CHAPTER 12

Analysis of the Degrees of Freedom in Steady-State Processes

12.1 Main Concepts 684

Your objectives in studying this chapter are to be able to

1. Identify the names and numbers of variables in the streams entering and leaving a processing unit, and the variables associated with the unit itself
2. Determine the number of independent equations for each processing unit, the constraints
3. Calculate the number of degrees of freedom (decision variables) for single units and combinations of units both without and with a reaction taking place
4. Specify the values of variables equal to the number of degrees of freedom for a unit

Now that you have accumulated some experience in making both material and energy balances, it is time to apply this knowledge to more complex problems. You have already encountered some simple examples of combined material and energy balances, as, for example, in the calculation of the adiabatic reaction temperature, where a material balance provides the groundwork for the implementation of an energy balance. An important aspect of solving complex problems is the determination that the degrees of freedom are indeed zero; that is, the problem is properly and completely specified.

Looking Ahead

In this chapter we show how to calculate the degrees of freedom for a continuous steady-state process.

12.1 Main Concepts

An important aspect of combined material and energy balance problems is how to ensure that the process equations or sets of modules are determinate, that is, have at least one solution, and ideally no more than one solution. The question is: How many variables are unknown and consequently must have their values specified in any problem? The **number of degrees of freedom** is the number of variables in a set of independent equations to which values must be assigned so that the equations can be solved.

Let N_d = number of degrees of freedom, N_v = number of variables, and N_e = number of equations (material balances, restrictions, specifications, constraints). Then for N_e independent equations in general

$$N_d = N_v - N_e \tag{12.1}$$

and we conclude that $N_v - N_e$ variables must be specified **as long as the N_e equations are still independent.** You do not have to write down the equations during the analysis but just identify them. Whether the equations are linear or nonlinear makes no difference.

In this chapter the analysis of the degrees of freedom for a process assumes that the process is a steady-state flow process as commonly assumed in design. If operations or control is of interest, you would base the analysis on an unsteady process in which the accumulation term would be taken into consideration. (Also, not all of the variables in a process can be manipulated, so the selection of which variables to specify is limited.)

Both extensive and intensive variables are included in the analysis in contrast with the degrees of freedom obtained from application of the phase rule in Chapter 8, which treats only intensive variables. What kinds of variables do you have to consider? Typical ones are

1. Temperature
2. Pressure
3. Either mass (mole) flow rate of each component in a stream, or the concentration of each component plus the total flow rate
4. Specific enthalpies (given in terms of temperature and pressure)
5. Heat flow, work (in the energy balance)
6. Recycle ratio
7. Specifications
8. Extent of reaction or fraction conversion

Some variables can be substituted for others, such as temperature and pressure for specific enthalpies, and stream flows for the recycle ratio.

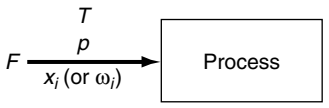


Figure 12.1 Stream variables

Examine the flow stream in Figure 12.1. Two modes of specifying the number of variables associated with a process stream (**stream variables**) exist (we assume the stream is a single phase in which no reactions occur; with more than one phase, each phase would be treated as a separate stream):

Using moles (or mass) flow rate		**Using compositions and total flow rate**	
	No.		No.
Temperature (T)	1	Temperature (T)	1
Pressure (p)	1	Pressure (p)	1
Component flow rates (n_i or m_i)	N_{sp}	Compositions (x_i or ω_i)	$N_{sp} - 1$
		Total flow rate (F)	1
Total	$N_{sp} + 2$		$N_{sp} + 2$

where N_{sp} is the number of **components (species)** in the stream. The count for the number of compositions is $N_{sp} - 1$ and not N_{sp} because of the implicit constraint that the sum of the mole (or mass) fractions is equal to 1.

Thus, you can conclude that the number of variables N_v needed to specify the condition of a stream completely is given by

$$N_v = N_{sp} + 2 \tag{12.2}$$

You should keep in mind that in a binary system, for example, in which one stream component is zero, for consistency you would count $N_{sp} = 2$ with the one component having a zero value treated as a constraint.

What kinds of equations are involved in the analysis of the degrees of freedom? A list would include

1. Independent material balances for each species (a total balance could be substituted for one species balance)
2. Energy balance
3. Phase equilibria relations, that is, equations that give the compositions between one species that exists in two (or more) phases; refer to Chapter 8
4. Chemical equilibrium relations

5. Implicit relations, such that the concentration of a species is zero in a stream
6. Explicit relations, such that a given fraction of a stream condenses
7. Extent of reaction or fraction conversion specified

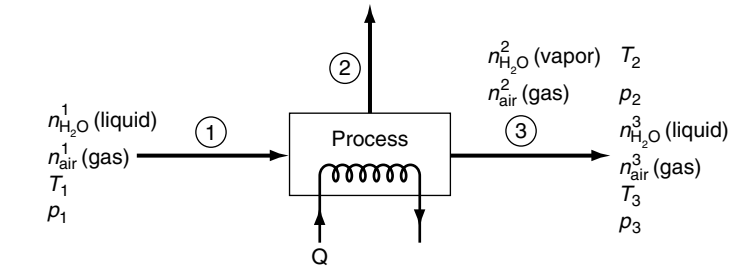
To illustrate an analysis for the degrees of freedom, examine Figures 12.2a and b, which show a simple steady-state isothermal, isobaric process involving three streams plus heat transfer. The count of the variables and equations is as follows:

Variables:

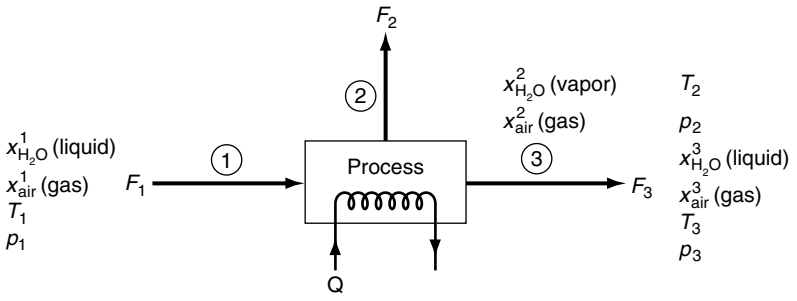
$(N_{sp} + 2) \times 3 = (2 + 2) \times 3 =$	12
Q	1
Total	13

Equations:

Material balances	2
Energy balance	1



a.



b.

Figure 12.2 A simple process with three streams. In Figure 12.2a the stream flows are expressed as mole flow rates, and in Figure 12.2b the stream flow is the total flow and the compositions of the species are given in mole fractions.

