

FDE 211-MATERIAL AND ENERGY BALANCES: MATERIAL BALANCES ON REACTIVE SYSTEMS

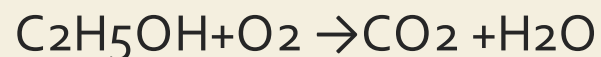
*Dr. Ilgın Paker Yıkıcı
Fall 2015*

Learning Objectives

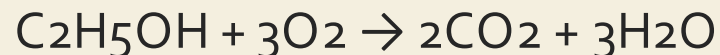
- Write a balanced chemical reaction and use stoichiometry to determine the corresponding amounts of participants in a reaction
- Understand the formulations of the material balance
- Write balance equations based on the extent of reaction
- Write balance equations involving atomic species
- Write balance equations using molecular species
- Use of the extent of reaction for a system of chemical reactions
- Use of component balance for a system of chemical reactions
- Apply the degrees of freedom analysis for a reactive system
- Define the features of combustion processes and properly apply material balances on them

Stoichiometric Equation

- It is an equation that relates the relative number of molecules or moles of participants (reactants and products) in a chemical reaction. To be valid, the equation must be balanced. For example, the following stoichiometric equation is not balanced:

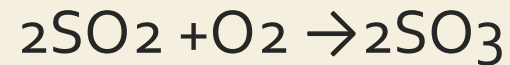


- The following equation is balanced because the number of atoms is the same on both sides of the equation (C, H, and O):



Stoichiometric Coefficients

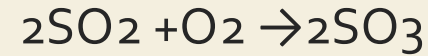
- These are the values preceding each molecular species, i , in a balanced stoichiometric equation. **Values are defined as positive for products and negative for reactants.** For the reaction,



$$v_{\text{SO}_2} = -2, v_{\text{O}_2} = -1, v_{\text{SO}_3} = 2$$

Stoichiometric Ratio

- It is the ratio of stoichiometric coefficients in a balanced stoichiometric equation. Consider the oxidation of sulfur dioxide:



- The following stoichiometric ratio is employed in solving material balance problems that involve this chemical reaction:
- 2mol SO₃ generated 1mol O₂ consumed
- Two reactants, A and B, are in stoichiometric proportion, if the ratio (moles of A present)/(moles of B present) equals their stoichiometric ratio determined from the stoichiometric equation.

Limiting Reactant

- A reactant is limiting if it is present in less than its stoichiometric proportion relatively to every other reactant. It is the reactant that would be the first to be consumed completely, if the reaction were complete. In order to find the limiting reactant, you balance the stoichiometric equation and then take the ratio of the reactant amount (mole, flow rate) in the feed to reactant stoichiometric coefficient, that is,

$$\frac{\dot{n}_i^o}{\nu_i} = \frac{\text{(molar flow rate of component } i \text{ in the feed)}}{\text{(stoichiometric coefficient of component } i\text{)}}$$

- The ratio with the lowest value corresponds to the limiting reactant.

Excess Reactants

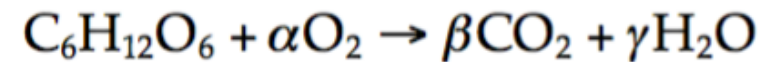
- All reactants, other than the limiting species, are termed excess reactants.
- **An excess reactant is not fully used up when the reaction is complete.**
- The fractional excess is the ratio of the amount by which the feed exceeds stoichiometric requirements divided by the stoichiometric requirement.
- The fractional excess of the reactant is the ratio of the excess to the stoichiometric requirement:

$$\text{Fraction excess of A} = \frac{(n_A)_{\text{feed}} - (n_A)_{\text{stoich}}}{(n_A)_{\text{stoich}}} \text{ or } \left(= \frac{(\dot{n}_A)_{\text{feed}} - (\dot{n}_A)_{\text{stoich}}}{(\dot{n}_A)_{\text{stoich}}} \right)$$

- where
(n_A)_{feed} is the amount (mole, flow rate) of an excess reactant, A, present in the feed to a reactor
- (n_A)_{stoich} is the stoichiometric requirement of A, or the amount needed to react completely with the limiting reactant.
- Percentage excess of A is 100 times the fractional excess.

How to balance a chemical equation

1. How many moles of atomic hydrogen and oxygen would be released in 1 mol of H_2O if the latter were broken up into its constituent parts?
2. A water drop is 0.05 g. How many moles are there in the drop? What would be the mass of air in the same number of moles (Mw of air is 29)?
3. How many kilograms of H_2 that can be obtained by the electrolysis of 1 kg of water?
4. Balance the equation for glucose oxidation (i.e., determine α , β , and γ):



Solution #1

- The number of moles of atomic hydrogen and oxygen that would be released if 1 mol of water were broken up into its constituent parts can be calculated as follows. Consider 1 mol of water broken up into its constituent parts.
- $\text{H}_2\text{O} \rightarrow 2\text{H} + \text{O}$
- There are two hydrogen atoms and one oxygen atom in a water molecule. Thus, 1 mol of water will release 2 mol of atomic hydrogen and 1 mol of atomic oxygen.

