Lecture Ten

(MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION by SPECIES MATERIAL BALANCES)

This Lecture discusses material balances for reacting systems. We begin by discussing material balances based on chemical species.

10.1 Species Material Balances

10.1.1 Processes Involving a Single Reaction
10.1.2 Processes Involving Multiple Reactions

Your Objectives in Studying this Lecture are :

- Carry out a degree of freedom analysis for processes involving chemical reaction(s).
- Formulate (تكوين او تركيب) and solve material balances using (a) species balances and (b) element balances.
- Decide (قرر) when element balances can be used as material balances.
- Determine (حدد) if a set of chemical reaction equations is a minimal set.
- Understand (يفهم) how the extent of reaction is determined for a process, and how to apply it in material balance problems.

10.1 Species Material Balances

10.1.1 Processes Involving a Single Reaction

The material balance for a species must be augmented to include generation and consumption terms when chemical reactions occur in a process, in terms of moles of species *i*;

يجب تطوير معادلة توازن المادة لتشمل حدي **مامستهلك وما متولد** من مادة في العملية الكيميائية بدلالة الأصناف الكيميائية عند حصول التفاعل الكيميائي في المنظومة .

$$
\left\{\begin{array}{l}\text{moles of}\\ i \text{ at } t_2\\ \text{in the}\\ \text{system}\end{array}\right\} - \left\{\begin{array}{l}\text{moles of}\\ i \text{ at } t_1\\ \text{in the}\\ \text{system}\end{array}\right\} = \left\{\begin{array}{l}\text{moles of } i\\ \text{entering}\\ \text{the system}\\ \text{between } t_2 \text{ and } t_1\end{array}\right\} - \left\{\begin{array}{l}\text{moles of } i\\ \text{leaving}\\ \text{the system}\\ \text{between } t_2 \text{ and } t_1\end{array}\right\} + \left\{\begin{array}{l}\text{moles of } i\\ \text{generated}\\ \text{by reaction}\\ \text{between } t_2 \text{ and } t_1\end{array}\right\} - \left\{\begin{array}{l}\text{moles of } i\\ \text{consumed}\\ \text{by reaction}\\ \text{between } t_2 \text{ and } t_1\end{array}\right\} \quad (10.1)
$$

Note that we have written Equation (1) in *moles* rather than *mass* because the *generation and consumption* terms are more conveniently represented in moles. To illustrate this idea, we use the *extent of reaction* that was discussed in previous lecture.

EXAMPLE 10.1: *Production of Ammonia*

Consider the well-known reaction of N_2 and H_2 to form NH_3. Figure.1 presents the process as an open, steady-state system operating for 1 min so that the accumulation terms are zero on the left-hand side of the equal sign in Equation (10.1). The data in Figure.1 are in g mol.
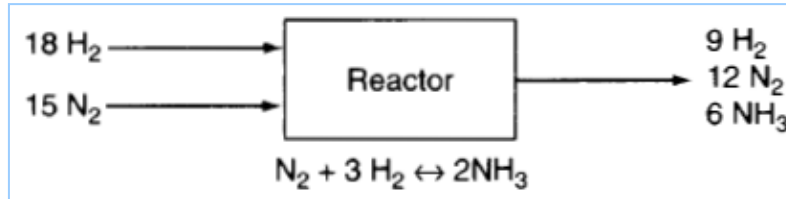
```
18 H₂  ──────────►  ┌──────────┐  ──────►  9 H₂
                    │ Reactor  │            12 N₂
15 N₂  ──────────►  └──────────┘            6 NH₃

         N₂ + 3 H₂ ↔ 2NH₃
```

Figure E10.1: A reactor to produce NH_3.

Solution:

Using Equation (1) you can calculate via a value in g mol for the generation or consumption, as the case may be, for each of the three species involved in the reaction:

$$NH_3 \text{ (generation):} \qquad 6 - 0 = 6 \text{ g mol}$$

$$H_2 \text{ (consumption):} \qquad 9 - 18 = -9 \text{ g mol}$$

$$N_2 \text{ (consumption):} \qquad 12 - 15 = -3 \text{ g mol}$$

As you know from the stoichiometry of the chemical reaction equation the respective three generation and consumption terms are related by the reaction equation. Given the value for the generation of NH_3, you can calculate the values for the consumption of H_2 and N_2 using the reaction equation. Thus, the generation and consumption terms are not independent, and you cannot specify more than one of the values without introducing a redundant (فائض) or inconsistent specification. In general, if you specify the value for the generation or consumption of one of the *N* species in a reaction, you are able to calculate the values of the *N - 1* other species from the chemical reaction equation.

