH4 (which contains 2% C2H6, an inert) is mixed with fresh O2 and recycle gas and fed to a reactor. The reaction chemistry is:

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_3\text{OH}
\]

The reactor is run at a conversion of 20% of the methane in the reactor feed. The reactor effluent is sent to a separator where all of the MeOH is removed but none of the other components. The overhead is recycled to the reactor after a purge is taken to maintain the C2H6 concentration at 10 mol%.

**Figure VII-1. Hypothetical Methanol Process**

Taking the reactor feed stream (Stream 3) as the tear stream and solving the linear material balance equations gives for CH4

\[
(E - 11) \quad f_{CH_4,3} = \frac{f_{CH_4,1}}{1 - (1 - P)(1 - C)}
\]

where \( P \) = the fraction purged to Stream 7 and
\( C \) = the fractional conversion across the reactor.

Keep in mind that we are assuming that the only component removed in the separator is MeOH. Thus, the separation coefficient \( s_i \) with respect to Stream 5 for all the other components is 1.0.

The tear stream solution for all the components other than CH4 and methanol (which is not recycled) is
Substituting Eqn. E-12 into E-13 and simplifying gives

$$\phi = \frac{f_{C_2H_6,3}}{F_3} = 0.1$$

where $F_3 = \sum_{i=1}^{nc} f_{i,3}$

This equation is linear in $P$ so its solution is straightforward. If the flow rate of Stream 1 (F1) is 100 mol/hr and that of Stream 2 is 50 mol/hr, then solving for $P$ gives $P = 0.02549$.

Unfortunately, not all design specs lead to linear equations for the associated model parameters. This is the case for the NH3 synthesis loop if we want to adjust its purge rate to keep the argon concentration in the reactor feed to 10%. This is because not all the $s_i$ are either 0 or 1.0. In this case it is easier to solve the problem using a spreadsheet. This was done by programming a cell to display the mol % of argon in the reactor feed and then adjusting the purge parameter until the spec is met. The following are the results that were obtained:

<table>
<thead>
<tr>
<th>$P$</th>
<th>Mol% Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>5.216</td>
</tr>
<tr>
<td>0.04</td>
<td>6.208</td>
</tr>
<tr>
<td>0.03</td>
<td>7.765</td>
</tr>
<tr>
<td>0.021525</td>
<td>10.000</td>
</tr>
<tr>
<td>0.02</td>
<td>10.562</td>
</tr>
</tbody>
</table>

Note that at the design spec purge rate, the yield is reduced to 6.29%.
In this section we look at some commonly used procedures for converging a flowsheet model using the sequential modular method of solution when some or all of the unit operations models are nonlinear. First we will look at the method direct iteration. This method is simple to use, highly reliable, and not sensitive to initial guesses of the tear streams. But, for tightly recycled processes it is quite inefficient. (By tightly recycled we mean processes for which the total flow rates of the tear streams are large compared to the fresh feed streams.)

The inefficiency of direct iteration was recognized early on and methods to accelerate it were developed. The best known of these is the method of Wegstein. Its convergence capabilities are explored in Part B of this section.

A. Convergence by Direct Iteration

As mentioned earlier the sequential modular method starts with an initial guess of the values of the tear stream vectors. The process is then calculated unit by unit in the sequence determined by the choice of tear streams. The result is a set of calculated values for the tear streams. If these do not agree with guessed values within a specified tolerance, a new set of values have to be guessed (or estimated) for the tear streams. If the previously calculated set are used as the new guesses, the procedure is referred to as direct iteration.

In order to learn something about the convergence characteristics of direct iteration as applied to flowsheets calculations, let us look at the simplest of all problems, that of the single-component, single-recycle process as shown in Figure VIII-1.

Stream 1 is mixed with Stream 3 in Mixer M-1 and sent to the Purge Splitter P-1 where it is separated into Streams 3 and 4. Stream 3 is obviously a recycle stream. Let us assume that the model for the Purge Splitter is nonlinear.

Fig. VIII-1. Purge Splitter Recycle Process
Let $X_i$ be the molar flow rate in Stream $i$ of a typical component present in this process. Then, the material balance equations for the process are:

For the Mixer M-1

(VIII-1) $X_2 = X_1 + X_3$

For the Purge Splitter P-1

(VIII-2) $X_3 = F[X_2, p]$, where $p$ is an operating parameter.

Now, let us solve Eqns. VII-1 and VII-2 iteratively. We start by assuming a value for $X_3$, call it $X_3(0)$ where $X_3(n)$ is the value of $X_3$ after $n$ iterations. Then,

$$X_2(1) = X_1 + X_3(0), \quad \text{and}$$

$$X_3(1) = F[X_2(1), p]$$

Let $E(n) = \text{the relative error in } X_3\text{ after the } n\text{th iteration. Then, if}$

$$E(1) = \frac{|X_3(1) - X_3(0)|}{X_3(1)} < \varepsilon$$

where $\varepsilon$ is a pre-assigned tolerance, the solution is finished. Otherwise, we must repeat the procedure, i.e.,

$$X_2(2) = X_1 + X_3(1), \quad \text{and}$$

$$X_3(2) = F[X_2(2), p]$$

If $E(2) < \varepsilon$, the solution is now finished. Otherwise, repeat the procedure until $E(n) < \varepsilon$ or $n > N_{\text{max}}$, where $N_{\text{max}}$ is the maximum number of iterations for which we are willing to continue the iterative procedure.

The question is, under what conditions does this procedure converge? The answer is, from numerical analysis (See Ostrowski, Chapter 4, or any other good text on numerical analysis), if $|dF/dX_3| < 1$, then the procedure will converge.

Let us examine this in a little more detail. Suppose $dF/dX_3 = 1-p = r$, where $p$ = the fraction of Stream 2 which is sent to Stream 4. Then, combining Eqns. VII-1 and VII-2 gives
(VIII-3) \[ X_2(n+1) = X_1 + r X_2(n) \]

If we start the iterative procedure with \( X_2(0) \), we have for the first few iterations

**Iteration 1:** \[ X_2(1) = X_1 + r X_2(0) \]

**Iteration 2:** \[ X_2(2) = X_1 + r [X_1 + r X_2(0)] = (1+r) X_1 + r^2 X_2(0) \]

**Iteration 3:** \[ X_2(3) = X_1 + r [(1+r)X_1 + r^2 X_2(0)] = (1+r+r^2) X_1 + r^3 X_2(0) \]

It can be shown that after \( n \) iterations,

(VIII-4) \[ X_2(n) = (1-r^{n+1})/(1-r) X_1 + r^n X_2(0) \]

Now, if an algorithm is to converge to a unique solution, the value of that solution should not depend on the initial assumed value \( X_2(0) \). For this to be the case,

(VIII-5) \[ \lim_{n \to \infty} r^n = 0 \]

This will only happen if \( r < 1 \), which is the condition for convergence of the nonlinear procedure. Also, if \( r < 1 \), the first term on the right hand side of Eqn. VII-4 becomes \( 1/(1-r) \), so the steady-state solution \( X_{2,ss} \) by iteration is

(VIII-6) \[ X_{2,ss} = 1/(1-r) X_1 \]

We get the same solution if we assume that \( X_2(n+1) = X_2(n) \) in Eqn. VII-3, which is reassuring. Of course, in the nonlinear case, we cannot solve directly for \( X_{2,ss} \). We can only estimate its value by the iteration.

We can make the following observations about the physical nature of the solution. First, \( r \) is the fraction of the component under consideration that is transferred from Stream 2 to Stream 3. If this component is a conserved quantity, then from physical considerations \( 0 < r < 1.0 \). In other words, if only conserved quantities are used in modeling the various unit operations in the process, then the input-output coefficients for all the process units must lie between 0 and 1.0. It can be shown that because of this, the direct iteration solution of a linear process always converges.
However, if in our simple example, $r \to 1.0$, the rate of convergence can be very slow. For instance, if $r = 0.9$, and we want $r^n < 0.0001$, 88 iterations will be required. If $r = 0.95$, 180 are necessary. Since values of $r = 0.9 - 0.95$ are not untypical in tightly recycled processes, it is obvious that convergence by direct iteration can require a lot of computer time for realistic process models.

Recycle has another effect on the process flowsheet other than making convergence slow. From Eqn. VII-6 we also see that it increases the internal stream flow rates by a factor of $1/(1-r)$ with respect to the feed streams to the process. This, in turn, will increase all the equipment sizes in the recycle loop for a fixed throughput.

In sequential modular simulation, the standard method for checking for convergence is to monitor the change from iteration to iteration of the tear set variables. For our simple example, the relative error $E_r$ is given by

\begin{equation}
E_r = \frac{|X_2(n+1) - X_2(n)|}{X_2(n+1)} \tag{VIII-7}
\end{equation}

However, a chemical process engineer is generally interested in how well the overall process material balance is converged. Let $E_o$ be the relative error in the overall material balance. For the process of Figure 10, it is given by

\begin{equation}
E_o = \frac{|X_4(n+1) - X_1|}{X_1} \tag{VIII-8}
\end{equation}

The question is, if $E_r = \delta$, what does $E_o =$? If the solution is close to convergence,

\begin{equation}
X_2(n+1) \approx \frac{1}{1-r} X_1 \tag{VIII-9}
\end{equation}

So,

\begin{equation}
E_r = (1-r) \frac{|X_2(n+1) - X_2(n)|}{X_1} \tag{VIII-10}
\end{equation}

Also,

\begin{equation}
E_o = \frac{|(1-r) X_2(n) - X_1|}{X_1} \tag{VIII-11}
\end{equation}

\begin{align*}
&= \frac{|X_2(n) - \{r X_2(n) + X_1\}|}{X_1} \\
&= \frac{|X_2(n) - X_2(n+1)|}{X_1}
\end{align*}

So,
The relative error in the overall material balance $E_o$ is a factor of $1/(1-r)$ larger than the relative error between iterations $E_r$. For instance, if $R = 0.9$, $E_o = 10 \times E_r$. It must be kept in mind that in tightly recycled processes, the relative error in the overall material balance can be an order of magnitude or more larger than the relative error from iteration to iteration $E_r$. It is $E_r$ that is the quantity usually monitored by the convergence checking routine in most simulation programs.

It is interesting to estimate how many iterations it will take to achieve convergence to a given tolerance. Suppose that for the system of Figure 11, we want to converge the simulation to a tolerance on $E_r$ of $0.0001$. The question is how many iterations will it take as a function of $r$? This obviously depends upon how close the initial guess of $X_2(0)$ is to the converged value. To keep things simple and straightforward, let us take this initial guess to be zero, i.e., $X_2(0) = 0$. Then, substituting Eqn. VIII-4 into Eqn. VIII-7 and solving for $n$ gives

$$(VIII-13) \quad n = \frac{\ln[\varepsilon/(1-r(1-\varepsilon))]}{\ln(r)} - 1$$

This is demonstrated numerically as follows:

<table>
<thead>
<tr>
<th>$r$</th>
<th>$n$</th>
<th>$E_o/E_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>5</td>
<td>1.25</td>
</tr>
<tr>
<td>0.5</td>
<td>12</td>
<td>2.0</td>
</tr>
<tr>
<td>0.7</td>
<td>22</td>
<td>3.33</td>
</tr>
<tr>
<td>0.9</td>
<td>65</td>
<td>10.0</td>
</tr>
<tr>
<td>0.95</td>
<td>121</td>
<td>20.0</td>
</tr>
<tr>
<td>0.99</td>
<td>459</td>
<td>100.0</td>
</tr>
</tbody>
</table>

We can see that the number of iterations required for a relative convergence to four significant figures grows quite rapidly as the system becomes more tightly recycled ($r \rightarrow 1.0$). Also, the error in the overall material balance $E_o$ increases substantially. If we want to converge the simulation to an overall material balance tolerance of $0.0001$, then it is easy to show that for $r = 0.99$, the number of iterations is 916 rather than 459, an increase of a factor of 2.0.