Solution #2

- The number of moles in an average rain drop contains 0.05 g water, which can be calculated considering the Mw of water (H₂O), that is, (2×1)+(1×16)=18 g/mol. The number of moles is, therefore,

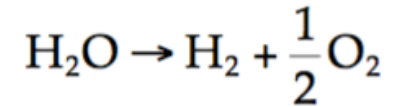
$$(n) = m / M_w = 0.05 \text{ g} / (18 \text{ g/mol}) = 2.78 \times 10^{-3} \text{ mol}$$

- The mass of air in the same number of moles as that of water is calculated as follows:

$$2.78 \times 10^{-3} \text{ mol} \left| \frac{29 \text{ g}}{\text{mol}} \right| = 0.08 \text{ g of air}$$

Solution #3

- Electrolysis is the use of electrical energy to turn water into H₂ and O₂. The relevant reaction is



- Thus, 1 mol of H₂O yields 1 mol of H₂. The number of moles in 1 kg of H₂O is $n = m/M_w = 1 \text{ kg}/(18 \text{ kg/kmol})$. Thus, (1/18) kmol of H₂O yields (1/18) kmol of H₂.
- Mass of (1/18) kmol H₂ = number of moles of H₂ multiplied by the M_w of hydrogen.

$$\text{Mass of (1/18) kmol H}_2 = \frac{1}{18} \cancel{\text{kmol}} \left| \frac{2 \text{ kg}}{1 \cancel{\text{kmol}}} \right| = \frac{1}{9} \text{ kg}$$

Solution #4

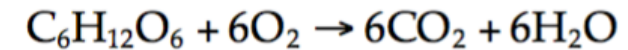
- β and γ are determined by balancing the number of each atom on both sides of the equation. In other words, the number of atoms on the left side of the equation must equal the number of atoms on the right side:

$$\text{C: } 6 = \beta$$

$$\text{H: } 12 = 2\gamma \Rightarrow \gamma = 6$$

$$\text{O: } 6 + 2\alpha = 2\beta + \gamma, \quad \alpha = 6$$

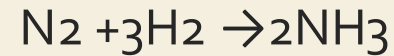
Thus, the balanced equation is



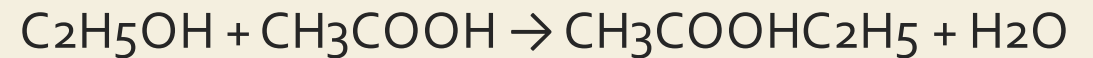
Limiting Reactant Example

For the following cases, determine which reactant is limiting and which is in excess as well as the percent excess for that component.

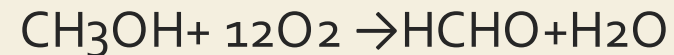
1. 2 mol of nitrogen (N₂) reacts with 4 mol of hydrogen (H₂) to form ammonia (NH₃) via the reaction:



2. 100 kg ethanol (C₂H₅OH) reacts with 100 kg of acetic acid (CH₃COOH) to form ethyl acetate:



3. 64 g of methanol (CH₃OH) reacts with 0.5 mol of oxygen (O₂) to form formaldehyde:



Solution #1

- Analysis: Divide feed component flow rate to its stoichiometric coefficient, and the lower value is the limiting reactant.
- The feed rate to stoichiometric ratio of both reactants is as follows:
- $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$
- 2.0/1 and 4.0/3
- This means that hydrogen (H_2) is the limiting reactant, since the ratio of hydrogen to its stoichiometric coefficient is lower than that of nitrogen. Accordingly, nitrogen is the component in excess.

Solution #1

The percent excess of nitrogen (N_2) can be calculated from

$$\% \text{ excess of } \text{N}_2 = \frac{(\text{N}_2)_{\text{feed}} - (\text{N}_2)_{\text{stoich}}}{(\text{N}_2)_{\text{stoich}}} \times 100\%$$

$$(\text{N}_2)_{\text{stoich}} = 4 \text{ mol H}_2 \left| \frac{1 \text{ mol N}_2}{3 \text{ mol H}_2} \right| = \frac{4}{3} \text{ mol N}_2$$

$$\% \text{ excess of } \text{N}_2 = \frac{\left(2 - \frac{4}{3}\right) \text{ mol N}_2}{\frac{4}{3} \text{ mol N}_2} \times 100\% = 50\%$$