Here is where the extent of reaction ξ becomes useful. Recall that for an open system

$$\xi = \frac{n_i^{out} - n_i^{in}}{v_i} \qquad i = 1, \cdots N \tag{10.2}$$

Where v_i is the stoichiometric coefficient of species i in the reaction equation. For the NH_3 reaction;

$$v_{NH_3} = 2$$

$$v_{H_2} = -3$$

$$v_{N_2} = -1$$

and the extent of reaction can be calculated via any species:

$$\xi = \frac{n_{NH_3}^{out} - n_{NH_3}^{in}}{\nu_{NH_3}} = \frac{6 - 0}{2} = 3$$

$$\xi = \frac{n_{H_2}^{out} - n_{H_2}^{in}}{\nu_{H_2}} = \frac{9 - 18}{-3} = 3$$

$$\xi = \frac{n_{N_2}^{out} - n_{N_2}^{in}}{\nu_{N_2}} = \frac{12 - 15}{-1} = 3$$

You can conclude for the case of a single chemical reaction that the specification of the extent of reaction provides the one independent quantity that accounts for all of the values of the generation and consumption terms for the various species in the respective implementations (عمليات تنفيذ) of Equation (1). The three species balances corresponding to the process in Figure 1 are:

Component	Out	In	=	Generation or Consumption
i	n_i^{out}	$-n_i^{in}$	=	$\nu_i \xi$
NH_3:	6	−0	=	2 (3) = 6
H_2:	9	−18	=	−3 (3) = −9
N_2:	12	−15	=	−1 (3) = −3

The term $\nu_i \xi$ corresponds to the moles of i generated or consumed.

Notes:

- For a closed, unsteady-state system the flows in and out would be zero, and Equation (1) would become;

$$\frac{n_i^{final} - n_i^{initial}}{\nu_i} = \xi \tag{10.3}$$

- If Equation (10.2) is applied to each species that reacts, the resulting set of equations will all contain the extent of reaction ξ. For the species that do not react, $\xi = 0$. In terms of the total molar flow in and the total molar flow out;

$$F^{out} = \sum_{i=1}^{S} n_i^{out}$$

$$F^{in} = \sum_{i=1}^{S} n_i^{in}$$

Where S is the total number of species in the system (n_i may be zero for some species). The material balance for the total molar flow is;

$$F^{out} = F^{in} + \xi \sum_{i=1}^{S} v_i \qquad (10.4)$$

you can calculate the value of ξ from the fraction conversion (or vice versa) plus information identifying the *limiting reactant*. In other cases, you are given sufficient information about the moles of a species entering and leaving the process so that ξ can be calculated directly. Now let's look at an example;

$$\xi = \frac{(-f)n^{in}_{limiting\ reactant}}{v_{limiting\ reactant}}$$

(10.5)

EXAMPLE 10.2: *Reaction in Which the Fraction Conversion is Specified*

The chlorination of methane occurs by the following reaction

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$
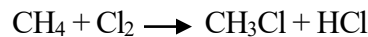
You are asked to determine the product composition if the conversion of the limiting reactant is 67%, and the feed composition in mole % is given as: 40% CH_4, 50 % Cl_2, and 10 % N_2.

Solution:

Steps 1, 2, 3, and 4

Assume the reactor is an open, steady-state process. Figure **E10.2** is a sketch of the process with the known information placed on it.
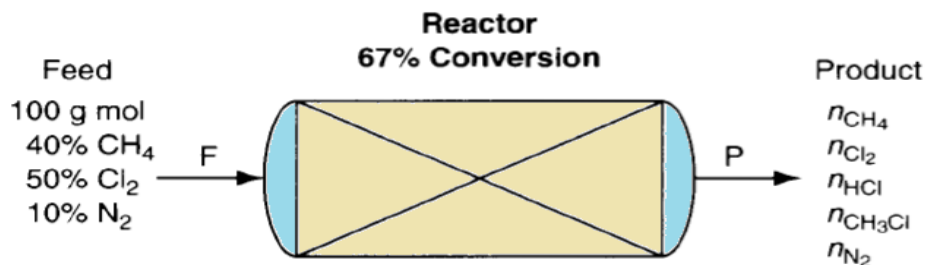
Reactor
67% Conversion