Phase equilibrium for H_2O	1
T is the same in all 3 streams	
$(T_1 = T_2 = T_3)$ 2 independent equations	2
p is the same in all 3 streams	
$(T_1 = T_2 = T_3)$ 2 independent equations	2
Total	8

Degrees of freedom:

$13 - 8 =$	5

The way in which the compositions are specified makes no difference in the analysis.

We now take up five simple processes in Example 12.1 and evaluate the number of degrees of freedom for each.

Example 12.1 Determining the Degrees of Freedom in a Process

We shall consider five typical processes, as depicted by the respective figures below, and for each ask the question: How many variables have to be specified [i.e., what are the degrees of freedom (N_d)] to make the problem of solving the combined material and energy balances determinate? All of the processes will be steady-state, and the entering and exit streams are single-phase streams.

a. Stream splitter (Figure E12.1a): We assume that $Q = W = 0$, and that the energy balance is not involved in the process. By implication of a splitter, the temperatures, pressures, and compositions of the inlet and outlet streams are identical. The count of the total number of variables, total number of constraints, and degrees of freedom is as follows:

Total number of variables		
$N_v = 3(N_{sp} + 2) =$	$3(N_{sp} + 2)$	
Number of independent equations		
Material balances	1	
Compositions of Z, P_1, and P_2		
are the same	$2(N_{sp} - 1)$	
$T_{P_1} = T_{P_2} = T_Z$	2	
$p_{P_1} = p_{P_2} = p_Z$	2	
Total number of degrees of freedom		$2N_{sp} + 3$ $N_{sp} + 3$

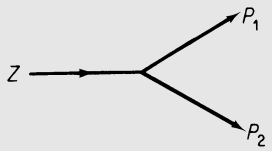


Figure E12.1a

(*Continues*)

Example 12.1 Determining the Degrees of Freedom in a Process (*Continued*)

Did you note that we counted N_{sp} material balances only once? Why? Let us look at some of the balances:

$$\text{Component 1: } Zx_{1Z} = P_1x_{1P_1} + P_2x_{1P_2}$$

$$\text{Component 2: } Zx_{2Z} = P_1x_{2P_1} + P_2x_{2P_2}$$

etc.

If $x_{1Z} = x_{1P_1} = x_{1P_2}$ and the same is true for x_2, and so on, only one independent material balance exists.

Do you understand the counts resulting from making the compositions equal in Z, P_1, and P_2? Write down the expressions for each component: $x_{iZ} = x_{iP_1} = x_{iP_2}$. Each set represents $2N_{sp}$ constraints. But you cannot specify every x_i in a stream, only $N_{sp} - 1$ of them. Do you remember why?

To make the problem determinate we might specify the values of the following decision variables:

Flow rate Z	1
Composition of Z	$N_{sp} - 1$
T_Z	1
p_Z	1
Ratio of split $\alpha = P_1/P_2$	1
Total number of degrees of freedom	$N_{sp} + 3$

b. Mixer (Figure E12.1b): For this process we assume that $W = 0$, but Q is not.

Total number of variables (3 streams + Q)	$3(N_{sp} + 2) + 1$
Number of independent equations	
Material balances	N_{sp}
Energy balance	1

$$\text{Total number of degrees of freedom} = 3(N_{sp} + 2) + 1 - (N_{sp} + 1) = 2N_{sp} + 6$$

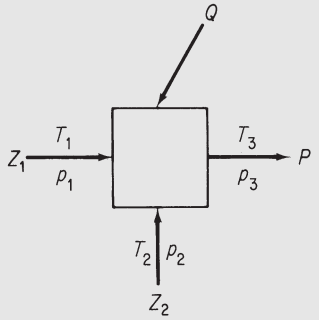


Figure E12.1b

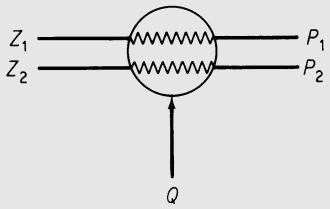


Figure E12.1c

c. Heat exchanger (Figure E12.1c): For this process we assume that $W = 0$ (but not Q).

Total number of variables		
$N_v = 4(N_{sp} + 2) + 1 =$		$4N_{sp} + 9$
Number of independent equations		
Material balances (streams 1 and 2)	2	
Energy balance	1	
Composition of inlet and outlet streams the same	$2(N_{sp} - 1)$	$2N_{sp} + 1$
Total number of degrees of freedom =		$2N_{sp} + 8$

One might specify four temperatures, four pressures, $2(N_{sp} - 1)$ compositions in Z_1 and Z_2, and Z_1 and Z_2 themselves to use up $2N_{sp} + 8$ degrees of freedom.

d. Pump (Figure E12.1d): Here $Q = 0$ but W is not.

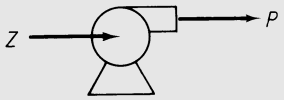


Figure E12.1d

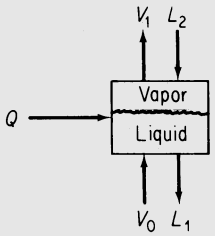


Figure E12.1e

Total number of variables		
$N_v = 2(N_{sp} + 2) + 1$		$2N_{sp} + 5$
Number of independent equations		
Material balances	1	
Composition of inlet and outlet streams the same	$N_{sp} - 1$	
Energy balance	1	$N_{sp} + 1$
Total number of degrees of freedom		$N_{sp} + 4$

e. Two-phase well-mixed tank (stage) at equilibrium (Figure E12.1e) (L, liquid phase; V, vapor phase): Here $W = 0$. Although two phases exist (V_1 and L_1) at equilibrium inside the system, the streams entering and leaving are single-phase streams. By equilibrium we mean that both phases are at the same temperature and pressure and that an equation is known that relates the composition in one phase to that in the other for each component.

Total number of variables (4 streams + Q)	$4(N_{sp} + 2) + 1$
Number of independent equations	
Material balances	N_{sp}

(*Continues*)

Example 12.1 Determining the Degrees of Freedom in a Process (*Continued*)

Energy balance	1
Composition relations at equilibrium	N_{sp}
Temperatures of the streams V_1 and L_1 in the two phases equal	1
Pressures of the streams V_1 and L_1 in the two phases equal	1

Total number of degrees of freedom $= 4(N_{sp} + 2) + 1 - 2N_{sp} - 3 = 2N_{sp} + 6$

In general you might specify the following variables to make the problem determinate:

Input stream L_2	$N_{sp} + 2$
Input stream V_0	$N_{sp} + 2$
Pressure	1
Q	1
Total	$2N_{sp} + 6$

Other choices are of course possible, but such choices must leave the equality constraints independent.