**B. Convergence Acceleration**

One can ask whether or not anything can be done to improve the rate of convergence of sequential modular simulations? The answer is yes. Instead of using the previously calculated value $X_2(n)$ for the $(n+1)$th iteration, let us develop a better estimate, call it $Y_2(n)$. A very simple strategy for doing this is

$$(VIII-14) \quad Y_2(n) = \alpha Y_2(n-1) + (1-\alpha) X_2(n)$$
Note that for $\alpha = 0$, this is equivalent to direct iteration and if $\alpha = 1$, no acceleration at all will take place. If $0 < \alpha < 1$, the effect is to damp the iterative procedure. For instance, if $\alpha = 0.5$, this amounts to averaging the previous guess and the current calculated value to produce the next guess. If the convergence is to be accelerated $\alpha$ must be negative.

Now, $\alpha$ is a parameter whose value must be determined in one manner or another. Let us see how this might be done. If an estimated value is to be used for each iteration, Eqn. VIII-3 becomes

$$X_2(n) = X_1 + r Y_2(n)$$  \hspace{1cm} (VIII-15) \\

So, from Eqn. VIII-14,

$$Y_2(n) = \alpha Y_2(n-1) + (1-\alpha)[X_1 + r Y_2(n-1)]$$  \hspace{1cm} (VIII-16) \\

Or,

$$Y_2(n) = \lambda Y_2(n-1) + \Phi$$  \hspace{1cm} (VIII-17)

where $\lambda = \alpha + (1-\alpha)r$ and $\Phi = (1-\alpha)X_1$.

Eqn. VIII-17 is similar in form to Eqn. VIII-3 where now $r$ becomes $\lambda$ and $X_1$ becomes $(1-\lambda)X_1$. Thus, the condition for convergence is $|\lambda| < 1.0$. Since $\alpha$ is a parameter at our disposal, we can choose it to make $\lambda$ take on any value we want. An obvious value is zero; convergence will then take place in one iteration. Solving for $\alpha$ for $\lambda = 0$ gives

$$\alpha = -r/(1-r)$$  \hspace{1cm} (VIII-18) \\

It is also possible to choose $\alpha$ such that $|\lambda| > 1$ in which case the sequential modular iterative procedure will diverge. What are the limits on $\alpha$ so that this will not happen. Since $\lambda$ is real if $\alpha$ is, we need to determine what values of $\alpha$ make $\lambda = +1$ and $\lambda = -1$. For $\lambda = +1$, we get

$$\alpha_{+1} = 1$$  \hspace{1cm} (VIII-18a) \\

which, as was previously established, is the value of $\alpha$ which results in no change from iteration to iteration. For $\lambda = -1$ we get

$$\alpha_{-1} = -(1+r)/(1-r)$$  \hspace{1cm} (VIII-18b)
Let us examine this numerically:

<table>
<thead>
<tr>
<th>$r$</th>
<th>$\alpha_0$</th>
<th>$\alpha_{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>-0.25</td>
<td>-1.50</td>
</tr>
<tr>
<td>0.5</td>
<td>-1.0</td>
<td>-4.00</td>
</tr>
<tr>
<td>0.7</td>
<td>-2.33</td>
<td>-5.67</td>
</tr>
<tr>
<td>0.9</td>
<td>-9.0</td>
<td>-19.0</td>
</tr>
<tr>
<td>0.95</td>
<td>-19.0</td>
<td>-39.0</td>
</tr>
<tr>
<td>0.99</td>
<td>-99.0</td>
<td>-199.0</td>
</tr>
</tbody>
</table>

We see that the value required for $\alpha_0$ increases rapidly as $r$ approaches 1.0 and that value of $\alpha_{-1}$ is asymptotically only twice that of $\alpha_0$. This, as will be seen, limits the extent to which this form of acceleration can be applied to real problems.

C. The Method of Wegstein

One of the first methods used to accelerate the convergence of sequential modular simulations was that of Wegstein. It is still used today; it is, for instance, the default method in ASPEN. It is based on the procedure outlined in Eqns. VIII-16 and VIII-18 which assumes that the value of $r$ is known. In real problems, it is not. Furthermore, if the problem is nonlinear (Why else would one do sequential modular simulation if the problem were not?), $r$ is not known. Furthermore, its value varies from iteration to iteration. Therefore, in order to use this acceleration procedure, one must have a means of estimating $r$.

This can be done as follows. Suppose we execute two direct iterations of the simulation. This can be expressed as follows:

\[(VIII-19a)\]
\[X_2(1) = X_1 + r X_2(0) \text{ and} \]
\[(VIII-19b)\]
\[X_2(2) = X_1 + r X_2(1).\]

Solving for $r$ gives

\[(VIII-20)\]
\[r = \frac{[X_2(2) - X_2(1)]/[X_2(1) - X_2(0)]}{\} \]

This is all well and good but what we are estimating in effect is a slope. The way in which Wegstein procedure is applied is component by component and tear stream by tear stream, ignoring all interactions. The effect of these interactions is to introduce errors into the estimation
of \( r \) for each component and each tear stream. As can be seen from the previous table, small errors in the estimation of \( r \), particularly when \( r \rightarrow 1.0 \), can result in choosing a value for \( r \) that will make the procedure unstable. This has led in practice to placing a bound on \( r \) that used in ASPEN is -5.0. As can be seen, this will reduce the efficiency of the procedure. For instance, for \( r = 0.99 \), \( r \) is only 0.94 instead of 0. However, it still helps since the number of iterations required for our example problem is reduced from 459 to about 120, a factor of almost 4.0.

Our investigation of convergence and convergence acceleration is quite limited. It is intended only to point out some of the difficulties that can be encountered in using present-day sequential modular simulators. Many of these simulators, such as ASPEN, have alternative algorithms available as well. These generally involve using Newton-Raphson or pseudo-Newton methods such as that of Broyden applied simultaneously to all of the tear set variables. These methods can also be used to solve simultaneously for the design specs and tear stream variables. This can result in a considerable saving of computer time for complex problems with many design specs. The drawback is that these methods are much more sensitive to initial guesses than those based on direct iteration or Wegstein. As a practical matter one has to experiment to determine which is best in a given situation.
IX. MIXING AND BLENDING PROBLEMS

Revised September 23, 1998

Many of the products produced by the chemical processing industries are mixtures or blends of various constituents. One example is gasoline. Today's gasoline must meet a number of specifications including octane rating, volatility, and oxygenate content. Another example is pharmaceutical products. For instance, each capsule in a bottle of Extra Strength Excedrin, an analgesic, contains 250 mg each of aspirin and acetaminophen and 65 mg of caffeine in addition to the binder. A third example is animal feed. The feed for, say, chickens must contain protein, fat, and carbohydrates in the proper ratios as well as the appropriate amounts of vitamins, minerals, and other nutrients.

In each example, the product is the result of the blending and mixing together of a number of individual constituents, many of which are themselves mixtures. We will refer to this process as mixing when the composition of the end product must meet exact composition specifications. For instance, each Excedrin capsule must contain 250 mg of aspirin, no more and no less. If the end product must merely meet its specifications in term of ranges, then we will refer to it as a blend. For instance, our chicken feed might be required to contain no less than 20% protein by weight and no more than 25%.

A mixture can be a mixture of gases (Air, for instance, is a mixture of oxygen, nitrogen, argon, carbon dioxide, and other trace gases.), liquids (Rubbing alcohol, for instance, is a mixture of isopropyl alcohol in water.), or solids (Premixed concrete, for instance, is a mixture of sand, cement, and lime.). A mixture that is liquid is quite often referred to as a solution. Mixtures of solids or gases have no special terminology.

A. Mixing

Mixtures can be specified on a weight basis, a molar basis, or a volume basis. A weight basis is commonly used for many large-scale commodities such as solutions containing one or more components that solids in their pure form. Many mixtures that are a solution of two liquids are characterized in terms of volume. Rubbing alcohol, for instance, which is generally 50 to 70% isopropyl alcohol by volume. Mixtures, particularly solutions for use in a chemical laboratory, are quite often characterized in terms of the number mols of a given constituent contained (usually) in a given volume of solution.

Let start with a simple example, namely, to make up 100 Kg of a 40% solution by weight of NaOH in water given available supplies of pure NaOH and pure water. All we would do is weight out 40 Kg of NaOH and 60 Kg of water and then dissolve the NaOH in the water (with due attention to safe handling).

However, if we only happen to have a solution of 60% NaOH in water and pure water available, then we have to do some material balance calculations.
Let $F_1$ be the Kg of NaOH solution which must be used and let $F_2$ be the Kg of water to be used. Then, an overall material balance for mixture is

(IX-1) \[ F_1 + F_2 = 100 \text{ Kg} \]

while a material balance on NaOH gives

(IX-2) \[ 0.6 F_1 + 0.0 F_2 = (0.4)(100) = 40 \text{ Kg}. \]

These two equations are easy enough to solve giving

\[ F_1 = \frac{40}{0.6} = 66.67 \text{ Kg} \quad \text{and} \quad F_2 = 100 - F_2 = 100 - 66.67 = 33.33 \text{ Kg}. \]

As a second example, consider making up a solution that approximates the composition of seawater, namely, 22,000 ppm by weight of NaCl and 13,000 ppm of MgCl2. Let us suppose that in addition to a supply of pure water, we have available a solution containing 5.0 wt% of NaCl and a second solution containing 4.0 wt% of MgCl2.

Since a target amount of solution has not been specified, let us choose 1000 Kg as a basis. In this 1000 Kg of solution we will need:

\[ (0.022)(1000) = 22 \text{ Kg of NaCl}, \]
\[ (0.013)(1000) = 13 \text{ Kg of MgCl2}, \]

and by difference, \[ 965 \text{ Kg of H2O}. \]

Let $W_1$ be the Kg of NaCl solution to be used, $W_2$ the Kg of MgCl2 solution to be used, and $W_3$ the Kg of pure H2O to be used.

We can write the following mass balances:

\[ W_1 + W_2 + W_3 = 1000 \text{ (overall mass balance)} \]
\[ 0.05 W_1 = 22 \text{ (NaCl balance)} \]
\[ 0.04 W_2 = 13 \text{ (MgCl2 balance)} \]

This is an easy problem to solve. Doing so gives

$W_1 = 440 \text{ Kg}$,
$W_2 = 325 \text{ Kg}$, and
$W_3 = 275 \text{ Kg}$.

Suppose instead that the two solutions have the following compositions:

Solution 1: 5% NaCl and 1% MgCl2 in H2O
Solution 2: 1% NaCl and 4% MgCl2 in H2O

The overall mass balance remains the same but the NaCl and MgCl2 balances become:

\[
\begin{align*}
0.05 W1 + 0.01 W2 &= 22 \\
0.01 W1 + 0.04 W2 &= 13
\end{align*}
\]

These two equations must be solved simultaneously. Doing so gives

\[
\begin{align*}
W1 &= 394.74 \text{ Kg}, \\
W2 &= 226.32 \text{ Kg}, \text{ and} \\
W3 &= 378.94 \text{ Kg}.
\end{align*}
\]

However, if the solutions have the compositions:

Solution 1: 5% NaCl and 3% MgCl2 in H2O and
Solution 2: 3% NaCl and 4% MgCl2 in H2O,

then W2 < 0. For this case there is no physically meaningful solution.