Feed
100 g mol
40% CH_4 F
50% Cl_2
10% N_2

P

Product
n_{CH_4}
n_{Cl_2}
n_{HCl}
n_{CH_3Cl}
n_{N_2}

Figure E10.2

Step 5

Select as a basis 100 g mol feed

Step 4

You have to determine the limiting reactant if you are to make use of the information about the 67% conversion. By comparing the maximum extent of reaction (refer to Chapter 9) for each reactant, you can identify the limiting reactant.

$$\xi^{max}(CH_4) = \frac{-n_{CH_4}^{in}}{v_{CH_4}} = \frac{-40}{(-1)} = 40$$

$$\xi^{max}(Cl_2) = \frac{-n_{Cl_2}^{in}}{v_{Cl_2}} = \frac{-50}{(-1)} = 50$$

Therefore, CH_4 is the limiting reactant. You can now calculate the extent of reaction using the specified conversion rate and Equation (10.5).

$$\xi = \frac{-f\, n_{lr}^{in}}{v_{lr}} = \frac{(-0.67)(40)}{-1} = 26.8 \text{ g moles reacting}$$

Steps 6 and 7

The next step is to carry out a degree-of-freedom analysis

Number of variables: 11

$$n_{CH_4}^{in},\ n_{Cl_2}^{in},\ n_{N_2}^{in},\ n_{CH_4}^{out},\ n_{Cl_2}^{out},\ n_{HCl}^{out},\ n_{CH_3Cl}^{out},\ n_{N_2}^{out},\ F,\ P,\ \xi$$

Number of equations: 11

Basis: $F = 100$

Species material balances: 5
$$CH_4,\ Cl_2,\ HCl,\ CH_3Cl,\ N_2$$

Steps 8 and 9

The species material balances (in moles) using Equation (10.2) give a direct solution for each species in the product:

$$n_{CH_4}^{out} = 40 - 1(26.8) = 13.2$$
$$n_{Cl_2}^{out} = 50 - 1(26.8) = 23.2$$
$$n_{CH_3Cl}^{out} = 0 + 1(26.8) = 26.8$$
$$n_{HCl}^{out} = 0 + 1(26.8) = 26.8$$
$$n_{N_2}^{out} = 10 - 0(26.8) = \underline{10.0}$$
$$100.0 = P$$

Therefore, the composition of the product stream is: 13.2% CH_4, 23.2% Cl_2, 26.8% CH_3Cl, 26.8% HCl, and 10% N_2 because the total number of product moles is conveniently 100 g mol. There are 100 g mol of products because there are 100 g mol of feed and the chemical reaction equation results in the same number of moles for reactants as products by coincidence.

Step 10

The fact that the overall mole balance equation is satisfied is not a consistency check for this problem.

10.1.2 Processes Involving Multiple Reactions

To extend the concept of the *extent of reaction* to processes involving multiple reactions, the question is do you just include a ξ for every reaction. The answer is no. *You should include in the species material balances only the ξ_i ; associated with a (nonunique) set of independent chemical reactions called the mini-mar set of reaction equations*. What this term means is the smallest set of chemical reactions equations that can be assembled that includes all of the species involved in the process. Analogous to a set of independent linear algebraic equations, you can form any other reaction equation by a linear combination of the reaction equations contained in the minimal set.

For example, look at the following set of reaction equations:

$$C + O_2 \longrightarrow CO_2$$

$$C + 1/2\ O_2 \longrightarrow CO$$

$$CO + 1/2\ O_2 \longrightarrow CO_2$$
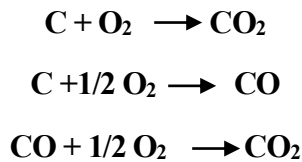
With these ideas in mind, we can state that for open, steady-state processes with multiple reactions, Equation (1) in moles becomes for component *i*

$$n_i^{out} = n_i^{in} + \sum_{j=1}^{R} v_{ij}\ \xi_j \qquad (10.6)$$

Where;

v_{ij} is the stoichiometric coefficient of species i in reaction j in the minimal set.

ξ_i is the extent of reaction for the jth reaction in the minimal set.

**R** is the number of independent chemical reaction equations (the size of the minimal set).

An equation analogous to Equation (6) can be written for a *closed, unsteady-state system*. The total moles, N, exiting a reactor are

$$N = \sum_{i=1}^{S} n_i^{out} = \sum_{i=1}^{S} n_i^{in} + \sum_{i=1}^{S}\sum_{j=1}^{R} v_{ij}\xi_j \qquad (10.7)$$

Where **S** is the number of species in the system. What Equation (7) means in words is add up the stochiometric coefficients for each independent reaction, multiply the sum by ξ for that reaction, and then sum the resulting products for each reaction to get **N**.