Example 12.2 Proper Process Specification

Figure E12.2 shows an isothermal separations column. At present the column specifications call for the feed mass fractions to be $\omega_{C_4} = 0.15$, $\omega_{C_5} = 0.20$, $\omega_{iC_5} = 0.30$, and $\omega_{C_6} = 0.35$; the overhead mass fractions to be $\omega_{C_5} = 0.40$ and $\omega_{C_6} = 0$; and the residual product mass fraction to be $\omega_{C_4} = 0$. Unless specified as 0, the component exists in a stream.

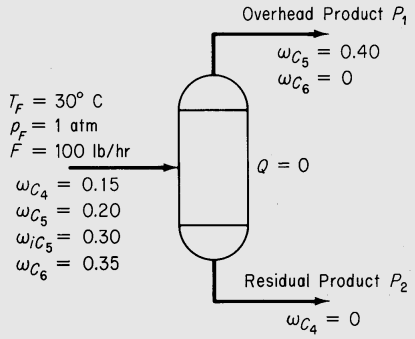


Figure E12.2

Given that $F = 100$ lb/hr, is the separator completely specified; that is, are the degrees of freedom $N_d = 0$? The streams P_1 and P_2 are not in equilibrium.

Solution

First we calculate N_v and then N_e. We will assume that all of the stream temperatures and pressures are identical. Number of variables N_v:

$$N_v = (N_{sp} + 2)(3) = (4 + 2)(3) = \underline{18}$$

Number of restrictions and equations give N_e:

Component mass balances (no reaction) = N_{sp} =	4	
$T_F = T_{P_1} = T_{P_2}$	2	
$p_F = p_{P_1} = p_{P_2}$	2	
Initial column specifications:		
(4 in F, 2 in P_1, and 1 in P_2 plus $T_F = 30°C$ and $p_F = 1$ atm)	9	
Total for N_e		17
Number of degrees of freedom N_d: 18 − 17 =		1

Note that only four factors can be specified in stream F, namely, the rate of F itself and three ωs; one of the ωs is redundant. One more variable must be specified for the process, but one that will not reduce the number of independent equations and restrictions already enumerated.

So far we have examined single units without a reaction occurring in the unit. How is the count for N_d affected by the presence of a reaction in the unit? The way N_v is calculated does not change except to add one extent of reaction variable for each reaction in the minimal set (refer to Chapter 5) if species balances are going to be used. As to N_r, all restrictions are deducted from N_v that represent *independent* restrictions on the unit. Thus the number of equations is not necessarily equal to the number of species (H_2O, O_2, CO_2, etc.) but instead is the number of independent equations that exist determined in the same way as we did in Chapters 3 to 6. Fixed ratios of materials such as the O_2/N_2 ratio in air or the CO/CO_2 ratio in a product gas would be a restriction, as would be a specified conversion fraction or a known molar flow rate of a material. If some degrees of freedom exist still to be specified, improper specification of a variable may disrupt the independence of equations and/or specifications previously enumerated in the enumeration of N_e, so be careful.

Example 12.3 Degrees of Freedom for a Process with a Reaction Taking Place in the System Using Element Balances

A classic reaction for producing H_2 is the so-called "water gas shift" reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Figure E12.3 shows the process data and the given information. How many degrees of freedom remain to be satisfied? For simplicity assume

(*Continues*)

Example 12.3 Degrees of Freedom for a Process with a Reaction Taking Place in the System Using Element Balances (*Continued*)

that the temperatures and pressures of all entering and exit streams are the same and that all streams are gases. The amount of water in excess of that needed to convert all of the CO completely to CO_2 is prespecified. Work = 0.

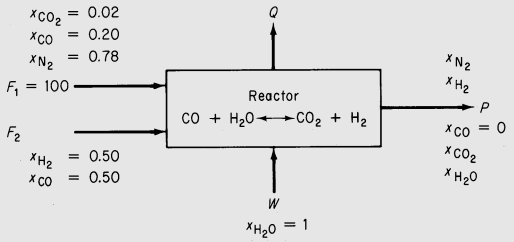


Figure E12.3

Solution

Let us use element material balances rather than species balances in the analysis.

N_v	$= 4(N_{sp} + 2) + 1 = 4(5 + 2) + 1 =$		29
	(+ 1 is for Q)		
N_e	Independent material balances		
	(C, O, N, H)	4	
	Energy balance	1	
	$T_{F_1} = T_{F_2} = T_W = T_P$	3	
	$p_{F_1} = p_{F_2} = p_W = p_P$	3	
	Compositions and flows specified:		
	In F_1 ($x_{H_2O} = x_{H_2} = 0$) including F_1	5	
	In F_2 ($x_{N_2} = x_{CO_2} = x_{H_2O} = 0$)	4	
	In W (all but x_{H_2O} are 0) only 4 of $5x_i$s are independent	4	
	In P ($x_{CO} = 0$)	1	
	Specified W	1	26
	$N_d = 29 - 26 =$		3

In the streams F_2 and W, only four compositions can be specified; a fifth specification is redundant. The total flows are not known. The given value of the excess water provides the information about the reaction products. Certainly, the temperature and pressure need to be specified, absorbing two degrees of freedom. The remaining degree of freedom might be the N_2/H_2 ratio in P, or the value of F_2, or the ratio of F_1/F_2, and so on.

Example 12.4 Degrees of Freedom for a Process Involving Multiple Reactions Using Species Balances

Methane burns in a furnace with 10% excess air, but not completely, so some CO exits the furnace, but no CH_4 exits. The reactions are

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$$
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
$$CO + 0.5O_2 \rightarrow CO_2$$

Carry out a degree-of-freedom analysis for this combustion problem.

Solution

For this example we will use species material balances in the analysis.

Figure E12.4 shows the process; all streams are assumed to be gases. Only two of the reactions are independent. Q is a variable here. For simplicity assume that the entering and exit streams are at the same temperatures and pressures.