The important fact to note about exact mixing problems is that for a solution to exist at all, the number of independent variables that can be adjusted must be exactly equal the number of specifications for the mixture. In the last example, there were three specifications (ppm NaCl, ppm MgCl2, and total weight of the solution) and three independent variables (W1, W2, and W3).

B. Blending

Blending problems arise when either there are more independent variables than there are specifications to be met or if some of the specifications are in the form of inequalities. In either case there is not a unique solution but rather a range of solutions. One can introduce, then, another consideration, namely, cost.

Let us look at the previous mixing problem as a blending problem to see how cost considerations can arise. Suppose that instead of having two solutions available, we have three, all of different compositions. If the problem is feasible at all, there range of combinations of the three solutions (plus the pure H2O) which will meet the specifications. Suppose that each solution has a different cost per Kg. Then the question is, which of all the possible combinations yields the lowest cost? This is what is traditionally known as an optimization problem.

On the other hand suppose that only solutions are available but that we relax the specification on NaCl. Instead of being exactly 22,000 ppm, suppose it only has to be between 18,000 and 24,000 ppm. Let us consider the situation where the two solutions have the compositions:
Solution 1: 5% NaCl and 1% MgCl2 in H2O
Solution 2: 1% NaCl and 4% MgCl2 in H2O

Further Solution 1 costs $0.05/Kg while Solution 2 costs $0.10/Kg. The cost of the pure water is negligible. What is the minimum cost recipe for this blending problem?

First, let us define an objective function which, in this case will be the total cost of the target solution:

\[ \Gamma = 0.05 W_1 + 0.10 W_2 \text{ (dollars)} \]

The material balance specifications now become

\[
0.05 W_1 + 0.01 W_2 \geq 18 \\
0.05 W_1 + 0.01 W_2 \leq 24 \\
0.01 W_1 + 0.04 W_2 = 13
\]

These three equations are known in optimization jargon as constraints. There are two additional constraints that must be satisfied to guarantee an physically meaningful solution to the optimization problem, namely,

\[ W_1 \geq 0 \quad \text{and} \quad W_2 \geq 0. \]

Note that both the objective function and the constraints are linear in the problem variables \( W_1 \) and \( W_2 \). When this is the case, the optimization problem has a very specific known a linear program. Linear programming or LP was developed over forty years ago and has been applied to many problems in planning, operations, and design. Very effective algorithms such as the Simplex Method have been developed for the solution of LP programs and problems involving thousands of constraints and thousands of variables are solved daily. These algorithms are widely available. Most of the popular spreadsheet programs have LP solvers as part of their repertoire.

Since we have only two variables, namely \( W_1 \) and \( W_2 \), we can explore the nature of the optimization problem graphically. This is shown in Figure IX-1. The MgCl2 exact constraint is the almost horizontal line and the two NaCl inequality constraints are the other two lines. The solution must lie to the right of the lower NaCl constraint and to the left of the upper one. It must also lie on the MgCl2 constraint. If we solve for the intersections of the two NaCl constraints and the MgCl2 constraint, we get, for the lower NaCl constraint, \( W_1 = 310.53 \) and \( W_2 = 247.37 \), while for the upper NaCl constraint, \( W_1 = 436.84 \) and \( W_2 = 215.78 \). If we evaluate the objective function at these two intersections, we get for the lower NaCl constraint

\[ \Gamma = (0.05)(310.53) + (0.1)(247.37) = 40.26 \]
and for the upper NaCl constraint

$$\Gamma = (0.05)(436.84) + (0.1)(215.78) = $43.42.$$ 

Any choice in between of W1 and W2 that lies on the MgCl2 constraint will have a value of between these two values. This is always the situation with an LP solution, namely, that the optimum lies at the intersection of constraint boundaries. The Simplex Method exploits this fact in finding the optimum solution for problems much larger than this one.
X. PLANT DATA ANALYSIS AND RECONCILIATION

Revised September 23, 1998
Up to this point we have been considering hypothetical processes, processes that exist only on paper. Equipment models have been chosen on the assumption that these describe the behavior of the process with sufficient accuracy for the purposes at hand. Flowsheet calculations have then been done, the results being presented in some form of a stream summary. If these calculations have been properly done, the stream summary satisfies the conservation of mass to as many significant figures as our computer will support.

Once a plant is built and operating, the situation changes. The chemical engineer's job is now to determine the performance of the actual, as-built plant rather than that of the hypothetical one on which the design is based. And this can only be done by the analysis of operating plant data.

A. Plant Data

Before proceeding to some examples, let us examine the nature of plant data. Data are the results of measurements. And measurements are subject to a number of potential difficulties.

1) The nature of measurements

Some measurements are direct but most are inferential. The determination of the weight of a sample using an old-fashioned swing-type gravimetric balance is direct. One puts the sample in one pan and adds weights of known denominations to the other pan until a balance is achieved. The two weights must be equal; the sample weight must be equal to the sum of the known weights added to the other pan of the balance.

Almost all other measurements are inferred. Temperature as measured by a mercury-in-glass thermometer is inferred from the length of the mercury column. The accuracy of the measurement depends on the uniformity of the bore of the thermometer and how well the dependence of the coefficients of thermal expansion of both the mercury and the glass are known. If a thermocouple is used, then the accuracy depends upon whether or not there is contamination of the junction weld and how well the dependence of the emf on temperature is known.

The two types of measurements most commonly used in plant material balance calculations are flow rate and stream composition. There are a variety of instruments used for each, all of which infer flow rate or composition from some other direct measurement. In the case of flow rate, the most widely used instrument is the orifice meter; mass flow rate is inferred from the measured pressure drop across the orifice. There are many other types of flow meters but their description is beyond the scope of these notes.

There are two ways in which composition is measured. One is on-line using an instrument called an analyzer. A small sample stream is continuously diverted to the analyzer. The measurement itself may be continuous in time, examples being infrared and ultra-violet Spectrometers. Or it may be periodic, a new analysis becoming available every so often, say
every ten seconds or every five minutes depending upon the requirements of the specific analysis. The most common example of this type of instrument is the gas chromatograph.

Some composition measurements are too difficult or too expensive to do on-line. In this case a discrete sample is taken in a sample flask and sent the plant analytical laboratory to be processed there. This is generally done on a frequency of one an hour to once per shift. Depending upon the complexity of the analysis, the results may not be available for anywhere from an hour to a day or more.

It is not necessary to know the specifics of every measurement to use plant data for material balances and other purposes. However, there are a few general characteristics of plant that should be kept in mind. Above, never assume (even if the on-line analyzer cost a half million dollars) that the data is correct. Beyond that one should know the following:

a) Zero and span

Every on-line measurement is good only over some predetermined range of values. The transducer that converts the primary signal into one that is compatible with the rest of the plant instrumentation is designed with a compromise between accuracy and range in mind. For example, suppose a reactor is to be run at temperature of 500 C with allowable excursions of 1.0 C. If a transducer is chosen with a range of 0 to 1000 C and an accuracy of 0.1% of span, then the best resolution it will give is 1.0 C. Since we must control to less than 1.0 C, this choice of transducer would not be acceptable. Choosing one with a range from 400 to 600 C with the small accuracy specification would give a of 0.2 C which is at least within the realm of possibility. It might be necessary to narrow the range even more (or buy a more accurate but more expensive transducer).

The lowest value for which the transducer provides an output is called the zero. For the second temperature transducer, this is 400 C. The range over which the transducer provides a useful output is called the span. This is 200 C for the second transducer. The important thing to keep in mind is that if the measurement is outside the range of the transducer, it is not valid. The best that can be said if the second temperature transducer indicates a temperature of 600 C is that the temperature is at least 600 C. We should know how the transducer fails. Some fail high while others fail low. Suppose our temperature transducer fails low. Then, if it reads 400 C, we do not know whether the temperature is 400 C or less or whether the transducer has failed and we have no idea what the temperature is.

b) Bias and error

There are two major sources of inaccuracy in an on-line measurement. One is error, and by this is meant random error. Suppose that the value of the variable being measured has not changed for the last hour but that when we read the transducer output every five minutes, we get a significantly different value, some higher, some lower than the others. In this case the error is
probably random and a good estimate of the underlying value would be to take the average of the 20 readings.

On the other hand, suppose that the instrument technician incorrectly calibrated the transducer so that its real zero is 390 C but its span is still 200 C. Or, suppose that the transducer has not been calibrated for a long time and its zero has drifted to the lower value. This means that every temperature measurement will be 10 C lower than the actual value. This is called bias.

c) Sampled versus continuous

Sampled measurements such as those described above are generally subject to much more random error than continuous on-line measurements. The opposite tends to hold for on-line measurements, namely that these subject to more bias but less random error than sampled measurements. There are many reasons for this. An important one is that most laboratory instruments are recalibrated much more often than plant instruments.

2) Plant material balances

Let us now consider the problem of determining plant performance from plant data. Two questions arise. The first is whether sufficient measurements are available to permit the calculation of those aspects of plant performance that are of interest. The second concerns the accuracy of the data.

It should be kept in mind that only a small fraction of all of the variables which characterize the complete performance of a plant are actually measured. For instance the complete performance of a distillation column is characterized by approximately 130 variables. In practice only about 15 would be measured.

Also, measurements are expensive. (Typically, 10% of the total investment in a plant is for instrumentation.) And some are very difficult and potentially unreliable. As a result, the number of measurements available represents a compromise between cost, feasibility, and sufficiency.

a) Surge Tank

Now let us consider a few simple examples. A surge tank is shown in Figure X-1. The instrumentation consists of flow meter on the inlet stream (FM1), another on the outlet stream (FM2), and a level meter (LM). Suppose the system is at steady state. This will be the case none of the measurements change with time. If this is the case, the inlet flow rate F1 as measured by FM1 should equal the outlet flow rate F2 as measured by FM2.
Suppose \( F_1 = 10,050 \text{ lb/hr} \) as measured and \( F_2 = 9,975 \text{ lb/hr} \). The two measurements differ by less than 1% which is well within the expected accuracy of most flow meters. Thus, we might conclude that the two measurements are fundamentally correct and agree to use the average of the two as the most correct value. On the other hand if \( F_1 = 11,050 \text{ lb/hr} \) and \( F_2 = 8,250 \text{ lb/hr} \), we recognize that we have a problem.

**Figure X-1. Surge Tank PID**

Further, with only this data, there is no way to determine which, if either is correct. Our only recourse is to call the instrument technician to check and recalibrate the two flow meters.

Let us note in passing that if we have only flow meter, we have no way of knowing whether or not it is even remotely correct. Having two allows us to check one against the other, which is an improvement. If one can calculate the same aspect of plant performance from two independent sets of data, the data are said to be redundant. As we will see, redundancy is the key to the effective use of plant data.