EXAMPLE 10.3: *Material Balances for a Process in Which Two Simultaneous Reaction Occur*

Formaldehyde (CH_2O) is produced industrially by the catalytic oxidation of methanol (CH_3OH) according to the following reaction:

$$CH_3OH + 1/2O_2 \rightarrow CH_2O + H_2O \tag{1}$$
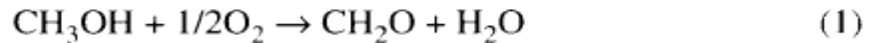
Unfortunately, under the conditions used to produce formaldehyde at a profitable rate, a significant portion of the formaldehyde reacts with oxygen to produce CO and H_2O, that is,

$$CH_2O + 1/2O_2 \rightarrow CO + H_2O \tag{2}$$
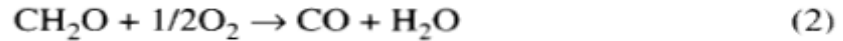
Assume that methanol and twice the stoichiometric amount of air needed for complete conversion of the CH_3OH to the desired products (CH_2O and H_2O) are fed to the reactor. Also assume that 90% conversion of the methanol results, and that a 75% yield of formaldehyde occurs based on the theoretical production of CH_2O by Reaction 1. Determine the composition of the product gas leaving the reactor.

Solution:

Steps 1, 2, 3, and 4

Figure E10.3 is a sketch of the process with y_i indicating the mole fraction of the respective components in P (a gas).
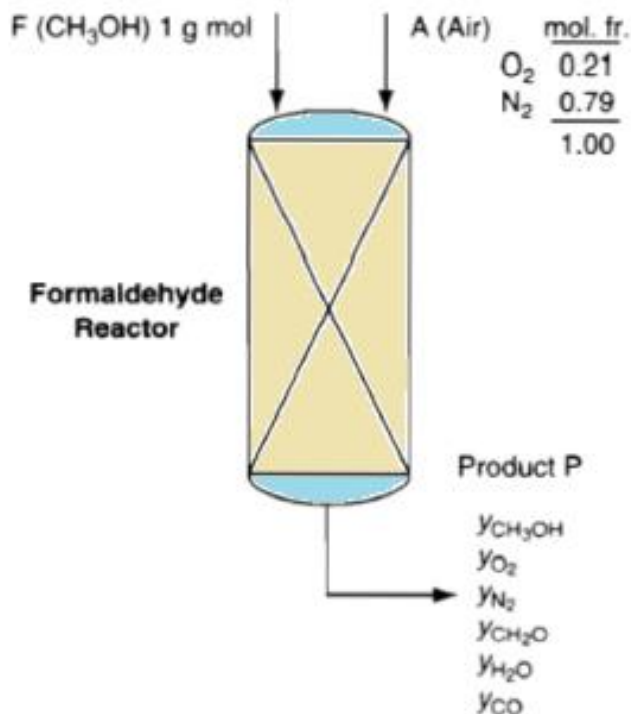

Figure E10.3: Formaldehyde Reactor.

Step 5

<div align="center">Basis: 1g mol F</div>

Step 4

You can use the specified conversion of methanol and yield of formaldehyde to determine the extents of reaction for the two reactions. Let ξ_1 represent the extent of reaction for the first reaction, and ξ_2 represent the extent of reaction for the second reaction. The limiting reactant is CH_3OH.

Use the fraction conversion, Equation (10.5): $\xi_1 = \dfrac{-0.90}{-1}(1) = 0.9$ g moles reacting

The yield is related to ξ_i as follows

By reaction 1: $n_{CH_2O}^{out,1} = n_{CH_2O}^{in,1} + 1(\xi_1) = 0 + \xi_1 = \xi_1$