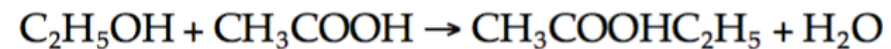
Solution #2

- Molecular weight of ethanol is 46 kg/kmol, acetic acid 60 kg/kmol, water 18 kg/kmol, and ethyl acetate 88 kg/kmol. First, you need to convert mass to mole. Thus,

$$\text{C}_2\text{H}_5\text{OH}: 100 \text{ kg} \left(\frac{1 \text{ kmol}}{46 \text{ kg}} \right) = 2.17 \text{ kmol C}_2\text{H}_5\text{OH}$$

$$\text{CH}_3\text{COOH}: 100 \text{ kg} \left(\frac{1 \text{ kmol}}{60 \text{ kg}} \right) = 1.67 \text{ kmol CH}_3\text{COOH}$$

The ratio of the feed rate to stoichiometric coefficient for each reactant is as follows:



$$\frac{2.17}{1} \qquad \frac{1.67}{1}$$

This means that acetic acid (CH_3COOH) is the limiting reactant. The component in excess is ethanol ($\text{C}_2\text{H}_5\text{OH}$). The percent excess of ethanol ($\text{C}_2\text{H}_5\text{OH}$) is

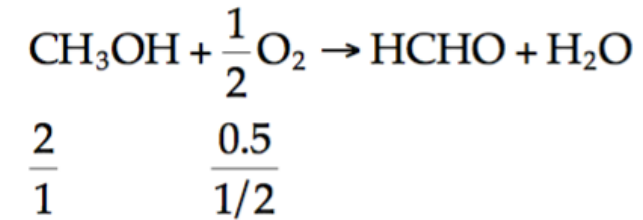
$$\% \text{ excess} = \frac{2.17 - 1.67}{1.67} \times 100\% = 30.0\%$$

Solution #3

- Molecular weight (g/mol) data: O₂=32, CH₃OH=32, H₂O=18, HCHO = 30
First, convert masses to mole. Thus,

$$\text{CH}_3\text{OH}: 64 \text{ g} \left(\frac{1 \text{ mol}}{32 \text{ g}} \right) = 2 \text{ mol CH}_3\text{OH}$$

The feed to stoichiometric ratio for each reactant is



- Oxygen (O₂) is the limiting reactant.

Solution #3

- The percent by which methanol is in excess is as follows:

The stoichiometric amount of methanol

$$(n_{\text{CH}_3\text{OH}})_{\text{stoich}} = (0.5 \text{ mol O}_2)_{\text{feed}} \left(\frac{1 \text{ mol CH}_3\text{OH consumed}}{1/2 \text{ mol O}_2 \text{ consumed}} \right) = 1 \text{ mol CH}_3\text{OH}$$

The percent excess of methanol

$$\% \text{ excess of CH}_3\text{OH} = \frac{(2 \text{ mol})_{\text{feed}} - (1 \text{ mol})_{\text{stoich}}}{(1 \text{ mol})_{\text{stoich}}} \times 100\% = 100\%$$

Fractional Conversion

- Chemical reactions do not occur instantaneously but rather proceed quite slowly. Therefore, it is not practical to design a reactor for the complete conversion of the limiting reactant. Instead, the reactant is separated from the reactor outlet stream and recycled back to the reactor inlet. The fractional conversion of a reactant A is the ratio of the amount reacted to the amount fed to the reactor:

$$f_A = \frac{(n_A)_{\text{reacted}}}{(n_A)_{\text{in}}} = \frac{(n_A)_{\text{in}} - (n_A)_{\text{out}}}{(n_A)_{\text{in}}}$$

Fractional Conversion

- The percentage conversion of component A is

$$\frac{(n_A)_{\text{reacted}}}{(n_A)_{\text{in}}} \times 100\% = \frac{(n_A)_{\text{in}} - (n_A)_{\text{out}}}{(n_A)_{\text{in}}} \times 100\%$$

- If no component is specified, then the fractional conversion (f) is based on limiting reactant:

$$f = \frac{(n_{\text{Lr}})_{\text{reacted}}}{(n_{\text{Lr}})_{\text{fed}}} = \frac{(n_{\text{Lr}})_{\text{in}} - (n_{\text{Lr}})_{\text{out}}}{(n_{\text{Lr}})_{\text{in}}}$$

where nLr is the number of moles of limiting reactant.

General Material Balance

- Mass balances are either integral mass balances or differential mass balances. An integral mass balance is a black box approach and focuses on the overall behavior of a system whereas a differential mass balance focuses on mechanisms within the system.