Our next example is shown in Figure X-2. The only difference between this surge tank and the previous one is the additional flow meter FM3 on the inlet stream. Suppose the measurements are \( F_1 = 10,050 \text{ lb/hr} \), \( F_2 = 9,975 \) and \( F_3 = 7,200 \). Clearly, something is amiss. However, if we chose not to think about it, we might just use the average over the three values which is 9075 lb/hr. F1 and F2 each differ from this value by about 10% while F3 is more than 20% low. Thus, this way of adjusting the data does not appear to be satisfactory. On the other hand, if we use the average of just F1 and F2, which is 10012.5 lb/hr, then F1 and F2 differ from this value be less than 1%. But F3 is low by 28%. Thus it would appear that F3 is in serious error and should be disregarded.

The value of redundant data is obvious. If we only had flow meters FM2 and FM3, there would be no way to identify which was in error. But with three, there is at least the possibility of determining which one is in error.
c) Flash Drum

Let us look next at the flash drum shown in Figure X-3. A feed stream containing nitrogen and water is flashed. Most of the nitrogen goes overhead while most of the water leaves as liquid in the bottom stream. All three streams are equipped with a flow meter. The feed stream has an analyzer AM1 which measures the amount of nitrogen in the stream. The overhead analyzer AM2 measures the amount of water in that stream while AM3 measures the amount of nitrogen dissolved in the liquid leaving the flash drum.

![Fig. XI-3. Flash Drum PID](image)

The following data have been taken at steady-state conditions:

- F1 (measured by FM1) = 25,015 Kg/hr
- F2 (measured by FM2) = 20,300 Kg/hr
- F3 (measured by FM3) = 4,920 Kg/hr
- N2 in feed = 70 mol%
- H2O in overhead = 4 mol%
- N2 in bottoms = 0.24 mol%

We would like to know the following:

i) What is the % of N2 in the feed which leaves in the overhead vapor? From a separation operations point of view, what is the recovery of N2?

ii) What is the separation factor for the flash drum?

**Digression:**

The separation factor is a measure of the completeness of separation produced by any item of separation equipment. Suppose that a feed stream, such as that to the flash drum, is separated into two output streams. If a separation occurs, then the composition of the two output streams must differ. The separation factor between two components is defined as follows:

Chose the component of most interest, generally a product or other valuable component. Call this component A and the other component B. Identify the stream in which that component A concentration should be higher than it is in the feed. Call this Stream 1 and the other output stream from the separator Stream 2. Then the separation factor between A and B (SF\textsubscript{AB}) is:
where $X_{I,J}$ is the composition or molar flow rate of component I in stream J. Properly defined, the separation factor is always greater than 1.0 if any separation takes place. For high purity separations, separation factors of 10,000 or more are not uncommon. Thus, the separation factor is useful measure of the effectiveness of a given separation.

End of Digression

Returning to our flash drum, suppose that we want to determine the fractional recovery of nitrogen and the separation factor. First, following good practice, we should examine the the quality of the data. We can see immediately that the feed rate is 25,015 Kg/hr while the total output is 25,220 Kg/hr. The discrepancy is not particularly significant compared to the expected errors in flow rate measurements.

The overall mass balance is not the only thing that needs to be checked. We must also check the individual component balances. The first thing to check is the validity of the analytical data, if possible. Some on-line analyzers such as IR and UV spectrometers only analyze for a specific component. If we know that the mixture is binary, then the amount of the second component can be inferred by difference.

Other analyzers such as gas chromatographs and mass spectrometers have the capability of determining the amount of each component present in a mixture. In this case, we can check the creditability of the analysis by summing up the amounts. If these are reported as mol or weight percents, the sum should equal 100%. Generally it will not do so exactly. If the sum is reasonable, say between 99% and 101%, we might simply renormalize the by dividing each component analysis by the sum.

For the example at hand we have only partial analyses, so no creditability check is possible. Let us do a mass balance on nitrogen. Before doing that, we must the measured mass flow rates into molar flow rates which requires computing the average molecular weight for each of the three streams. These are:

$$
\text{MWfeed} = (0.7)(28.014) + (0.3)(18.016) = 25.015
$$

$$
\text{MWvapor} = (0.96)(28.014) + (0.04)(18.016) = 27.614
$$

$$
\text{MWbottoms} = (0.0024)(28.014) + (0.9976)(18.016) = 18.040
$$

The molar flow rates of the three streams are:

$$
F_{1\text{molar}} = (25015/25.015) = 1000.00 \text{ Kmol/hr}
$$

$$
F_{2\text{molar}} = (20300/27.614) = 735.13 \text{ Kmol/hr}
$$

$$
F_{3\text{molar}} = (4920/18.040) = 272.73 \text{ Kmol/hr}
$$

\[ \frac{(X - 1)}{SF_{AB}} = \frac{x_{A,1}x_{A,2}}{x_{B,1}x_{B,2}} \]
The N2 balance is:

\[
\begin{align*}
\text{N}_2\text{in} & = (1000.)(0.7) = 700.00 \text{ Kmol/hr} \\
\text{N}_2\text{out} & = (735.13)(0.96) \\
& \quad + (272.73)(0.0024) \\
& = 705.72 + 0.654 = 706.37 \text{ Kmol/hr}
\end{align*}
\]

The balance is not in serious error (less than 10%) but notice that the amount of N2 leaving in the vapor alone exceeds the amount in the feed. Moisture analyses can somewhat unreliable unless precautions are taken to prevent condensation and adsorption. If the overhead vapor analysis were 4.9% H2O instead 4.0%, the balance would be almost exact. Since this correction is in the right direction if there were condensation of H2O in the sample line, we will accept it.

B. Data Reconciliation

Data reconciliation is the adjustment of the raw plant data so that the material balances computed the adjusted data are exact. The previous examples have employed what we might term ad hoc data reconciliation, i.e., adjustments based on technical judgment as to what measurements are most likely to be in error. One might ask if such reconciliation is necessary if the errors associated with the raw data are not excessive. The answer should be clear from the second example. Without even a small adjustment, the calculation of the fractional recovery of N2 is meaningless.

The ad hoc approach is fine if the problem is relatively small. Different choices of adjustments can be made. The one that leads to exact balances with the most reasonable adjustments of the data can then be selected. If the problem is large involving, say, an entire section of a plant, the ad hoc procedure becomes unwieldy since the number of choices grows factorially.

A more structured approach is required. This has been the subject of extensive research over the past thirty years. What one wants is a procedure that, for one, identifies measurements that are in gross error and, for the other, determines what are the most logical adjustments to be made to the remaining data. There are many approaches to this problem, some of which are outlined in the book by Mah (1990). It is beyond the scope of these notes to go into any of these. Our purpose here has been to introduce the reader to the nature of the problems that arise in dealing with actual plant data.
We are now in a position to calculate the required quantities. The fractional recovery \( fr \) of N2 in the overhead vapor is

\[
fr = (0.951)(735.13)/700. = 0.9987
\]

Note that if we had used the unadjusted analysis, \( fr \) would be greater than 1.0 which is not a useful result. The separation factor \( S_f \) is

\[
S_f = (0.951/0.0024)/(0.049/0.9976) = 8067
\]

XI. THE ELEMENTS OF DYNAMIC PROCESS MODELING

Revised September 23, 1998
Up to this point almost all of our attention has been focused on processes operating in the continuous steady state. While this is a useful idealization for many purposes, in reality processes do not operate in the steady state. Their true behavior is dynamic, their state changing with time due to disturbances of various kinds and deliberate changes in the required operating conditions. Furthermore, many processes are operated in the unsteady-state mode for one reasons or another. This includes batch processes such as are commonly used in the manufacture of fine chemicals and pharmaceuticals. Some processes or parts thereof, are operated in the cyclic mode, examples being pressure swing absorbers (PSA) and fixed bed reactors with a rapid catalyst decay/regeneration cycle.

Thus a full understanding of the behavior of any process requires that we look at its dynamics. Dynamic process modeling, when done fully, is very a very demanding undertaking (Denn 1985, Franks 1972, Ramirez 1989, Silebi and Schiesser 1992). Our intent here is to provide an introduction to such modeling and the solution of simple dynamic process problems.

We will look at two systems that are typical of various processing operations, namely, the liquid-filled continuous stirred tank, and the well-mixed vapor drum or gasholder. In each case we are interested in both the changes in total inventory as a function of the total flow rates into and out of the system and the changes in inventory of individual components as functions of both total flow rates and feed compositions.

In the case of the liquid-filled tank, one concern is its total inventory. If the flow rates into the tank exceed those leaving it for a long enough period of time, the tank will overflow. If the tank happens to be our bathtub, the result will be a wet floor or perhaps damage to the ceiling of the room below. If the tank happens to be in a chemical plant and contains a corrosive or toxic solution, the results could be far more serious. If, on the other hand, our tank is a drinking-water supply tank and the flow rates out exceed the flow rates in for long enough, the tank will run dry with unpleasant consequences.

In the case of a gasholder, pressure is the measure of total inventory. If the flow rate of gas into the holder exceeds that leaving, the pressure will increase. If the supply pressure exceeds the design pressure of the holder, eventually the pressure in the holder will exceed its design pressure. As a result, the holder may rupture or burst with potentially disastrous con-sequences.

Thus, there are several reasons for developing a dynamic model of a process. If the process is inherently dynamic, being either batch on cyclic in operation, then only a dynamic model makes sense. Even if the process is intended to be operated in the continuous steady state, its underlying behavior is dynamic. Steady state operation can only be achieved by good control. In turn, good control can only be achieved through a proper understanding of the process dynamics.

We are also interested in what happens when things fail. Suppose the control valve that controls the level in a tank fails? What are the consequences as a function of time? How long does the operator have to take remedial action? What sort of safety features should be included in
the process design so this catastrophic event will be prevented? Again, a dynamic model is
required to predict the course of events both without and with the safety system. The use of
dynamic models for hazard evaluation is a very important part of chemical engineering de-sign
and operations analysis.

A. Conservation of Mass for Dynamic Systems

In what follows the principle of conservation of mass will be applied to the two systems in
which we are interested. In order to carry our analysis, some assumptions are required:

1) Control volume is well mixed

In dynamic modeling it is important to know how the physical quantities that describe the
state of system (such as composition and temperature) vary throughout the control volume. In
general these will vary over the three spatial coordinates and the model equations will be partial
differential equations (PDE's) in time and the three spatial dimensions. While such models have
the most potential to accurately represent the dynamic performance of the system, they are
relatively difficult to solve. For many systems some simplifying assumptions are reasonably valid
and allow us to reduce the number of spatial dimensions that must be considered. If the system
involves flow through a cylindrical vessel or pipe (often the case in chemical processing), we can
assume that the spatial distribution is axisymmetrical and thereby reduce the number of spatial
dimensions to two. If the flow is highly turbulent, we can assume that the turbulent mixing is
intense enough that at any point along axis, the fluid is well mixed. (This is the so-called plug-flow
idealization.) It reduces the number of spatial dimensions to one. Still we are faced with the
solution of partial differential equations in time and one spatial dimension, a more manageable
prospect than the general case but one that can present some difficulties.

The assumption that leads to the simplest of dynamic models is that of well mixedness. It
is assumed that within the control volume the fluid is intensely mixed, either by turbulence
generated by the flow through the control volume or by the use of mechanical mixing device such
as a motor-driven agitator. Variables such as temperature and composition are assumed to have
the same value over the entire control volume at any in point in time. Therefore, no spatial
dimension is involved and the model equations become ordinary differential equations (ODE's).
The control volume for which this assumption is most commonly made is an agitated tank through
which fluid continually flows (hence the terminology continuous stirred tank or CST).