By reaction 2: $n_{CH_2O}^{out,2} = n_{CH_2O}^{in,2} - 1(\xi_2) = n_{CH_2O}^{out,1} - \xi_2 = \xi_1 - \xi_2$

$$\text{The yield is } \frac{n_{CH_2O}^{out,2}}{F} = \frac{\xi_1 - \xi_2}{1} = 0.75$$

$$\xi_2 = 0.15 \text{g moles reacting}$$

You should next calculate the amount of air (A) that enters the process. The entering oxygen is twice the required oxygen based on Reaction 1, namely

$$n_{O_2}^A = 2\left(\frac{1}{2}F\right) = 2\left(\frac{1}{2}\right)(1.00) = 1.00 \text{ g mol}$$

$$A = \frac{n_{O_2}^A}{0.21} = \frac{1.00}{0.21} = 4.76 \text{ g mol}$$

$$n_{N_2}^A = 4.76 - 1.00 = 3.76 \text{ g mol}$$

Steps 6 and 7

The degree-of-freedom analysis is

Number of variables: 11

$$F, A, P, y_{CH_3OH}^P, y_{O_2}^P, y_{N_2}^P, y_{CH_2O}^P, y_{H_2O}^P, y_{CO}^P, \xi_1, \xi_2$$

Number of equations: 11

Basis: $F = 1$ g mol

Species material balances: 6

$$CH_3OH, O_2, N_2, CH_2O, H_2O, CO$$

Calculated values in Step 4: 3

$$A, \xi_1, \xi_2$$

Implicit equation: 1

$$\Sigma y_i^P = 1$$

Step 8

Because the variables in Figure E10.3 are y_i^P and not n_i^P, direct use of y_i^P in the material balances will involve the nonlinear terms $y_i^P P$. Consequently, to avoid this situation, let us first calculate P using Equation (10.7):

$$P = \sum_{i=1}^{S} n_i^{in} + \sum_{i=1}^{S}\sum_{j=1}^{R} v_{i_j} \xi_j$$

$$= 1 + 4.76 + \sum_{i=1}^{6}\sum_{j=1}^{2} v_{i_j} \xi_j$$

$$= 5.76 + [(-1) + (-^1{}_2) + (1) + 0 + (1) + 0]\,0.9$$

$$+ [0 + (-^1{}_2) + (-1) + 0 + (1) + (1)]\,0.15 = 6.28 \text{ g mol}$$

The material balances after entering the values calculated in Step 4 are:

$$n_{CH_3OH}^{out} = y_{CH_3OH}\,(6.28) = 1 - (0.9) + 0 = 0.10$$

$$n_{O_2}^{out} = y_{O_2}\,(6.28) = 1.0 - (^1{}_2)(0.9) - (^1{}_2)(0.15) = 0.475$$

$$n_{CH_2O}^{out} = y_{CH_2O}\,(6.28) = 0 + 1\,(0.9) - 1\,(0.15) = 0.75$$

$$n_{H_2O}^{out} = y_{H_2O}\,(6.28) = 0 + 1\,(0.9) + 1\,(0.15) = 1.05$$

$$n_{CO}^{out} = y_{CO}\,(6.28) = 0 + 0 + 1\,(0.15) = 0.15$$

$$n_{N_2}^{out} = y_{N_2}\,(6.28) = 3.76 - 0 - 0 = 3.76$$

Step 10

You can check the value of P by adding all of the n_i^{out} above.

Step 9

The six equations can be solved for the y_j:

$$y_{CH_3OH} = 1.6\%. \qquad y_{O_2} = 7.6\%. \qquad y_{N_2} = 59.8\%.$$

$$y_{CH_2O} = 11.9\%. \quad y_{H_2O} = 16.7\%. \quad y_{CO} = 2.4\%.$$

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Lecture Ten/ Tutorials

(MATERIAL BALANCES FOR PROCESSES INVOLVING REACTION by SPECIES MATERIAL BALANCES)

PROBLEM: *Processes Involving a Single Reaction*

P.10.1 *A Reaction in Which the Fraction Conversion is to Be Calculated*

Mercaptans, hydrogen sulfide, and other sulfur compounds are removed from natural gas by various so-called "sweetening processes" that make available otherwise useless "sour" gas. As you know H_2S is toxic in very small quantities and is quite corrosive to process equipment.

A proposed process to remove H_2S is by reaction with SO_2:

$$2H_2S(g) + SO_2(g) \longrightarrow 3S(s) + 2H_2O(g)$$
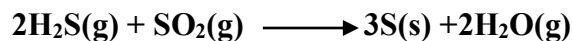
In a test of the process, a gas stream containing 20% H_2S and 80% CH_4 was combined with a stream of pure SO_2. The process produced 5000 Ib of S(s), and in the product gas the ratio of SO_2 to H_2S was equal to 3, and the ratio of H_2O to H_2S was 10. You are asked to **determine the fractional conversion of the limiting reactant, and the feed rates of the H₂S and SO₂ streams.**