Differential Balance

- A differential balance is a material balance at a given instant in time and deals with rates, that is, amount/unit time. Typically, a differential material balance may be written more precisely in a mathematical form as

$$\frac{dm}{dt} = \dot{m}_{\text{in}} - \dot{m}_{\text{out}} + \dot{G} - \dot{C}$$

Where **dm/dt** denotes the rate of change of the material, **G** and **C** denote the rate of generation and consumption.

Differential Balance

- There are a couple of special cases:
- For the steady-state case,
- $0 = \text{in} - \text{out} + \text{generation} - \text{consumption}$

$$0 = \dot{m}_{\text{in}} - \dot{m}_{\text{out}} + \dot{G} - \dot{C}$$

- For the case without chemical reaction,

$$\text{in} = \text{out}; \quad \dot{m}_{\text{in}} = \dot{m}_{\text{out}}$$

Integral Balance

- An integral balance deals with the entire time of the process at once and uses amounts rather than rates at steady state; none of the process variables change with time. For transient process that begins with time = t_0 and ends at a later time t_f , the general integral material balance equation is

$$m_{t_f} - m_{t_0} = \int_{t_0}^{t_f} m_{\text{in}} dt - \int_{t_0}^{t_f} m_{\text{out}} dt + \int_{t_0}^{t_f} \mathfrak{R} dT$$

where

m_{t_f} is the mass of system content at final time

m_{t_0} is the mass of system content at initial time

\mathfrak{R} is the generation/consumption term

Integral Balance

- This is significant for component with reactive systems only. The term is positive for produced material and negative if the material is consumed. The stoichiometric equation of the reaction imposes constraints on the relative amounts of reactants and products in the input and output streams. The simple relation “input equals output” holds for steady-state processes under the circumstances explained in the figure below.

Validity of “Input = Output” for a Steady-State Process

Type of Balance	Without Chemical Reaction	With Chemical Reaction
Total mass	Yes	Yes
Total moles	Yes	No
Mass of a chemical compound	Yes	No
Moles of a chemical compound	Yes	No
Moles of an atomic species	Yes	Yes

Formulation Approaches of Mass Balance

- There are three approaches in the formulation of material balances with reaction, that is, **the extent of reaction method**, **the atomic balance method**, and **the molecular species method**.
- For multiple reactions, sometimes, it is more convenient to use the atomic balance approach. Generally, atomic species balances lead to the most straightforward solution procedure, especially when more than one reaction is involved.
- Molecular species balances require more complex calculations than either of the other two approaches and should be used only for simple systems involving one reaction.
- Each approach provides the same results, but one method may be more convenient than the other for a given problem

Extent of Reaction Method for a Single Reaction

- The extent of reaction (ξ or $\dot{\xi}$) is the amount (in moles or molar flow rate) of a species converted in a reaction divided by the species stoichiometric coefficient. Therefore, the extent of reaction is a quantity that characterizes the reaction since it is based on the stoichiometric equation. As such, the extent can be very useful in simplifying material balance calculations. The extent of reaction ξ (or $\dot{\xi}$) has the same units as n (or \dot{n}) divided by the moles (stoichiometric) reacting.
- For a continuous process and single reaction at steady state: $\dot{n}_i = \dot{n}_i^o + \nu_i \dot{\xi}$

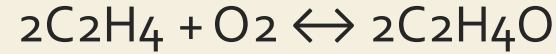
where \dot{n}_i^o and \dot{n}_i are the molar flow rates of species i in the feed and outlet streams, respectively. For a batch process,

$$n_i = n_i^o + \nu_i \xi$$

where n_i^o and n_i are the initial and final molar amounts of species i , respectively.

Problem Production of Ethylene Oxide

- Ethylene oxide is produced by the reaction of ethylene with oxygen as per the following reaction:



- The feed to the reactor contains 5 mol ethylene, 3 mol oxygen, and 2 mol ethylene oxide. Draw and label the process flow sheet. Write the material balance equations as a function of the extent of reaction.

Solution

- Use the extent of reaction method. From the definition of the extent of reaction for a single reaction,

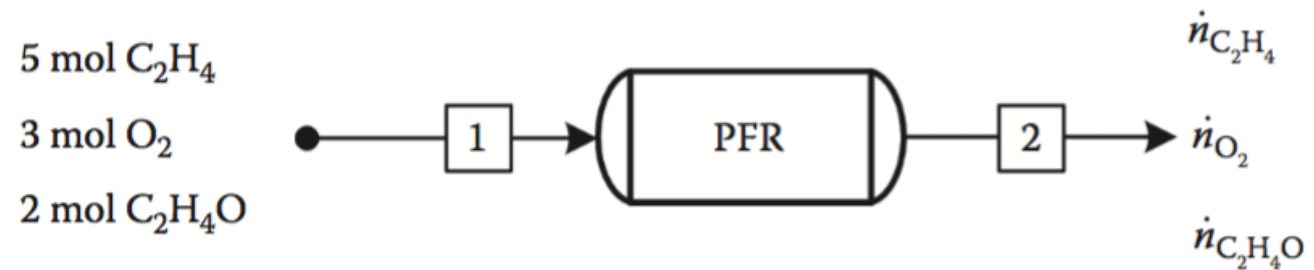
$$\dot{n}_i = \dot{n}_i^0 + \nu_i \dot{\xi}$$