2) System is isothermal at all times

This is an assumption of convenience for our present analysis necessitated by the fact that
our only tool at this point is the mass balance. It is easily removed by applying the First Law of
Thermodynamics (conservation of energy) but this is beyond the scope of these notes. So, we will assume that the temperature of the system is constant with respect to time.

Fig. XI-1. Surge and Mixing Tank

B. Surge and Mixing Tanks

Consider the agitated tank shown in Figure XI-1. There is a liquid flow in of flow rate \( F_1 \) and a liquid flow out of flow rate \( F_2 \). There can, of course, be more than one input stream to the tank; inclusion of additional feed streams is straightforward. So is the inclusion of additional output streams.

First, let us chose a control volume. We could chose the entire volume of the tank but this is not directly related to how much liquid there is in the tank. Let us chose instead the actual volume of liquid in the tank at time \( t \). This means if the height \( h \) of liquid in the tank varies with time, so will the control volume. If the tank has a constant cross section area \( S \), then the control volume at any time is \( Sh \).

Let \( \Psi \) = the holdup of a conserved quantity of in the control volume. If quantity of interest is the total mass of liquid in the tank, then \( \Psi = Sh\rho \) where \( \rho \) = the fluid density in, say, lb-mols/ft\(^3\). If we are interested instead in amount of the \( i \)th component, then \( \Psi_i = Shx_i \) where \( x_i \) = the mol fraction of the \( i \)th component in the tank. (Under the assumption of well mixedness, this will be the same everywhere throughout the control volume.)

Let us calculate the change in inventory over a very small time interval \( \Delta t \) starting at time \( t \). This will be given by

\[
\Psi_i(t + \Delta t) - \Psi_i(t) = (F_1 x_{i,1})^{(a)} \Delta t - (F_2 x_{i,2})^{(a)} \Delta t
\]

Where the superscript \( (a) \) denotes the average over the time interval \( \Delta t \). Also, \( x_{i,1} \) and \( x_{i,2} \) are the mol fractions of the \( i \)th component in Streams 1 and 2 respectively and \( F_1 \) and \( F_2 \) are the corresponding total molar flow rates. Also, if there are a total of \( nc \) components in the mixture, Eqn. XI-1 represents a set of \( nc \) equations, one for each component.
Note: Unless specifically mentioned, all dynamic mass balances in this section will be derived on a molar basis. In non-reacting systems, mols are conserved. In reacting systems, care must be taken to include terms to account for the extent of reaction for each component. This will be illustrated in this example.

\[
(\text{XI - 2}) \quad \frac{\Psi_i(t + \Delta t) - \Psi_i(t)}{\Delta t} = (F_1 \ x_{i,1})^{(a)} - (F_2 \ x_{i,2})^{(a)}, \quad i = 1, \ldots, nc
\]

Let us divide Eqn. XI-1 by \( \Delta t \) which gives

\[
(\text{XI - 3}) \quad \frac{d\Psi_i}{dt} = F_1 \ x_{i,1} - F_2 \ x_{i,2}, \quad i = 1, \ldots, nc
\]

Taking the limit of the left-hand side as \( \Delta t \to 0 \) gives

The limit of the left-hand side is merely the derivative and, in the limit, the average values in right-hand side become the point values at time \( t \).

Earlier, we related \( \Psi_i \) to the mol fraction \( x_i \) of the \( i \)th component in the control volume. One of the physical consequences of withdrawing fluid from a well-mixed control volume is that it has to be some of the same fluid that is in the control volume, i.e., its temperature and composition must be equal to those in the control volume. Therefore, \( x_{i,2} \) must equal \( x_{i,1} \). (For clarity, we will use \( x_{i,2} \) to represent \( x_i \).) Applying this fact and the definition of \( \Psi_i \) to Eqn. XI-3 gives

\[
(\text{XI - 4}) \quad \frac{d[Sh \ x_{i,2}]}{dt} = F_1 \ x_{i,1} - F_2 \ x_{i,2}, \quad i = 1, \ldots, nc
\]

Let us take stock of the situation. We have \( nc \) ODE's. But we have \( nc+1 \) variables, namely the \( nc \) mol fractions \( x_{i,2} \) and the liquid height \( h \). Clearly, we need one more equation. This can be obtained by invoking the closure condition on mol fractions, namely, where \( j \) refers to any stream or control volume. Now, Eqn. XI-5 represents a problem. It is an algebraic equation which states that the sum of the mol fractions of the \( j \)th stream or control volume must equal unity at all times. While Eqns. XI-4 and XI-5 comprise a set of \( nc+1 \) equations to go with the set of \( nc+1 \) variables for the system, this set of \( nc+1 \) equations is of mixed type. They are what is known as a set of differential and algebraic equations or DAE's for short.
For a number of reasons, we would like the equations representing the dynamic behavior of a system to be a pure set of ODE's of the form

\[
\frac{dy_i}{dt} = f_i(y_1, y_2, \ldots, y_n, z_1, \ldots, z_m)
\]

\[
\frac{dy_2}{dt} = f_2(y_1, y_2, \ldots, y_n, z_1, \ldots, z_m)
\]

\[
\ldots
\]

\[
\frac{dy_n}{dt} = f_n(y_1, y_2, \ldots, y_n, z_1, \ldots, z_m)
\]

of a system to be a pure set of ODE's of the form

where the \( y_i \) are the state variables (i.e., those variables which describe the internal state of the system) and the \( z_j \) are the input variables which drive the system. For our CST, \( h \) and the \( x_{i,2} \), while \( F_1, F_2 \), and the \( x_{i,1} \) are the input variables. There are excellent software packages (such as ODEPACK) available for solving sets of ODE's of the form of Eqn. XI-6. And, for the purposes of control system design, the dynamic equations for the system also need to be in that form.

So let us see how to convert Eqns. XI-4 and XI-5 from a set of DAE's to ODE's. First, expand the derivative in Eqn. XI-4 using the chain rule of differentiation. Assume for the moment that the density \( \rho \) is constant. We get

\[
\frac{d}{dt} \left( \sum_{i=1}^{nc} x_{i,2} \right) = F_1 \sum_{i=1}^{nc} x_{i,1} - F_2 \sum_{i=1}^{nc} x_{i,2}
\]

that the density \( \rho \) is constant. We get

\[
\frac{d}{dt} \left( \sum_{i=1}^{nc} x_{i,2} \right) = F_1 \sum_{i=1}^{nc} x_{i,1} - F_2 \sum_{i=1}^{nc} x_{i,2}
\]

Now let us sum Eqn. XI-7 over \( I \) which gives

\[
\frac{d}{dt} \left( \sum_{i=1}^{nc} x_{i,2} \right) = 0
\]

If Eqn. XI-5 is differentiated with respect to time for Stream 2, we get

Substituting Eqns. XI-5 and XI-9 into Eqn. XI-8 gives
Eqn. XI-10 is known the overall mass balance and could be derived directly. However, the approach outlined avoids confusion with regard to whether or not all of the equations are independent.

If the density $\rho$ is not constant but is a function of composition (and more generally temperature as well), this does not change how to reduce the equations to a set of pure ODE's but it does introduce some additional terms into Eqn. XI-10.

Now let us substitute Eqn. XI-10 into Eqn. XI-7. The component mass balance becomes

$$\frac{d}{dt} \left( S \rho \frac{dh}{dt} \right) + x_{i,2} ( F_1 - F_2 ) = F_1 x_{i,1} - F_2 x_{i,2}, \text{ or}$$

$$\frac{d}{dt} \left( S \rho \frac{dx_{i,2}}{dt} \right) = F_1 (x_{i,1} - x_{i,2}), \ i = 1, \ldots, nc$$

Except for dividing through by some constants, Eqns. XI-10 and XI-11 are a set of nc+1 equations in the form required by Eqn. XI-6.

Now that we have this dynamic model, what can we do with it? One thing is dynamic simulation. We can write a computer program that uses a standard set of routines for integrating ODE's (IMSL and ODEPACK are two such) to solve these equations for specified variations in the input variables. The computed responses of the state variables then tell us something about the behavior of the system. This is generally what must be done since the model equations are nonlinear. However, for some simple situations the model equations can be solved analytically. Let us look at some.

Suppose we are only interested in how the liquid height $h$ (also called the liquid level) in the tank varies with time as the flow rates in and out vary. For this we only need to solve Eqn. XI-10. Let us suppose that prior to time $t = 0$, $F_1$ and $F_2$ are equal but at time $t = 0$ one or the other is changed to a new, constant value. Let this difference be $\Delta F = F_1 - F_2$. Suppose also that at $t=0$, $h(t) = h^0$. Then, direct integration of Eqn. XI-10 gives

$$h(t) = h^0 + \frac{1}{S \rho} \Delta F \ t$$

We see that if $\Delta F > 0$, then $h$ increases linearly with $t$ for as long as the imbalance in flow rates continues. A new steady state value of $h$ will never be reached, at least not until the tank
overflows, at which point our model in its present form no longer applies, there being two flows out of the system. Conversely, if $\Delta F < 0$, $h$ will decrease until the tank runs dry.

One might ask how this can be prevented. One is by manually adjusting one of the flow rates to exactly match the other. Now, if this is to be done by manual control, a number of problems arise. Suppose that the flow in is truly constant, i.e., does not vary with time. Then we must set the output flow rate exactly equal to it using the available plant instrumentation. The lesson of Chapter X should be that, with well-maintained instrumentation, we can set the output flow rate almost equal to the input flow rate but very likely there will be a small error in one direction or the other. Therefore $h$ will change with time, very slowly perhaps, but change it will. Occasional readjustments will be necessary. The situation will be worse if the input flow rate varies with time. Frequent readjustments may be necessary making manual control a labor-intensive activity.

Instead, we might want to use an automatic controller to maintain $h$ at some desired value or setpoint. Let this value be $h_s$. The simplest control law we can use is proportional control. If the output flow rate is to be adjusted to compensate for variations in the input flow rate, then the control law will have the form

$$(XI - 13) \quad F_2 = F_2^0 - K_c (h_s - h)$$

where $F_2^0$ and $K_c$ are adjustable controller parameters. In particular, $K_c$ is controller proportional gain. Let us assume that prior to turning on the controller at $t = 0$, the system has been lined out so that $F_2^0 = F_1$ and $h = h_s$. Also at $t = 0$ let there be a change in net flow rate $\Delta F$. Then, Eqn. XI-11 becomes

$$(XI - 14) \quad \frac{dh}{dt} = \left( \frac{\Delta F}{K_c} + h_s \right) \frac{1}{\tau_c} - \frac{h}{\tau_c}$$

where $\tau_c = \frac{S \rho}{K_c}$

$$(XI - 15) \quad h(t) = h_s + \frac{\Delta F}{K_c} (1 - e^{-\frac{t}{\tau_c}})$$

Solving by the standard method for a 1st order ODE and keeping in mind that $h(0) = h_s$ gives

We see that the controller will maintain the level at the set point $h_s$ except for an offset that increases with $t$ to a final value of $\Delta F/K_c$. This offset can be made smaller by increasing $K_c$. However, a more sophisticated control law might do better but this gets into the subject of process control. The important point is that our model can be used to show how a control system can be used to improve system performance.
Suppose we are interested in the composition dynamics of the well-mixed tank. There are a number of questions we might like to answer about its dynamic behavior. One concerns the time it will take the output of the tank to come to a new steady state following a sudden change in the input composition. If this change takes place instantaneously, it is commonly referred to as a step change. Let us suppose that prior to \( t = 0 \) the tank has been operated with a input of constant composition. Then the output will have the same composition. (This is the steady-state solution of Eqn. XI-11.) Then, at \( t = 0 \), the input composition is instantly increased by a fixed amount. This leads to a problem of the form

\[
(XI - 16) \quad \frac{d x_{i,2}}{dt} = \frac{I}{\tau_m} \left( x_{i,1} - x_{i,2} \right)
\]

where \( x_{i,1}(t) = x_{i,1}^0 \) for \( t < 0 \)

and \( x_{i,2}(t) = (1 + \beta) x_{i,1}^0 \) for \( t \geq 0 \)

also \( \tau_m = \frac{Sh \rho}{F_i} \) (the residence time or mixing time constant)

The solution to this equation is

\[
(XI - 17) \quad x_{i,2}(t) = x_{i,1}^0 \left[ 1 + \beta \left( 1 - e^{-t/\tau_m} \right) \right]
\]

Note that at \( t = 0 \) the output is equal to the initial value. As \( t \) increases, the exponential term goes to zero and the output approaches

\[
x_{i,2}(t) \rightarrow (1 + \beta) x_{i,1}^0
\]

When \( t = \tau_m \) the solution will have reached 63.2% of its final value. Thus the time constant tells us how fast the system will respond to a sudden change in input. In the case of the well-mixed tank, the time constant is the residence time or the ratio of the holdup in the tank to the flow rate leaving it. For a given flow rate, this residence time can be varied by varying the active volume of the tank. Thus the designer can adjust the transient behavior of the tank by choosing the appropriate volume.