$N_v = 3(6 + 2) + 1 + 2 =$		27
(+1 is for Q and +2 for the extent of reactions)		
N_e		
Species material balances	6	
Energy balance	1	
$T_A = T_F = T_P$	2	
$p_A = p_F = p_P$	2	
Compositions specified:		
In A ($N_{sp} - 1$) some 0	5	
In F ($N_{sp} - 1$) some 0	5	
In P	1	11
Percent excess air A:		1
		23

$N_d = 27 - 23 = 4$

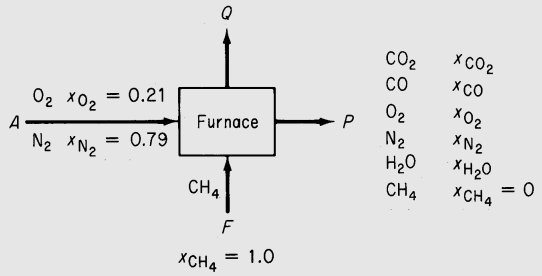


Figure E12.4

To have a well-defined problem you should specify (a) the temperature, (b) the pressure, (c) either the feed rate, or the air rate, or the product rate, and (d) either the CO/CO_2 ratio or the fraction of CH_4 converted to CO or alternatively to CO_2.

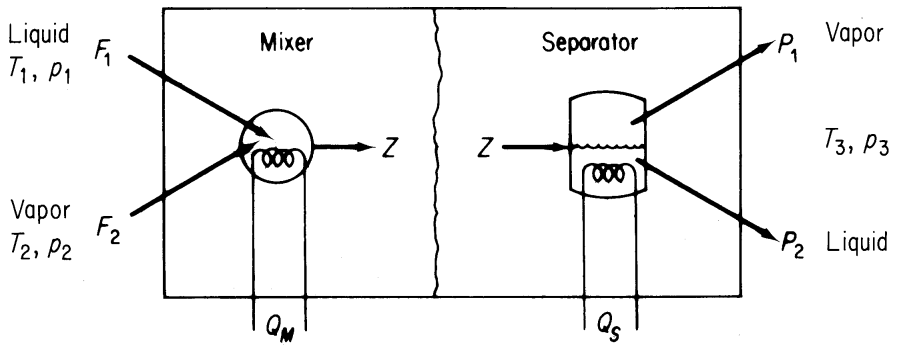


Figure 12.3 Degrees of freedom in combined units

You can compute the degrees of freedom for combinations of like or different simple processes by proper combination of their individual degrees of freedom. In adding the degrees of freedom for units, you must eliminate any double counting for either variables or constraints and take proper account of interconnecting streams whose characteristics are often fixed only by implication.

Examine the mixer-separator in Figure 12.3. For the mixer considered as a separate unit, from Example 12.1b, $N_d = 2N_{sp} + 6$. For the separator, an equilibrium unit:

$N_v = 3(N_{sp} + 2) + 1 =$		$3N_{sp} + 7$
N_e:		
Material balances	N_{sp}	
Equilibrium relations	N_{sp}	
Energy balance	1	
$T_Z = T_{P_1} = T_{P_2}$	2	
$p_Z = p_{P_1} = p_{P_2}$	2	$2N_{sp} + 5$
$N_d = (3N_{sp} + 7) - (2N_{sp} + 5) =$		$N_{sp} + 2$

The sum of the mixer and separator is $3N_{sp} + 8$.

You must deduct redundant variables and add redundant restrictions as follows:

Redundant variables:	
Remove 1 Q	1
Remove Z	$N_{sp} + 2$
Redundant constraints:	
1 energy balance	1

Then $N_d = (3N_{sp} + 8) - (N_{sp} + 3) + 1 = 2N_{sp} + 6$, the same as in Example 12.1e.

Example 12.5 Degrees of Freedom in a System Composed of Several Units

Ammonia is produced by reacting N_2 and H_2:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Figure E12.5a shows a simplified flowsheet. All of the units except the separator and lines are adiabatic. The liquid ammonia product is essentially free of N_2, H_2, and A. Assume that the purge gas is free of NH_3. Treat the process as four separate units for a degree-of-freedom analysis, and then remove redundant variables and add redundant constraints to obtain the degrees of freedom for the overall process. The fraction conversion in the reactor is 25%.

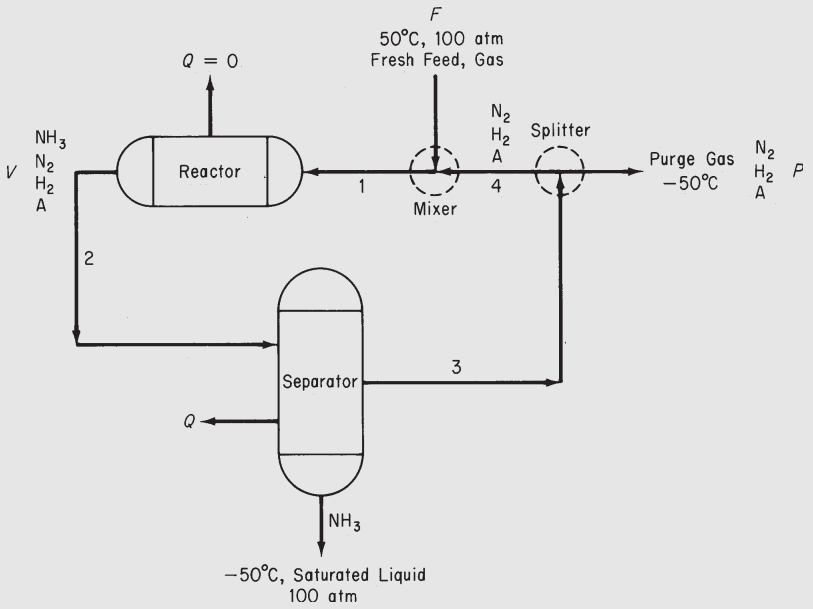


Figure E12.5a

Solution

Mixer:

$N_v = 3(N_{sp} + 2) + 1 = 3(6) + 1 =$	19
N_e:	
Material balances (H_2, N_2, A only)	3
Energy balance	1
Specifications:	
NH_3 concentration is zero	3
$T_P = -50°C$	1
$T_F = 50°C$	1

(*Continues*)

Example 12.5 Degrees of Freedom in a System Composed of Several Units (*Continued*)

Assume that $p_F = p_{\text{mix out}} = p_{\text{split}} = 100$	3	
$Q = 0$	1	13
$N_d = 19 - 13 =$		6

Reactor:

$N_v = 2(N_{\text{sp}} + 2) + 1 = 2(6) + 1 + 1$ (for ξ) =		14
N_e:		
Material balances (H, N, NH_3, A)	4	
Energy balances	1	
Specifications:		
NH_3 entering = 0	1	
$Q = 0$	1	
Fraction conversion	1	
$p_{\text{in}} = p_{\text{out}} = 100$ atm	2	
Energy balance	1	11
$N_d = 14 - 11 =$		3

Separator:

$N_v = 3(N_{\text{sp}} + 2) + 1 = 3(6) + 1 =$		19
N_e:		
Material balances	4	
Energy balance	1	
Specifications:		
$T_{\text{out}} = -50°\text{C}$	1	
$p_r = p_{\text{in}} = p_{NH_3} = 100$	3	
NH_3 concentration is 0 in recycle gas	1	
N_2, H_2, A are 0 in liquid NH_3	3	13
$N_d = 19 - 13 =$		6

Splitter:

$N_v = 3(N_{\text{sp}} + 2) = 3(6) =$		18
N_e:		
Material balances	1	
Specifications:		
NH_3 concentration = 0	1	
Compositions same $2(N_{\text{sp}} - 1)$	6	
Stream temperatures same = $-50°\text{C}$	3	
Stream pressures same = 100 atm	3	14
$N_d = 18 - 14$		4

The total number of degrees of freedom is 19 less the redundant information, which is as follows:

Redundant variables in interconnecting streams being eliminated:

Stream 1: (4 + 2) =	6
Stream 2: (4 + 2) =	6
Stream 3: (4 + 2) =	6
Stream 4: (4 + 2) =	6
	24

Redundant constraints being eliminated:

Stream 1:	
NH_3 concentration = 0	1
p = 100 atm	1
Stream 2:	
p = 100 atm	1
Stream 3:	
NH_3 concentration = 0	1
p = 100 atm	1
$T = -50°$ C	1
Stream 4:	
NH_3 concentration = 0	1
$T = -50°$ C	1
p = 100 atm	1
	9

Overall the number of degrees of freedom should be

$$N_d = 19 - 24 + 9 = 4$$

We can check the count for N_d by making a degree-of-freedom analysis about the entire process as follows:

Examine Figure E12.5b.

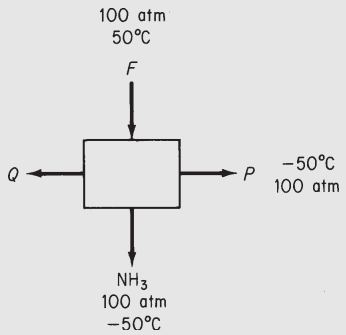


Figure E12.5b

(*Continues*)

Example 12.5 Degrees of Freedom in a System Composed of Several Units (*Continued*)

$N_v = 3(4 + 2) + 1 + 1$ (for ξ) =		20
N_e:		
Material balances (H_2, N_2, NH_3, A)	4	
Energy balance	1	
Specifications:		
Stream F ($T = 50°C$, $p =$ 100 atm, $NH_3 = 0$)	3	
NH_3 stream ($T = -50°C$, $p = 100$ atm, three components have 0 concentration)	5	
Purge stream ($T = -50°C$, $p = 100$ atm, $NH_3 = 0$)	3	16
$N_d = 20 - 16$ =		4

We do not have the space to illustrate additional combinations of simple units to form more complex units, but Kwauk[1] prepared several excellent tables summarizing the variables and degrees of freedom for distillation columns, absorbers, heat exchangers, and the like. Also read the references at the end of this chapter.

Looking Back

In this chapter we described how to determine the number of degrees of freedom involved in a process, that is, the number of additional values of variables that have to be specified to get a solution to a problem.

Self-Assessment Test

Questions

1. Is there any difference between the number of species present in a process and the number of components in the process?
2. Why are there $N_{sp} + 2$ variables associated with each stream?
3. Determine the number of degrees of freedom for a still (see Figure SAT12.1P3).

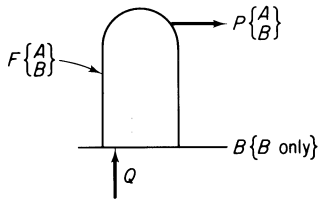


Figure SAT12.1P3

[1]M. Kwauk, *AIChE J.*, **2**, 2 (1956).

4. Determine the number of degrees of freedom in the following process (Figure SAT12.1P4):

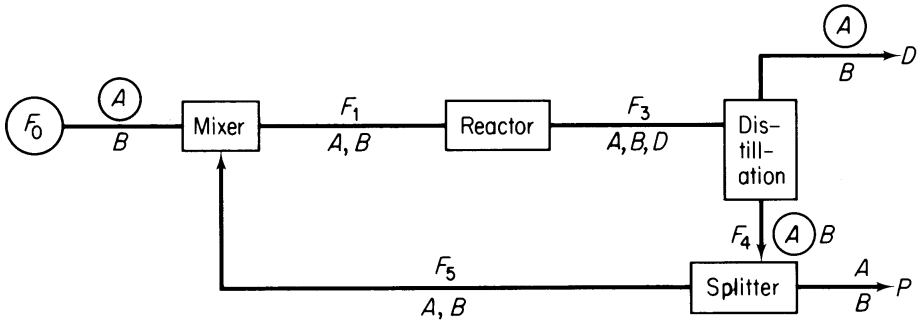


Figure SAT12.1P4

The encircled variables have known values. The reaction parameters in the reactor are known as the fraction split at the splitter between F_4 and F_5. Each stream is a single phase.

5. Figure SAT12.1P5 represents the schematic flowsheet of a distillation tower used to recover gasoline from the products of a catalytic cracker. Is the problem completely specified; that is, is the number of degrees of freedom equal to zero for the purpose of calculating the heat transfer to the cooling water in the condenser?