Compound mole balance:

$$\text{C}_2\text{H}_4 : n_{\text{C}_2\text{H}_4} = n_{\text{C}_2\text{H}_4}^0 - 2\xi = 5 - 2\xi$$

$$\text{O}_2 : n_{\text{O}_2} = n_{\text{O}_2}^0 - \xi = 3 - \xi$$

$$\text{C}_2\text{H}_4\text{O} : n_{\text{C}_2\text{H}_4\text{O}} = n_{\text{C}_2\text{H}_4\text{O}}^0 + 2\xi = 2 + 2\xi$$



Production of Ethylene Oxide

Solution

Total material balance is the sum of the component balance equations:

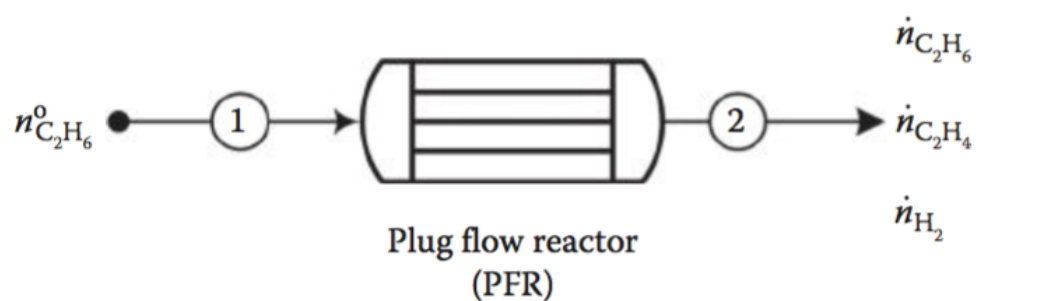
$$n = n^{\circ} - \xi = 10 - \xi$$

where

$$n^{\circ} = n_{\text{C}_2\text{H}_4}^{\circ} + n_{\text{O}_2}^{\circ} + n_{\text{C}_2\text{H}_4\text{O}}^{\circ}$$

Element or Atomic Balance Method

- Element balances have no generation or consumption terms (atoms are not generated or consumed), and the mass balance is simplified to input equals output for continuous, steady-state processes. The element balance is based on the number of moles of that element regardless of the number of moles of the compound. The number of moles of each compound must be multiplied by the number of atoms of the element in the compound in order to obtain the number of moles of the element.
- For instance, in the ethane dehydrogenation process, there are 2 mol of carbon atom for every mole of ethane.
- The atomic balance for each element, C and H, is expressed as