It is also instructive to look at the behavior of the tank when the input varies sinusoidally with respect to time. As in the previous case, suppose the tank is at steady state at \( t = 0 \) at which time the input concentration begins to vary sinusoidally. The mathematical expression of this situation is
The solution is

\[
\frac{dx_{i,2}}{dt} = \frac{I}{\tau_m} (x_{i,t} - x_{i,2})
\]

where \( x_{i,t} (t) = x_{i,1}^0 \) for \( t < 0 \)

and \( x_{i,2} (t) = x_{i,1}^0 [1 + \alpha \sin(\omega t)] \) for \( t \geq 0 \)

where \( \omega = \text{the frequency at which the input is varied} \)

The solution is

\[
(x - 19) x_{i,2} (t) = x_{i,1}^0 \frac{\alpha (\tau_m \omega)^2}{(\tau_m \omega)^2 + 1} e^{i/\tau_m}
\]

\[
+ x_{i,1}^0 (1 + \frac{\alpha}{(\tau_m \omega)^2 + 1} [\sin(\omega t) - \tau_m \omega \cos(\omega t)])
\]

\[
(x - 20) x_{i,2} (t) = x_{i,1}^0 [1 + \frac{\alpha}{\sqrt{(\tau_m \omega)^2 + 1}} \sin(\omega t + \phi)]
\]

where \( \phi = -\tan^{-1}(\tau_m \omega) \)

Note the solution consists of two terms. The first is multiplied by a decaying exponential in time (the same exponential that appears in the step response transient) and therefore goes to zero after enough time. The second term continues as a function of time and represents, in effect, a sinusoidal steady state. Applying some trigonometric identities, we can rewrite the steady-state part of Eqn. XX-19 as Note that the output is also a sinusoid and of the same period at the input sinusoid. However the output lags behind the input by a factor which is called the phase lag or phase angle. This phase angle is essentially zero at low frequencies, i.e., frequencies for which \( \tau_m \omega \ll 1 \). At high frequencies, the phase angle approaches -\( \pi/2 \) (or -90 degrees). Also, the amplitude of the output sinusoid compared to the input sinusoid decreases as the frequency increases. What this means physically is that variations in the input which are extremely rapid compared to the residence time will be strongly attenuated (or filtered out) by the tank while those which are relatively slow will pass through with little or no attenuation. This relationship of the amplitude ratio (or gain) and the phase angle of a physical system is known as its frequency response. The frequency response is a powerful tool for the dynamic analysis of systems and for the design their control systems.

Let us now look at how chemical reaction can be included in our mathematical model of the well-mixed tank. Consider the case of single reaction whose rate per unit volume is given by \( r \). Let \( a_i \) be the stoichiometric coefficient for the \( i \)th component for this reaction. \( R_i \), the rate at which the \( i \)th component is generated by reaction in the tank, is given by
Now, \( R_i \) is just another input term in the component mass balance. Including this in Eqn. XI-4 gives

\[
(XI - 22) \quad \frac{d[Sh_i x_{i,2}]}{dt} = F_1 x_{i,1} - F_2 x_{i,2} + a_i S h r, \quad i = 1, \ldots, nc
\]

To get the overall mass balance, we do as we did before, namely sum Eqn. XI-22 over \( i \). Doing so and collecting terms gives the reacting version of Eqn. XI-10, namely,

\[
(XI - 23) \quad Sh \frac{dh}{dt} = F_1 - F_2 + \sigma S h r
\]

where \( \sigma = \sum_{i=1}^{nc} a_i \)

Again, using Eqn. XI-23 to put Eqn. XI-22 in standard form gives, for the component mass balance

\[
(XI - 24) \quad Sh \frac{dx_{i,2}}{dt} = F_1 (x_{i,1} - x_{i,2}) + (a_i - x_{i,2} \sigma) S h r, \quad i = 1, \ldots, nc
\]

C. Gas Holders

Let now look briefly at another version of the well-mixed tank, namely, a vapor drum or gas holder. The major differences between this system and the well mixed tank previously analyzed are:

1) The gas or vapor completely fills the available volume. (Needless to say, a vapor drum must be closed while a mixing tank can be open at the top.)
2) While assuming constant density for a liquid is not a bad first approximation, it definitely is for a gas.

Thus, the major the major difference between the two systems will be in variable used to track changes in inventory. For the mixing or surge tank, it is the liquid height \( h \). For the vapor drum it is the gas pressure \( P \) inside the drum.

Consider the vapor drum shown in Figure XI-2. Except that it must be a closed volume, it is very similar to the liquid-filled, well-mixed tank of Figure XI-1. Thus, we would expect the mass balance equations to be similar and indeed they are. The only difference is in the overall mass balance. In Eqn. XI-10 (non-reacting system) or Eqn. XI-23 (reacting system), it was assumed that \( \rho \) is constant and that \( h \) varies with time. In the case of the flash drum, the situation is reversed and the overall mass balance becomes

\[
(XI - 25) \quad Sh \frac{d\rho}{dt} = F_1 - F_2
\]

However, \( \rho \) is not a state variable but is a function of several state variables including pressure, temperature, and composition. At the beginning of this section, we stipulated that our considerations would be limited to isothermal systems. Also, to keep the analysis within hand, let us assume that \( \rho \) is described by the ideal gas law. If a molar basis is used, then \( \rho \) is also independent of composition. This leaves only pressure. Applying the chain rule of differentiation to Eqn. XI-25 gives

\[
(XI - 26) \quad Sh\left(\frac{\partial \rho}{\partial P}\right)\left(\frac{dP}{dt}\right) = F_1 - F_2
\]

The ideal gas law states that \( \rho = P/RT \). Carrying out the partial differentiation indicated in Eqn. XI-26 provides a useable form of the overall mass balance, namely,

\[
(XI - 27) \quad \frac{Sh\rho}{P} \frac{dP}{dt} = F_1 - F_2
\]

The reader should verify that the component mass balances are the same for both the mixing tank and the gasholder.
XII. PROCESS SIMULATORS
Process simulators are computer programs for performing the kinds of process flowsheet calculations described in these notes. These are of particular utility for simulating processes using the more accurate, rigorous unit operations models. A good process simulator offers a broad selection of such models. In addition, present day simulators have comprehensive physical properties systems offering a wide choice of equations of state, activity coefficient models, etc., as well as extensive databases of physical properties data for both pure components and binary mixtures. They also have extensive capabilities for flowsheet convergence and optimization. Many also provide an elementary, though useful, equipment sizing and cost estimation capability.

The following are some commercially available process simulators.

A. Steady State

Two of the most widely used steady-state process simulators are ASPEN PLUS (Aspen Technology, Inc., Cambridge, MA) and PRO-IV (Simulation Sciences, Fullterton, CA). Both of these programs offer a large variety of unit operations models, a substantial physical properties system and database, and robust methods for flowsheet convergence and optimization. ASPEN PLUS also provides a conceptual level equipment sizing and cost estimation capability.

Hyprotech and COADE also offer steady-state simulators particularly suited for use on high-end desktop computers. Aspen Technology also provides desktop capability.

B. Dynamic

For many years about the only dynamic simulator that was readily available was DYFLO developed by Roger Franks of DuPont. It is still used in many quarters as attested to by the fact that Franks's book, originally published in 1972, is still in print. DYFLO, while quite useful, requires considerable effort and skill on the part of the user.

Dynamic process simulators of reasonable reliability are just beginning to become commercially available. One is SPEEDUP that was originally developed by Roger Sargent and John Perkins at Imperial College and is now offered commercially by Aspen Technology. Another is OTIS which is currently be commercialized by Simulation Sciences. Hyprotech has recently come to the market with HYSIS. The leading academic dynamic simulators are ASCEND (developed by A. Westerberg and colleagues at Carnegie-Mellon) and DIVA (developed by E. Gilles and colleagues at the University of Stuttgart). Another, more recent, simulator that originated at Imperial College but is now commercially available is gPROMS.
The use of real-time dynamic simulators for personnel training has grown considerably in recent years. Several companies, such as ABB Simcon, offer a complete of services in this area from process modeling to development of a set of training exercises for use with the simulator.

Dynamic simulation is undergoing rapid development. Its use for both engineering simulation and personnel training has lead to a demand for simulators that are easy to use and that can provide realistic simulations of real processes. Heretofore, the development of dynamic simulator models has been a time-consuming and error-prone activity. The most recent trend is the development of modeling environments that allow the user to configure new equipment models with a minimum of effort. Two such systems are MODEL.LA developed by Stephanopoulos at MIT and ForeSee being developed at CCNY.
BIBLIOGRAPHY

Revised October 12, 1999


The proper handling of reaction stoichiometry in material balance calculations is of the utmost importance. It must be done correctly, otherwise the calculations are at best valueless and, if the errors are not caught, downright dangerous. The purpose here is to provide some guidelines to avoiding the most types of errors.

The recommended procedure for any reactor calculations for which a set of reactions is known is as follows:

1) Convert any series reactions to parallel reactions.

While series reactions may be correct from the point of view of chemical kinetic mechanisms, we are only interested here in getting the material balance bookkeeping straight. This is more readily done if all the reactions are in parallel form.

2) Divide all reactions through by the stoichiometric coefficient of the key component(s)

Conversion and selectivity are based on one or more key components. The correct interpretation of these is easier if all the key components have a stoichiometric coefficient of -1. For most simple reaction systems there will only be one key component. However, there are more complex systems for which there may be more than one key component. This will depend on the reaction chemistry and the conversion and selectivity definitions. Note that each reaction can have only one key component.

3) Convert all reaction system performance specifications to a molar basis

Reactor performance specifications are generally made on a weight basis, e.g., (1) convert a specified number of pounds of a key raw material to products and byproducts or (2) produce a given number of kilograms of a specified product. Although raw materials are bought and product sold by weight, reactions take place in mols.

4) Calculate the extents of reaction of all key components first

Since the selectivity structure is based on the extents of reaction of the key components, these should obviously be calculated first. This is straightforward since in 2) we have insured that all key components have unity stoichiometric coefficients.