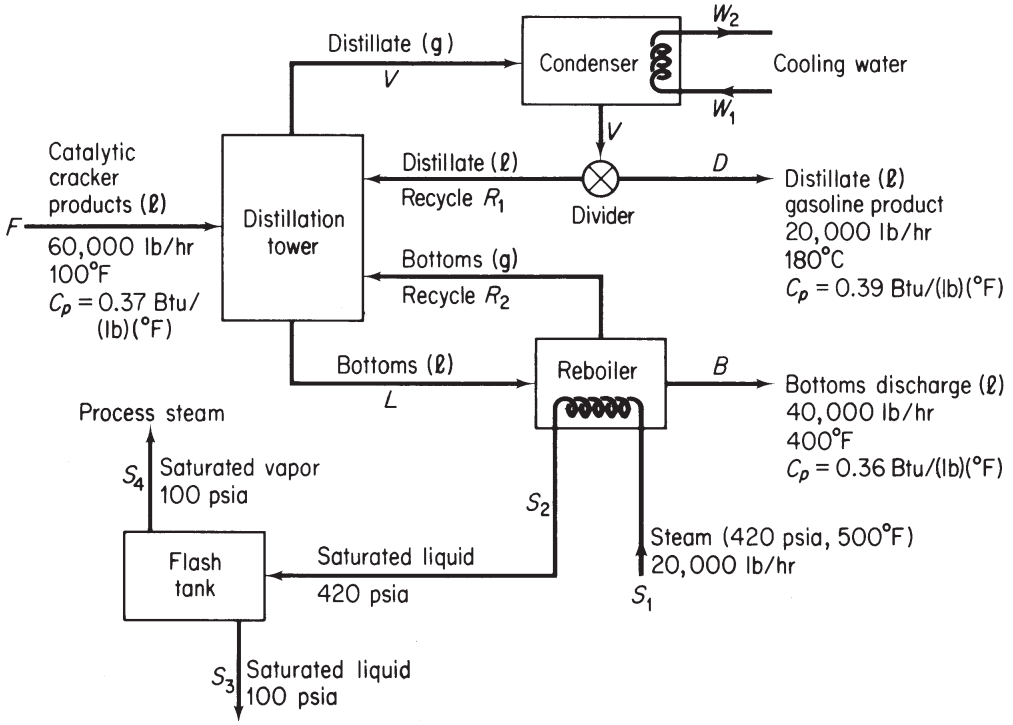


Figure SAT12.1P5

Thought Problems

1. If one or more of the variables in a process can take on only integer values (such as number of stages in a column or number of reactors in a series of reactors), will the analysis of degrees of freedom have to be changed?
2. What other variables in some processes might have to be included in the count of variables for a stream to add to $(N_{sp} + 2)$?

Discussion Question

How should a computer code handle the calculation of the degrees of freedom so that a naive user does not overspecify or underspecify the problem?

Supplementary References

Pham, Q. T. "Degrees of Freedom of Equipment and Processes," *Chem. Eng. Sci.,* **49,** 2507 (1994).

Ponton, J. W. "Degrees of Freedom Analysis in Process Control," *Chem. Eng. Sci.,* **49,** 2089 (1994).

Smith, B. D. *Design of Equilibrium Stage Processes,* Chapter 3, McGraw-Hill, New York (1963).

Sommerfeld, J. T. "Degrees of Freedom and Precedence Orders in Engineering Calculations," *Chem. Eng. Educ.,* 138 (Summer, 1986).

Problems

Problems in this chapter will not be rated according to the degree of difficulty.

12.1 Determine the number of degrees of freedom for the condenser shown in Figure P12.1.

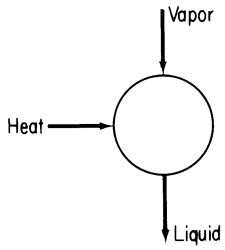


Figure P12.1

12.2 Determine the number of degrees of freedom for the reboiler shown in Figure P12.2. What variables should be specified to make the solution of the material and energy balances determinate?

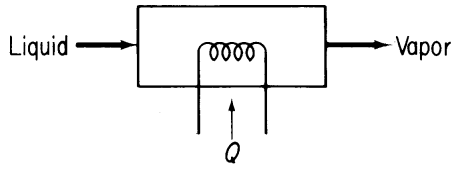


Figure P12.2

12.3 How many variables must be specified for the furnace shown in Figure P12.3 to absorb all the degrees of freedom?

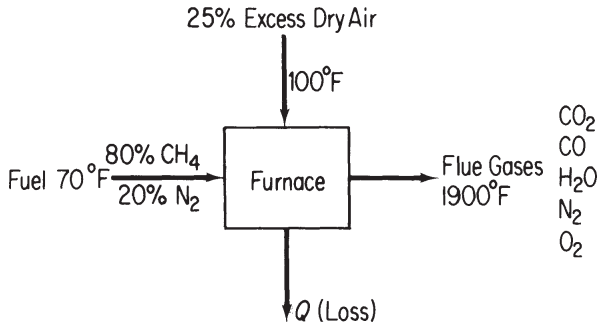


Figure P12.3

12.4 Figure P12.4 shows a simple absorber or extraction unit. S is the absorber oil (or fresh solvent), and F is the feed from which material is to be recovered. Each stage has a Q (not shown); the total number of equilibrium stages is N. What is the number of degrees of freedom for the column? What variables should be specified?

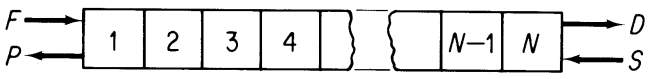


Figure P12.4

12.5 In a reactor model, rather than assume that the components exit from the reactor at equilibrium, an engineer will specify the r independent reactions that occur in the reactor, and the extent of each reaction, ξ_i. The reactor model must also provide for heating or cooling. How many degrees of freedom are associated with such a reactor model? See Figure P12.5.

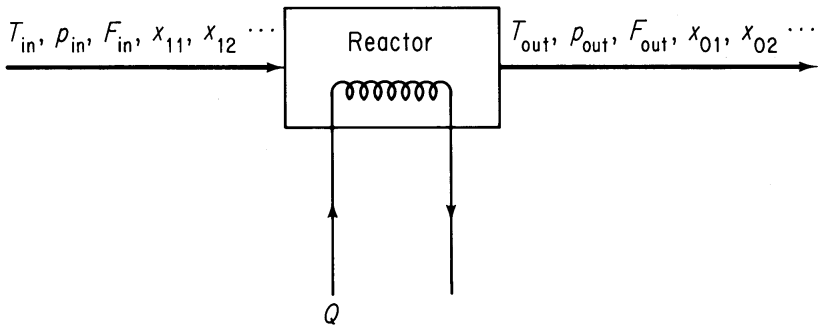


Figure P12.5

12.6 Set up decomposition schemes for the processes shown in Figure P12.6. What additional variables must be specified to make the system determinate if (a) the feed conditions are known, or (b) the product conditions are specified?

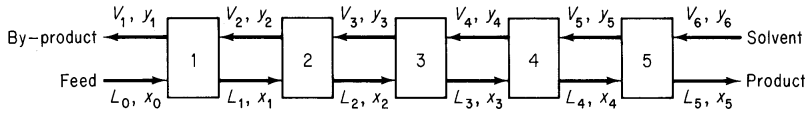


Figure P12.6

12.7 Determine whether or not the following problems are determinate in the sense that all of the values of the material flows can be calculated.

a. A vapor mixture containing 45 wt % ammonia, the balance being water, and having an enthalpy of 1125 Btu/lb is to be fractioned in a bubble-cap column operating at a pressure of 250 psia. The column is to be equipped with a total condenser. The distillate product is to contain 99.0 wt % ammonia and the bottom product is to contain 10.0 wt % ammonia. The distillate and the reflex leaving the condenser will have an enthalpy of 18 Btu/lb (Figure P12.7a).