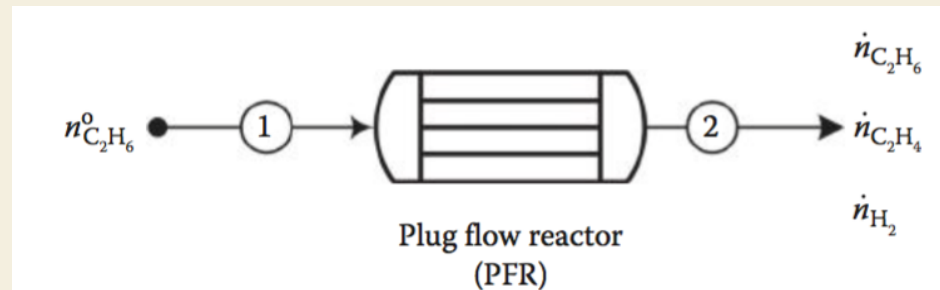


$$C: 2n_{C_2H_6}^o = 2n_{C_2H_4} + 2n_{C_2H_6}$$

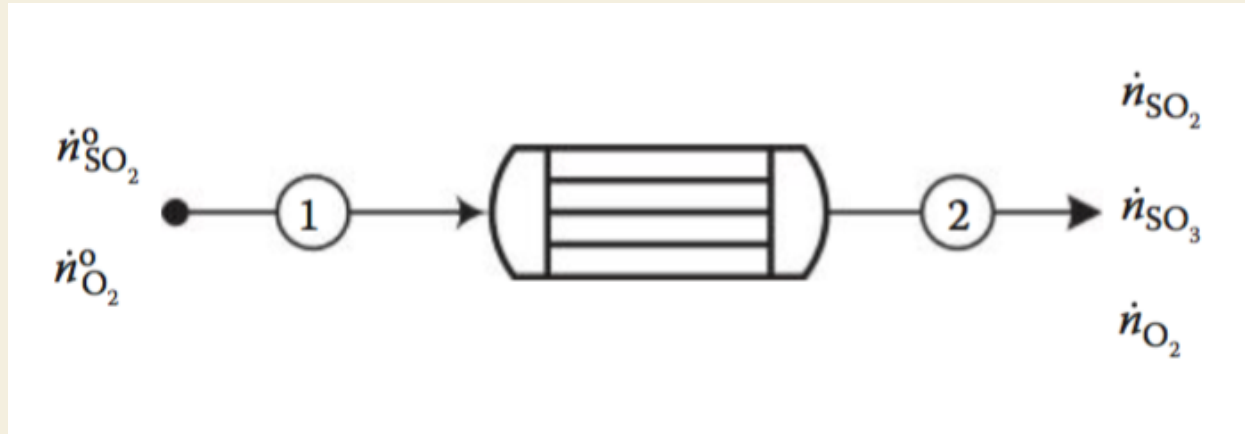
$$H: 6n_{C_2H_6}^o = 4n_{C_2H_4} + 6n_{C_2H_6} + 2n_{H_2}$$

Molecular or Component Balance Approach

- When applying molecular or component balances, consumption and generation terms need to be considered according to the problem at hand. Therefore, the general mass balance for steady-state flow processes becomes



- In the oxidation of sulfur dioxide process, $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3$, suppose that 5 mol/h of O_2 is consumed.



- From the stoichiometric equation and using molecular species balance, the number of moles of SO_3 generated is

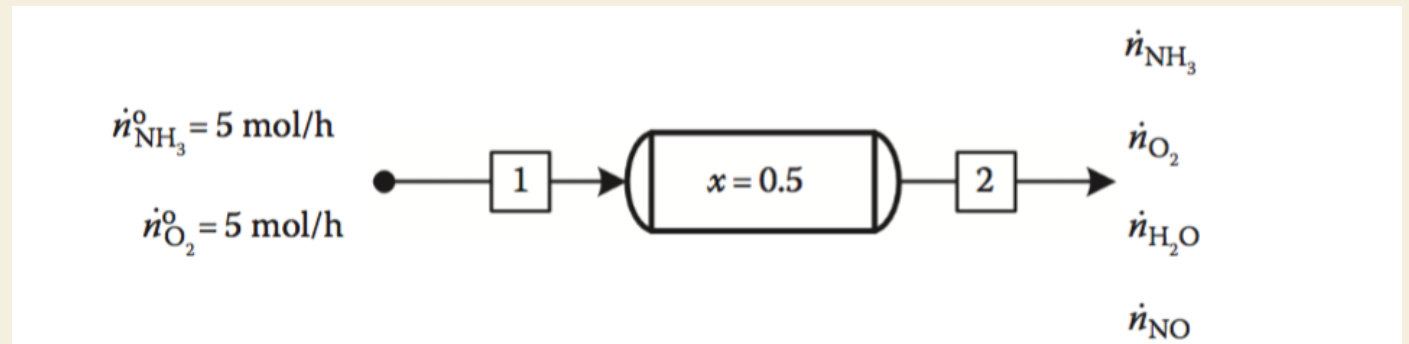
(5 mol of O consumed/h) * 1 mol/h SO_3 generated / $\frac{1}{2}$ mol O_2 consumed/h = 10 mol/h SO_3 produced

- Using the molecular species balance, the number of moles of SO_3 leaving the reactor is

$$\dot{n}_{\text{SO}_3} = 0 + 10 - 0 = 10 \text{ mol/h}$$

Extent of Reaction, Atomic Balance, and Molecular Species Balance Methods Example

- Ammonia is burned to form nitric oxide and water:
$$4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$$
- The fractional conversion of oxygen is 0.5. The inlet molar flow rate is 5 mol/h of NH_3 and 5 mol/h of oxygen. Calculate the exit component molar flow rates using the three methods:
 - a. Extent of reaction method
 - b. Atomic balance approach
 - c. Molecular species balance approach



- Basis: All results are based on 1 h of operation.