5) Calculate the extents of reaction of all other components based on their stoichiometric coefficients and the selectivity structure
Keep in mind that the selectivity of a key component to a particular product or byproduct is the ratio of the mols of the key component converted to the target product or byproduct to the totals mols of key component converted via all applicable reactions.

6) Calculate the stream summary for both the reactor feed and the effluent

Do this on both a molar and a weight basis.

7) Check the overall and conserved species balances

Do pounds in equal pounds out? This is a simple check if the calculations have been done by spreadsheet. If there is a significant error, something has done wrong in the calculations. If it is small, the error probably stems from not using consistent molecular weights. (Note: The molecular weights given in Perry's Handbook are not consistent due to round-off.) The conserved species balances are most readily checked on a molar basis.
APPENDIX B. EVALUATION OF EQUIPMENT MODEL PARAMETERS

In order to utilize the linear material balance technique, one must be able to estimate reasonable values for all the equipment model parameters. Let us look at the parameters required for each of the four models described in Chapter IV:

1) Mixer (MIX)

No parameters are required for this model.

2) Reactor (REACT)

We require $\Delta_i$ (extent of reaction) for each component. This is generally known in one of three ways:

a. The rate of each reaction $r_j$ is specified in, say, kmol/hr.

Then extent of reaction of the $i$th component is given by

$$\Delta_i = \sum_{j=1}^{nr} a_{ij} r_j$$

(b) The conversion $C_k$ and selectivities $S_{kj}$ for each of a set of key components are specified.

Then, for the $k$th key component, its extent of reaction is given by

$$\Delta_k = - C_k f_{in,k}$$

For the other components in the reaction set assigned to the $k$th key component

$$\Delta_i = - S_{k,j} a_{i,j} \Delta_k$$

3) Separator (SEPAR)

SEPAR can be applied directly to simple separators such as a flash drum or simple distillation column. For more complex separators (more than one feed or more than two output streams), an appropriate model will have to be developed as demonstrated in Appendix C. For SEPAR we require $s_i$ for each component in the feed to the separator.
Most separators in use in large-scale continuous plants work on the principle of the equilibrium stage. The physical quantity that best characterizes the performance of this type of equipment is the relative volatility. Thus, before beginning a material balance model, one should estimate the relative volatilities of the components involved. These estimates do not have to be highly accurate. What one want to know is the ranking of the components by relative volatility and a reasonable estimate of the numerical values, particularly if any of these are less than, say, 1.2.

a. Flash Drum

If the feed to the flash drum consists of a number of components with very high relative volatilities compared to the others, then one can assume that these components will be almost entirely in the vapor leaving the drum while the low volatility components leave almost entirely in the liquid. Thus, \( s_i \) will be approximately 1.0 for the high volatility components and 0.0 for the low.

The most general way to specify the performance of a flash drum is to specify the fraction of the feed that is to leave as vapor. Let \( \gamma = V/F \). Then we can solve the Rachford-Rice Equation for \( \gamma \). If \( k_R \) is the k-value of the reference component, then we must solve

\[
(B - 1) \sum \frac{(\alpha, k_R - 1)z_i}{\alpha, k_R \gamma + 1 - \gamma} = 0
\]

for \( \gamma \). Then the component flow rates for the liquid are given by

\[
(B - 2) \quad f_{L,i} = \frac{(1 - \gamma)}{\gamma \alpha, k_R + 1 - \gamma} f_{F,i}
\]

So, if \( s_i \) is defined with respect to the vapor, then

\[
(B - 3) \quad s_i = 1 - \frac{f_{L,i}}{f_{F,i}}
\]

b. Simple Distillation Column

In general we know the specs on the key components, either purity specs or fractional recovery specs. If the separation between the keys essentially complete, then a good first approximation is to assume that all the components lighter than the light appear in the distillate while all the components heavier than the heavy key leave in the bottoms.
If there are components whose volatilities are intermediate between the key components or the separation between the keys is only partially complete, then we can estimate the distribution of the key components using the Fenske Equation.

1) Calculate $N_{\text{min}}$ based on the specification $s$ of the key components.
2) Choose one of the key components as the reference component.
3) Calculate the distribution of the non-key components using

$$ (B - 4) \ (d / b)_i = \alpha_i^{N_{\text{min}}} (d / b)_R $$

where all the relative volatilities are with respect to the reference component.

4) Flow Split (FSPLIT)

The flow split parameter $P$ is specified by the process engineer. It may be adjusted to achieve a specified flow rate or composition spec in a recycle stream.
APPENDIX C. COMPLEX EQUIPMENT MODELS

October 13, 1999

Complex equipment models can be developed using a combination of the four basic equipment models developed in Chapter IV. We give a typical example, that for an absorber that has two feeds: the vapor entering at the bottom and the absorption liquid entering at the top. This is shown in Figure C-1.

The absorber is modeled as two simple separators, S-11 for the vapor phase and S-12 for the liquid phase. The components absorbed from the vapor are added to the components not stripped from the liquid in mixer M-2. M-1 does the same for the non-absorbed vapor-phase components and the stripped liquid-phase components. Evaluation of the separation coefficients for both phases can be done for dilute systems using the Kremser Equation. The details are given in Appendix E.

A similar approach can be used for constructing models for other complex equipment items.
The following is the spreadsheet for the Ammonia Synthesis Loop example presented in Section VII. The upper part of the spreadsheet contains the problem input data. One column, the reactor deltas, is not input but is computed based on the molar flow rate of N2 in Stream 3 and the specified conversion.

The lower part of the spreadsheet is the stream summary that is shown in Section VII. Streams 1 and 2 are input data. Each molar flow rate for Stream 3 is calculated based on the tear stream solution (Eqns. E-8 and E-10). The other streams are then calculated sequentially based on Eqns. E-1 through E-5.

Also shown in the upper part of the spreadsheet is the mol% of Argon in Stream 3. This is calculated directly from the stream summary. Every time a new value for P is entered, the entire flowsheet is recalculated including the mol% of Argon. This provides the mechanism for adjusting P to achieve the design spec of 10 Mol% Argon by trial and error.

<table>
<thead>
<tr>
<th>Comp</th>
<th>si</th>
<th>ai</th>
<th>Delta</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.999</td>
<td>-3.0</td>
<td>-648.96</td>
<td>2.016</td>
</tr>
<tr>
<td>N2</td>
<td>0.998</td>
<td>-1.0</td>
<td>-216.32</td>
<td>28.014</td>
</tr>
<tr>
<td>Ar</td>
<td>0.998</td>
<td>0.0</td>
<td>0.00</td>
<td>39.948</td>
</tr>
<tr>
<td>NH3</td>
<td>0.010</td>
<td>2.0</td>
<td>432.64</td>
<td>17.031</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Comp</th>
<th>ST1</th>
<th>ST3</th>
<th>ST4</th>
<th>ST6</th>
<th>ST7</th>
<th>ST8</th>
<th>ST9</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>750.00</td>
<td>2632.13</td>
<td>1983.17</td>
<td>1981.19</td>
<td>1.98</td>
<td>99.06</td>
<td>1882.13</td>
</tr>
<tr>
<td>N2</td>
<td>250.00</td>
<td>865.28</td>
<td>648.96</td>
<td>647.66</td>
<td>1.30</td>
<td>32.38</td>
<td>615.28</td>
</tr>
<tr>
<td>Ar</td>
<td>10.00</td>
<td>192.68</td>
<td>192.68</td>
<td>192.29</td>
<td>0.39</td>
<td>9.61</td>
<td>182.68</td>
</tr>
<tr>
<td>NH3</td>
<td>4.15</td>
<td>436.79</td>
<td>436.79</td>
<td>432.42</td>
<td>0.22</td>
<td>4.15</td>
<td></td>
</tr>
<tr>
<td>Total mol/hr</td>
<td>1010.00</td>
<td>3694.23</td>
<td>3261.60</td>
<td>2825.51</td>
<td>436.09</td>
<td>141.28</td>
<td>2684.23</td>
</tr>
<tr>
<td>MWavg</td>
<td>8.83</td>
<td>10.10</td>
<td>11.44</td>
<td>10.58</td>
<td>17.02</td>
<td>10.58</td>
<td>10.58</td>
</tr>
<tr>
<td>Total lb/hr</td>
<td>8914.98</td>
<td>37314.01</td>
<td>37314.01</td>
<td>29893.71</td>
<td>7420.29</td>
<td>1494.69</td>
<td>28399.03</td>
</tr>
</tbody>
</table>
APPENDIX E. THE KREMSER MODEL OF GAS ABSORBERS

Revised September 26, 1999

The preliminary design of staged gas absorption systems and liquid-liquid extractors can generally be accomplished with a modest amount of effort using the Kremser Equation. This is particularly the case if the components to be absorbed or extracted from a process stream are "dilute", i.e., present in the stream at relatively low concentrations. The system must also be essentially isothermal which is generally the case for liquid-liquid extractors but not always so with gas absorbers. Also, the vapor-liquid or liquid-liquid equilibrium should not be a strong function of composition. This requirement is satisfied for dilute solutions due to the small concentration range of either an absorbed or extracted component.

Consider the staged absorber shown in Figure E-1. The column contains N stages (6 are shown) that, for the moment, we will take to be 100% efficient. Vapor feed enters below the bottom tray of the column (Tray #1) and liquid absorbent enters on the top or Nth tray. Yin is the mol fraction in the feed of a typical component being absorbed; Yout is the mol fraction of that component leaving the column. Similarly, Xin and Xout are the mol fractions of that component in the liquid entering and leaving the column.

There are two cases of interest. For the first, the rating case, we are told how many trays there are in the column (N), what the vapor and liquid feed rates (V and L) are, and what the inlet compositions Yin and Xin are. The problem is to determine the separation performance of the column, i.e., what are Yout and Xout? For the second case, that of design, we are told what V, Yin, and Xin are as well as the value of Yout that the column is to achieve. The problem is to determine suitable values of L and N.

A. The Kremser Model

Let us start with a mass balance around the nth tray for a typical component. This gives
If the tray is at thermodynamic equilibrium, then

\[ \text{(2)} \quad y_n = k_n x_n \]

Substituting Eqn. 2 into Eqn. 1 gives

\[ \text{(3)} \quad V_{n-1} k_{n-1} x_{n-1} (V_n k_n + L_n) x_n + L_{n+1} x_{n+1} = 0 \]

In general we would also need an energy balance and an overall mass balance to complete the performance equations for the tray. We eliminate this requirement by making some simplifying assumptions:

a) \( y_n \ll 1.0 \) and \( x_n \ll 1.0 \), i.e., the feeds to the column are dilute with respect to the components to be transferred from one phase to the other. Therefore there will be a negligible change in \( V \) and \( L \) from tray to tray. As a result, we have

\[ \text{(4)} \quad V_n = V_{n-1} = V \quad \text{and} \quad L_n = L_{n+1} = L \]

i.e., \( V \) and \( L \) are constant from tray to tray.

b) The column is isothermal and isobaric. This means that \( k_n \) does not vary from tray to tray, i.e., \( k_n = k \).

With these assumptions, Eqn. 3 becomes

\[ \text{(5)} \quad S x_{n-1} (S + 1) x_n + x_{n+1} = 0 \]

Where \( S = V k / L \). This quantity is known as the stripping factor for the component in question.