b. An engineer designed an extraction unit (Figure P12.7b) to recover oil from a pulp using alcohol as a solvent. The inerts refer to oil-free and solvent-free pulp. Several of the streams are shown as F_0 and F_1. Notice

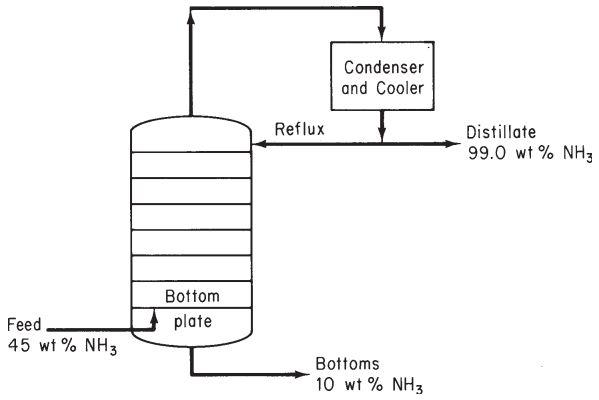


Figure P12.7a

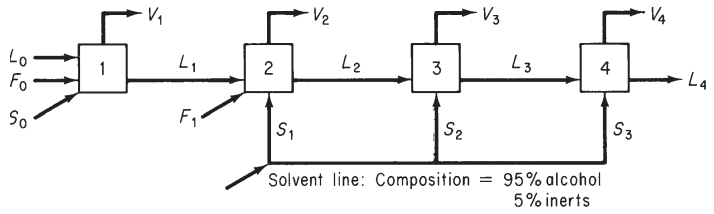


Figure P12.7b

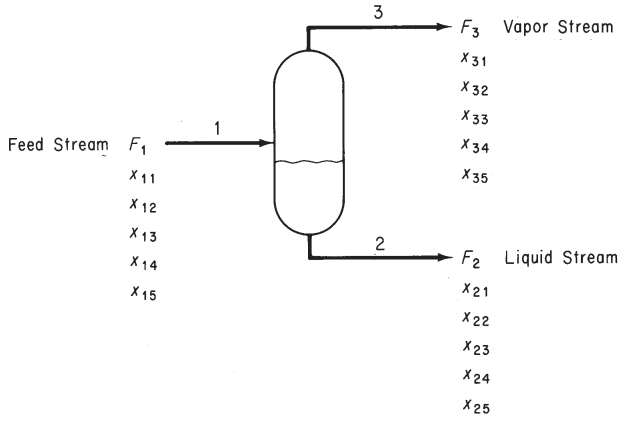
that the extracts from the first two stages were not clear but contained some inerts. (Both V_1 and V_2 contain all three components: oil, solvent, and inerts.) Equal amounts of S_1 and L_1 were added to stage 2. There are 2 lb of L_2 for each pound of V_2 leaving the second stage.

The raffinate from stage 1, L_1, contains 32.5% alcohol, and also in this same stream the weight ratio of inerts to solution is 60 lb inert/100 lb solution. The remaining raffinate streams, L_2, L_3, and L_4, contain 60 lb inert/100 lb alcohol. The L_2 stream contains 15% oil.

12.8 Examine Figure P12.8. Values of F_1, x_{11}, x_{12}, x_{13}, x_{14}, and x_{15} are known. Streams F_2 and F_3 are in equilibrium, and the three streams all have the same (known) temperatures and pressures. Is the problem completely specified, underspecified, or overspecified? Assume that the values of K in the equilibrium relations can be calculated from the given temperatures and pressures.

12.9 Book[2] describes a mixer–heat exchanger section of a monoethylamine plant that is illustrated in Figure P12.9 along with the notation. Trimethylamine recycle enters in stream 4, is cooled in the heat exchanger, and is mixed with

[2]N. L. Book, *Structural Analysis and Solution of Systems of Algebraic Design Equations*, Ph.D. dissertation, University of Colorado (1976).



Description of the variables:

F_i – Molar flow for i^{th} stream

x_{ij} – Mole fraction of j^{th} component in i^{th} stream

K_j – Phase–equilibrium coefficient for the j^{th} component

The design variables are:

The Feed Stream, F_1, x_{11}, x_{12}, x_{13}, x_{14}

The Phase–Equilibrium coefficients, K_1, K_2, K_3, K_4, K_5

Figure P12.9

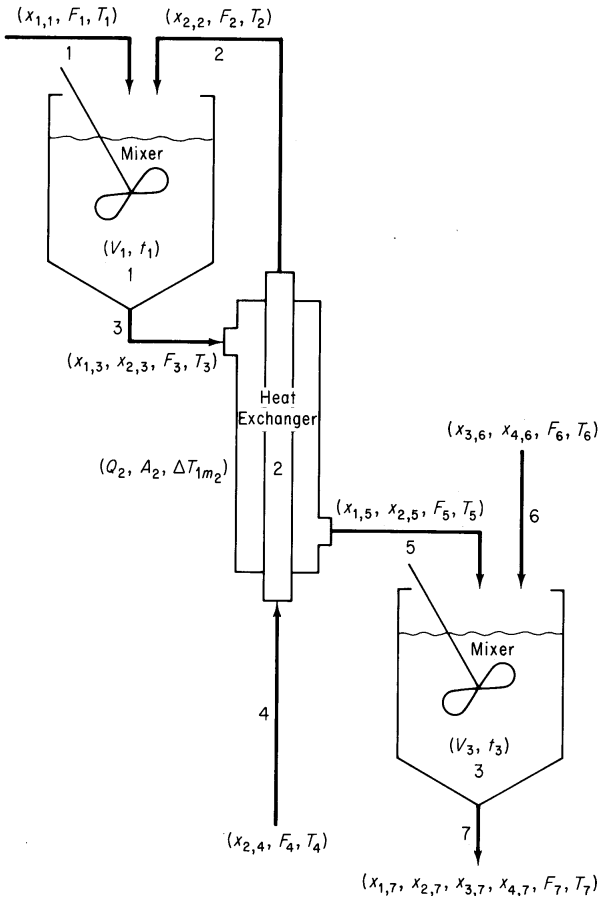


Figure P12.10

water from stream 1 in mixer 1. The trimethylamine-water mixture is used as the cold-side fluid in the heat exchanger and is then mixed with the ammonia-methanol stream from the gas absorber in mixer 3. The mixture leaving mixer 3 is the reaction mixture which feeds into the preheater of the existing plant.