Extent of reaction method

- The material balance can be written using the extent of reaction method as follows:

$$n_i = n_i^o + \nu_i \xi$$

where $\nu_{\text{NH}_3} = -4$, $\nu_{\text{O}_2} = -5$, $\nu_{\text{NO}_2} = 4$, and $\nu_{\text{H}_2\text{O}} = 6$
Material balance of each component is then

$$\text{NH}_3 : n_{\text{NH}_3} = n_{\text{NH}_3}^o - 4\xi$$

$$\text{O}_2 : n_{\text{O}_2} = n_{\text{O}_2}^o - 5\xi$$

$$\text{NO} : n_{\text{NO}} = n_{\text{NO}}^o + 4\xi$$

The total number of moles at the outlet of the reactor:

$$n = n^{\circ} + (-4 - 5 + 4 + 6)\xi = n^{\circ} + \xi$$

where

$$n^{\circ} = n_{\text{NH}_3}^{\circ} + n_{\text{O}_2}^{\circ} + n_{\text{NO}}^{\circ} + n_{\text{H}_2\text{O}}^{\circ}$$

The total material balance equation is

$$n = n^{\circ} + \xi$$

Inlet molar feed rates:

$$n_{\text{NH}_3}^{\circ} = 5 \text{ mol/h}, \quad n_{\text{O}_2}^{\circ} = 5 \text{ mol/h}, \quad n_{\text{NO}}^{\circ} = 0, \quad n_{\text{H}_2\text{O}}^{\circ} = 0$$

- The reactor single pass conversion based on oxygen component is given by

Conversion = $f = \frac{n_{\text{O}_2}^{\circ} - n_{\text{O}_2}}{n_{\text{O}_2}^{\circ}}$, substituting known quantities.

$0.5 = \frac{5 - n_{\text{O}_2}}{5}$, the exit number of moles of oxygen is $n_{\text{O}_2} = 2.5$ mol.

Substituting n_{O_2} in oxygen component mole balance equation and solve for ξ

$$n_{\text{O}_2} = n_{\text{O}_2}^{\circ} - 5\xi$$

$$2.5 = 5 - 5\xi$$

The extent of reaction is $\xi = 0.5$

Substituting the value of $\xi = 0.5$ and the initial molar flow rates of each component into components mole balance equations, the final results are then

$$n_{\text{O}_2} = 2.5 \text{ mol/h}, \quad n_{\text{NH}_3} = 3 \text{ mol/h},$$

$$n_{\text{H}_2\text{O}} = 3 \text{ mol/h}, \quad n_{\text{NO}} = 2 \text{ mol/h}$$

Atomic balance approach

- Atomic balance on atoms involved in the reaction (N, O, H)— this is based on reactor inlet and outlet streams and not on the stoichiometry of the reaction equation:

$$\text{N: } 5 = n_{\text{NH}_3} + n_{\text{NO}}$$

$$\text{O: } 2(5) = 2(n_{\text{O}_2}) + n_{\text{H}_2\text{O}} + n_{\text{NO}}$$

$$\text{H: } 3(5) = 3n_{\text{NH}_3} + 2n_{\text{H}_2\text{O}}$$

- The single pass conversion, f_{O_2}

$$f_{\text{O}_2} = \frac{n_{\text{O}_2}^{\circ} - n_{\text{O}_2}}{n_{\text{O}_2}^{\circ}} = 0.5 = \frac{5 - n_{\text{O}_2}}{5}, \quad n_{\text{O}_2} = 2.5 \text{ mol}$$

- Substituting n_{O_2} in the O atomic balance and rearranging equations
- $5 = n_{NH_3} + n_{NO}$
- $5 = n_{H_2O} + n_{NO}$
- $15 = 3n_{NH_3} + 2n_{H_2O}$

Subtracting Equation 2 from Equation 1 leads to

$$0 = n_{NH_3} - n_{H_2O}, \quad \text{hence, } n_{NH_3} = n_{H_2O}$$

Substitution of $n_{NH_3} = n_{H_2O}$ in Equation 3

$$15 = 3n_{NH_3} + 2n_{NH_3}$$

$$5n_{NH_3} = 15, \quad n_{NH_3} = 3 \text{ mol}$$

Since $n_{NH_3} = n_{H_2O}$, accordingly, $n_{H_2O} = 3 \text{ mol}$

Substitute n_{H_2O} in Equation 2 to get the value of n_{NO}

$$5 = n_{H_2O} + n_{NO}$$

$$5 = 3 + n_{NO}, \quad n_{NO} = 2 \text{ mol}$$

The final results are

$$n_{O_2} = 2.5 \text{ mol/h}, \quad n_{NH_3} = 3 \text{ mol/h}, \quad n_{H_2O} = 3 \text{ mol/h},$$

$$n_{H_2O} = 3 \text{ mol/h}, \quad n_{NO} = 2 \text{ mol/h}$$

Molecular species approach

- The limiting reactant is oxygen:

$$\text{Conversion} = f = 0.5 = \frac{\text{Moles reacted}}{\text{Moles in the feed}} = \frac{\text{Mole reacted}}{5}$$