Eqn. 5 is a difference equation. Before we can solve it, we must establish the boundary conditions which are, for the vapor feed to the bottom of the column (\( n=0 \)),

\[ x_0 = y_{in} / k \]

And, for the liquid feed to the top of the column (\( n=N+1 \)),

\[ x_{N+1} = y_{top} / k \]
\[x_{N+1} = x_{\text{in}}.\]

To solve Eqn. 5 we assume a solution of the form

\[x_n = c \lambda^n\] (6)

Substituting Eqn. 6 into Eqn. 5 and collecting terms gives a characteristic equation of the form

\[\lambda^2 - (S + 1) \lambda + S = 0\] (7)

Solving Eqn. 7 for its characteristic values gives \(\lambda_1 = 1\) and \(\lambda_2 = S\). Our assumed solution (Eqn. 6) now has the form

\[x_n = c_1 \lambda_1^n + c_2 \lambda_2^n\] or

\[x_n = c_1 + c_2 S^n\] (8a) (8b)

Applying the boundary conditions, solving for \(c_1\) and \(c_2\), and collecting terms gives

\[x_n = \frac{S^{N+1} - S^n}{S^{N+1} - 1} \frac{y_{\text{in}}}{k} + \frac{S^n - 1}{S^{N+1} - 1} x_{\text{in}}\] (9)

We are generally interested how much is absorbed, namely the difference between \(y_{\text{out}} (= y_N)\) and \(y_{\text{in}}\). This is given by

\[y_{\text{out}} = S^N \frac{S - 1}{S^{N+1} - 1} y_{\text{in}} + \frac{S^n - 1}{S^{N+1} - 1} k x_{\text{in}}\] (10)

Now, let us define a fractional removal factor as

\[\Phi = \frac{y_{\text{out}} - y_{\text{in}}}{k x_{\text{in}} - y_{\text{in}}}\] (11)

Rearranging Eqn. 10 gives
First, let us look at some limiting cases for Eqn. 10 as we let the number of trays increase to infinity. For $S < 1$, we have

\[
\lim_{N \to \infty} y_{\text{out}} \to 0 + k \ x_{\text{in}}
\]

For $S > 1$, we have

What can we learn from these limiting cases? From Eqn. 13 we see that if we want to reduce the amount of material in the vapor feed to zero, $S$ must be $< 1$. In this case, the amount of the component in question in the vapor leaving the column will be equal to the amount in equilibrium with the liquid feed to the top of the column. If we are using a "clean" absorbent, then $x_{\text{in}} = 0$ and we can theoretically have a clean vapor leaving the column. However, economics and environmental considerations dictate that we reuse the absorbent. This means separating the absorbed material from it and recycling it back to the absorber. Since no separation using finite means can be 100% complete, $x_{\text{in}}$ will generally not be zero.

If, instead of absorbing material from a vapor, we want to remove it from a liquid using a vapor (a procedure known as stripping), then Eqn. 14 provides guidance. This shows that if we have a clean stripping vapor ($y_{\text{in}} = 0$), then we can theoretically reduce the amount of material in the liquid leaving the column to zero. Otherwise, $x_{\text{out}}$ is in equilibrium with $y_{\text{in}}$.

**B. Absorber Design**

1) Selection of Operating Conditions

The value of $S$ can be set by the designer by adjusting any of a number of variables. Usually $V$ is set by process considerations. So if we want to enhance absorption, we must make $S < 1$ by either making $k$ sufficiently small or $L$ sufficiently large. $L$ can be made large up to a point. For a given $V$ there is a limit on how large $L$ can be without causing mal-operation of the column.
k can be made small by raising the pressure and in some cases by lowering the temperature. If the component being absorbed is subcritical and obeys Raoult's Law with respect to the absorbent, then

\[ (15) \quad k = \frac{P^0(T)}{P_{col}} \]

where \( P^0(T) \) = the vapor of the absorbed component. It is obvious that \( k \) can be reduced by either increasing the column operating pressure \( P_{col} \) or by reducing the temperature \( T \) of the absorbent. Generally the available feed pressure will determine the column operating pressure; it is seldom economic to compress the feed to a higher pressure. The absorbent temperature cannot generally be reduced below a the available cooling water temperature plus a suitable approach temperature. Otherwise refrigeration will be required which is expensive. Thus, it is clear that design of an absorber system is requires the evaluation of alternatives and some design optimization.

2) Tray Requirements

If the absorber performance is specified, then fractional removal factor is known and Eqn. 12 can be solved for \( N \). This gives a familiar form of the Kremser Equation

\[ (16) \quad N = \frac{\ln \left[ \frac{\phi - I}{\phi S - I} \right]}{\ln S} \]

Let us examine how the choice of \( S \) affects the tray requirements as a function. Table 1 gives an idea of the relationship.

<table>
<thead>
<tr>
<th>( S )</th>
<th>0.9</th>
<th>0.95</th>
<th>0.99</th>
<th>0.999</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.95</td>
<td>7.2</td>
<td>13.0</td>
<td>34.8</td>
<td>76.6</td>
</tr>
<tr>
<td>0.90</td>
<td>6.1</td>
<td>10.1</td>
<td>22.7</td>
<td>43.8</td>
</tr>
</tbody>
</table>

Table 1.
We see that for high fractional removals ($\phi > 0.99$), the tray requirements are quite high for $S > 0.7$ to 0.8. Since tray efficiencies for absorption are lower than those for distillation (25 to 40% is typical), ideal tray requirements should not exceed 15 to 25 if the column height is not to be excessive (> 100 ft at a tray spacing of 2.0 ft.). Thus adjusting $L$ to give $S \leq 0.8$ is useful rule of thumb for choosing a reasonable starting point for a design.

The effect of tray efficiency can also be included in the Kremser model. If we use the Murphree Vapor Phase efficiency $E_{MV}$ defined as

$$E_{MV} = \frac{y_n - y_{nl}}{k \ x_n - y_{nl}}$$

we can solve for the actual tray requirement $N_{\text{Actual}}$ and the overall column efficiency $E_{O}$ which gives

$$E_{O} = \frac{N_{\text{Ideal}}}{N_{\text{Actual}}} = \frac{\ln[(1 - E_{MV}) + S \ E_{MV}]}{\ln S}$$

where $N_{\text{Ideal}}$ is given by Eqn. 16. We see that the actual tray requirement is independent of and is a function only $S$ and $E_{MV}$. The overall column efficiency $E_{O}$ as a function of these last two variables is shown in Table 2.

<table>
<thead>
<tr>
<th>$E_{MV}$</th>
<th>0.95</th>
<th>0.9</th>
<th>0.8</th>
<th>0.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.9</td>
<td>0.898</td>
<td>0.895</td>
<td>0.889</td>
<td>0.882</td>
</tr>
<tr>
<td>0.8</td>
<td>0.796</td>
<td>0.791</td>
<td>0.781</td>
<td>0.769</td>
</tr>
<tr>
<td>0.5</td>
<td>0.494</td>
<td>0.456</td>
<td>0.472</td>
<td>0.456</td>
</tr>
<tr>
<td>0.3</td>
<td>0.295</td>
<td>0.289</td>
<td>0.277</td>
<td>0.264</td>
</tr>
</tbody>
</table>

We see that there is not much difference between $E_{MV}$ and $E_{O}$ over most of this table. The maximum error ($S=0.6$, $E_{MV}=0.3$) is 12%. Thus, for preliminary design, setting $E_{O} = E_{MV}$ will not introduce a significant error.

C. Absorber-Stripper Systems
Absorbing a component from a gas stream into a liquid (mass separating agent or MSA) merely transfers a separation problem from one stream to another if our goal is to recover the absorbed component in a relatively pure form. Even if all we want to do is throw it away or burn it, we still have the problem of dealing with the MSA. The flow rate of this stream will generally be several times larger than the molar flow rate of the component being absorbed. If it is an expensive solvent, we must reuse it for our absorption system to be economic. This means separating most of the absorbed component from it before recycling it back to the absorber. Even if the MSA is water and relatively inexpensive, we may still have to reuse it for environmental reasons if the material being absorbed is toxic, carcinogenic, or merely smells bad. The question arises as to what is the most economical separation system for this task.

![Figure E-2](image)

The two most common choices are stripping and distillation. Since distillation is a separate subject, we will only consider stripper in these notes. A schematic diagram of an absorber-stripper system is shown in Figure E-2. The absorber is similar to that shown in Fig. E-1 except that the liquid stream leaving the bottom of the column goes to the stripper. A stripping vapor of flow rate $V_S$ is used to strip the component of interest from the liquid feed to the stripper.

Now, having a stripper will do little good if the concentration of the absorbate in the vapor leaving the stripper is not considerably higher than it is in the feed to the absorber. We have already established that the absorber must be designed so that its stripping factor $S_A < 1$. This sets a value for $L$. Therefore, the first design decision for the stripper is the value of $V_S$.

Let us assume that the Kremser model applies to the stripper as well as the absorber. As in the case of the absorber itself, let us look at the limiting case of infinite trays. From Eqn. 14, $X_{S\text{out}} = 0$ for clean stripping vapor ($Y_{\text{Sin}} = 0$) if $S_S > 1$. Now, if we use the same rule of thumb for $S_S$ as we do for $S_A$, $S_S 1/0.8 = 1.25$. Therefore $S_S/S_A = 1.25/0.8 = 1.6$. 

104
This means that

\[(19) \quad \frac{V_S}{V_A} \cdot \frac{K_S}{K_A} = 1.6\]

Thus, for \(V_S\) to be much less than \(V_A\), \(K_S\) must be much greater than \(K_A\). How can this be accomplished? Two of the most commonly used ways are by pressure swing and by thermal swing, quite often a combination of both.

Let us consider pressure swing first. Suppose that the absorber operates at a pressure of 10 atm and we choose to operate the stripper at 1 atm. Then, from Eqn. 15, \(K_S = 10 K_A \) so \(V_S = 0.16 V_A\). This is an improvement but not an overwhelming one. We have only increased the concentration of the absorbate by a factor of 6.25. It is obvious that, unless the absorber pressure is very high, stripping by pressure swing only is not very effective.

Suppose that the absorber is run at a temperature just above that of cooling water, say 30°C, and that we heat the bottoms of the absorber to a much higher temperature before feeding it to the stripper. If the absorbate is subcritical and follows Raoult's Law, we would expect a substantial increase in \(K\) going from the absorber to the stripper. As an example, suppose we are absorbing methanol in water and we operate the absorber at 30°C and the stripper at 85°C. Then \(K\) in the absorber will be about 0.25 atm while that in the stripper will be about 2.0 atm, an improvement of a factor of 8.0. If we operate the stripper almost at the atmospheric boiling point of water, then the improvement will be closer to a factor of 15.0.

If the absorber also operates at 10 atm, then the overall improvement by the combination of pressure and temperature swing is on the order of 50 to 100 depending upon the operating temperature of the stripper.

Recovering the absorbate from the stripping vapor may still be a problem. If the amount of vapor is small enough, the absorbate can be recovered by condensation if that is our purpose. On the other hand, if the absorber is used for pollution control, the overhead from the stripper can be sent directly to an incinerator to recover the heating value of the absorbate. There are many possibilities.

It should be kept in mind that the above analysis is based on the limiting behavior of absorbers and strippers for infinite trays. Since the number of trays must be finite, there will be some unstripped absorbate in the bottoms of the stripper, some of which will, on recycle, appear in the overhead of the absorber (refer to Eqn. 10). The amount left in the stripper bottoms becomes another design decision subject to optimization.