Table P12.9 lists the 31 equations that represent the process in Figure P12.10. C_i is a heat capacity (a constant), F_i a flow rate, A area (a constant), ΔT_{lm} a long mean temperature difference

$$\frac{(T_4 - T_5) - (T_2 - T_3)}{\ln[(T_4 - T_5)/(T_2 - T_3)]}$$

U is a heat transfer coefficient (a constant), V_i a volume, y_i the molar flow rate of component i, x_i the mole fraction of component i, Q the heat transfer rate, and ρ_i the molar density (a constant). The question is: How many degrees of freedom exist for the process?

Table P12.9 List of Equations to Model the Process

Material Balance Equations
Mole fraction equations
1. $x_{1,1} - 1 = 0$
2. $x_{2,2} - 1 = 0$
3. $x_{1,3} + x_{2,3} - 1 = 0$
4. $x_{2,4} - 1 = 0$
5. $x_{1,5} + x_{2,5} - 1 = 0$
6. $x_{3,6} + x_{4,6} - 1 = 0$
7. $x_{1,7} + x_{2,7} + x_{3,7} + x_{4,7} - 1 = 0$
Flow balance equations
8. $F_1 + F_2 - F_3 = 0$
9. $F_2 - F_4 = 0$
10. $F_3 - F_5 = 0$
11. $F_5 + F_6 - F_7 = 0$
Component balance equations
12. $x_{1,1}F_1 - y_1 = 0$
13. $x_{1,3}F_3 - y_1 = 0$
14. $x_{1,5}F_5 - y_1 = 0$
15. $x_{1,7}F_7 - y_1 = 0$
16. $x_{2,2}F_2 - y_2 = 0$
17. $x_{2,3}F_3 - y_2 = 0$
18. $x_{2,4}F_4 - y_2 = 0$
19. $x_{2,5}F_5 - y_2 = 0$
20. $x_{2,7}F_7 - y_2 = 0$
21. $x_{3,6}F_6 - y_3 = 0$
22. $x_{3,7}F_7 - y_3 = 0$
23. $x_{4,6}F_6 - y_4 = 0$
24. $x_{4,7}F_7 - y_4 = 0$

(*Continues*)

Table P12.9 List of Equations to Model the Process (*Continued*)

Balance Equations
Energy balance equations
25. $C_1F_1T_1 + C_2F_2T_2 - C_3F_3T_3 = 0$
26. $C_4F_4T_4 - Q_2 - C_2F_2T_2 = 0$
27. $C_3F_3T_3 + Q_2 - C_5F_5T_5 = 0$
28. $C_5F_5T_5 + C_6F_6T_6 - C_7F_7T_7 = 0$
Equipment specification equations
29. $V_1 - (F_3)\left(\frac{V_1}{F_1}\right)/\rho_3 = 0$
30. $Q_2 - U_2A_2 (T_{lm2} = 0$
31. $V_3 - (F_7)\left(\frac{V_3}{F_3}\right)/\rho_7 = 0$

12.10 Cavett proposed the following problems as a test problem for computer-aided design. Four flash drums are connected as shown in Figure P12.10. The temperature in each flash drum is specified, and equilibrium is assumed to be independent of composition so that the vapor-liquid equilibrium constants are truly constant. Is the problem properly specified, or do additional variables have to be given? If the latter, what should they be? The feed is as follows:

Component	**Feed**
1. Nitrogen and helium	358.2
2. Carbon dioxide	4965.6
3. Hydrogen sulfide	339.4
4. Methane	2995.5
5. Ethane	2395.5
6. Propane	2291.0
7. Isobutane	604.1
8. *n*-Butane	1539.9
9. Isopentane	790.4
10. *n*-Pentane	1192.9
11. Hexane	1764.7
12. Heptane	2606.7
13. Octane	1844.5
14. Nonane	1669.0
15. Decane	831.7
16. Undecane plus	1214.5
Total	27,340.6

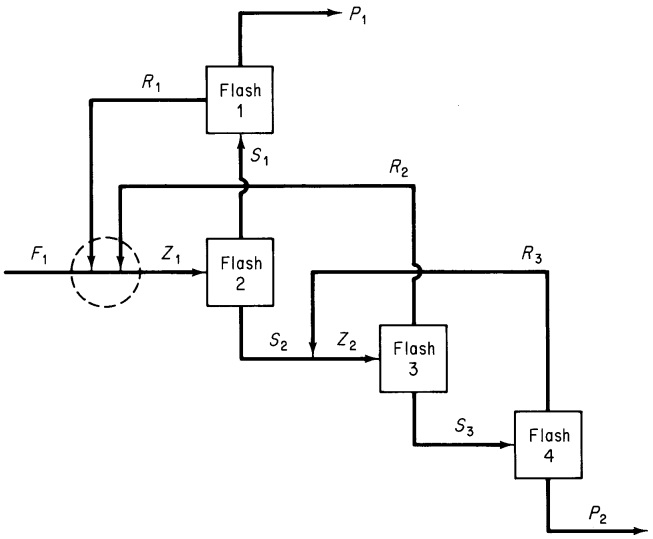


Figure P12.10

12.11 The flowsheet (Figure P12.11) has a high-pressure feed stream of gaseous component *A* contaminated with a small amount of *B*. It mixes first with a recycle stream consisting mostly of *A* and passes into a reactor, where an exothermic reaction to form *C* from *A* takes place. The stream is cooled to condense out component *C* and passed through a valve into a flash unit. Here most of the unreacted *A* and the contaminant *B* flash off, leaving a fairly pure *C* to be withdrawn as the liquid stream. Part of the recycle is bled off to keep the concentration of *B* from building up in the system. The rest is repressurized in a compressor and mixed, as stated earlier, with the feed stream. The number of parameters/variables for each unit is designated by the number within the symbol for the unit. How many degrees of freedom exist for this process?

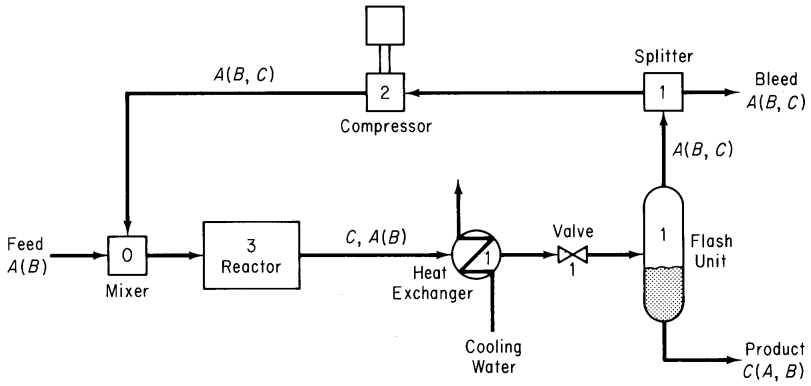


Figure P12.11