Solution

Steps 1, 2, 3, and 4

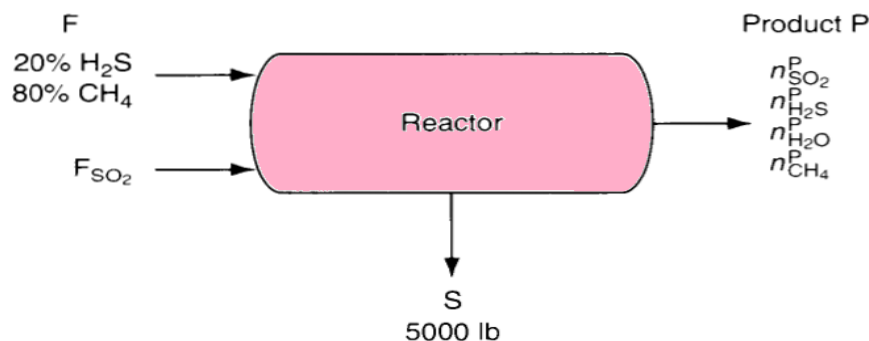Figure **P10.1** is a diagram of the process with the known data inserted.

Figure P10. 1

Step 5

The obvious basis is 5000 lb S (156.3 lb mol S)

Steps 6 and 7

The next step is to carry out a degree-of-freedom analysis.

Number of variables: 11 : $n_{H_2S}^F$, $n_{CH_4}^F$, F_{SO_2}, $n_{SO_2}^P$, $n_{H_2S}^P$, $n_{H_2O}^P$, $n_{CH_4}^P$, ξ, F, P, S

Number of equations: 11 : Basis: $S = 5000$ lb (156.3 lb mol)

Species material balances: 5 H_2S, CH_4, SO_2, H_2O, S

Specifications: 4 (3 independent)

$$x^F_{H_2S} = 0.20 \text{ or } x^F_{CH_4} = 0.80, \ (n^P_{SO_2}/n^P_{H_2S}) = 3, \ (n^P_{H_2O}/n^P_{H_2S}) = 10$$

Implicit equations: 2

$$\Sigma n^P_i = P \quad \Sigma n^F_i = F \text{ (redundant if you use both specifications in } F)$$

The degrees of freedom are zero, and the problem is exactly specified.

Step 8

The species balances in pound moles after introduction of most of the specifications are:

$$S: \quad 156.3 = 0 + 3 \, \xi \tag{a}$$

$$H_2S: \quad n^P_{H_2S} = 0.20F - 2 \, \xi \tag{b}$$

$$SO_2: \quad n^P_{SO_2} = F_{SO_2} - 1 \, \xi \tag{c}$$

$$H_2O: \quad n^P_{H_2O} = 0 + 2 \, \xi \tag{d}$$

$$CH_4: \quad n^P_{CH_4} = 0.80F + 0 \, (\xi) \tag{e}$$

The remaining specifications are

$$n^P_{SO_2} = 3n^P_{H_2S} \tag{f}$$

$$n^P_{H_2O} = 10n^P_{H_2S} \tag{g}$$

Equations (a) through (g) comprise seven independent equations and seven unknowns.

Step 9

If you solve the equations without using a computer, you should start by calculating ξ from Equation (a)

$$\xi = \frac{156.3 \text{ mol}}{3} = 52.1 \text{ mol rxn}$$

Then Equation (d) gives

$$n^P_{H_2O} = 2(52.1) = 104.2 \text{ lb mol } H_2O$$

Next, Equation (g) gives

$$n^P_{H_2S} = \frac{1}{10} n^P_{H_2O} = 10.4 \text{ lb mol } H_2S$$

and Equation (f) gives

$$n_{SO_2}^P = 3(10.4) = 31.2 \text{ lb mol } SO_2$$

If you solve the rest of the equations in the order (b), (c), and (e), you find

$$F = 573 \text{ lb mol}$$
$$F_{SO_2} = 83.3 \text{ lb mol}$$
$$n_{CH_4}^F = 458 \text{ lb mol}$$

Finally, you can identify H_2S as the limiting reactant because the molar ratio of SO_2 to H_2S in the product gas (3/1) is greater than the molar ratio in the chemical reaction equation (2/1). The fractional conversion from Equation (10.5) is the consumption of H_2S divided by the total feed of H_2S

$$f = \frac{-(-2)\xi}{0.2F} = \frac{(2)(52.1)}{(0.2)(573)} = 0.91$$

Step 10

Because of the coincidence of the equality of moles of reactants and products for this particular reaction, you cannot use the overall mole balance for this process as a consistency check.