$$\text{Moles of O}_2 \text{ reacted} = 0.5 \times 5 = 2.5 \text{ mol}$$

$$\text{Moles of O}_2 \text{ exiting the reactor} = 5 - 2.5 = 2.5 \text{ mol}$$

$$\text{Moles of NH}_3 \text{ consumed} = 2.5 \text{ mol O}_2 \text{ consumed}$$

$$\times \frac{4 \text{ mol NH}_3 \text{ consumed}}{5 \text{ mol of O}_2 \text{ consumed}} = 2 \text{ mol}$$

$$\text{Moles of NH}_3 \text{ leaving the reactor} = \text{in} - \text{consumed} = 5 - 2 = 3 \text{ mol}$$

$$\text{Moles H}_2\text{O generated} = 2.5 \text{ mol O}_2 \text{ consumed}$$

$$\times \frac{6 \text{ mol H}_2\text{O generated}}{5 \text{ mol of O}_2 \text{ consumed}} = 3 \text{ mol}$$

$$\text{Moles of NO generated} = 2.5 \text{ mol O}_2 \text{ consumed}$$

$$\times \frac{4 \text{ mol NO generated}}{5 \text{ mol of O}_2 \text{ consumed}} = 2 \text{ mol}$$

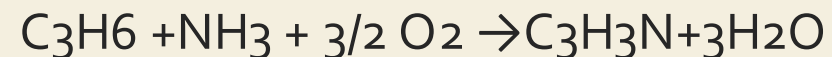
- The final values of exit stream component molar flow rates are:
- $n_{\text{O}_2} = 2.5 \text{ mol/h}$
- $n_{\text{NH}_3} = 3 \text{ mol/h}$
- $n_{\text{H}_2\text{O}} = 3 \text{ mol/h}$
- $n_{\text{NO}} = 2 \text{ mol/h}$

Summary

- The extent of reaction method and molecular species balance require the specification of the stoichiometric equation.
- By contrast, the stoichiometric equation is not needed in atomic balance.
- All of the three methods lead to the same results.

Problem

- The feed contains 10 mol% propylene (C₃H₆), 12 mol% ammonia (NH₃), and 78 mol% air. **Hint: Air is 21% O₂ and 79% N₂.**
- A fractional conversion of 30% of the limiting reactant is achieved.
- Taking 100 mol of feed as a basis, determine which reactant is limiting, the percentage by which each of the other reactants is in excess, and the molar amounts of all product gas.
- Use all methods of solution.
- Acrylonitrile (C₃H₃N) is produced by the reaction of propylene, ammonia, and oxygen:



Determining limiting reactant

- The limiting reactant is found by determining the lowest n_i/v_i ratio:

$$\text{C}_3\text{H}_6 \text{----} 10/1 = 10$$

$$\text{NH}_3 \text{----} 12/1 = 12$$

$$\text{O}_2 \text{----} (78 \times 0.21)/1.5 = 16.38$$

Then C_3H_6 is the limiting reactant!

- The percent excess of ammonia is:

$$\% \text{NH}_3 \text{ in excess} = ((n_{\text{feed}} - n_{\text{stoich}}) / n_{\text{stoich}}) \times 100 = ((12 - 10) / 10) \times 100 = 20 \%$$

- The percent excess of oxygen:

$$\% \text{O}_2 \text{ in excess} = ((n_{\text{feed}} - n_{\text{stoich}}) / n_{\text{stoich}}) \times 100 = ((16.38 - 15) / 15) \times 100 = 9.2 \%$$

Extent of reaction method

- Using the extent of reaction method for single reaction, $n_i = n_i^0 + \nu_i \xi$

$$\text{C}_3\text{H}_6 : n_{\text{C}_3\text{H}_6} = 10 - \xi$$

$$\text{NH}_3 : n_{\text{NH}_3} = 12 - \xi$$

$$\text{O}_2 : n_{\text{O}_2} = (0.21 \times 78) - 1.5 \xi$$

$$\text{C}_3\text{H}_3\text{N} : n_{\text{C}_3\text{H}_3\text{N}} = 0 + \xi$$

$$\text{H}_2\text{O} : n_{\text{H}_2\text{O}} = 0 + 3\xi$$

- Conversion of the limiting reactant (C_3H_6):

$$0.3 = (10 - n_{\text{C}_3\text{H}_6})/10, \quad n_{\text{C}_3\text{H}_6} = 7 \text{ mol}$$

- Substituting $n_{\text{C}_3\text{H}_6}$ in C_3H_6 component balance equation $7 = 10 - \xi$, $\xi = 3$
- Substitute $\xi = 3$ in the rest of component mole balance equations to get the number of moles of all components leaving the reactor, the values supposed to be as follows:
- $n_{\text{C}_3\text{H}_6} = 7 \text{ mol}$, $n_{\text{NH}_3} = 9 \text{ mol}$, $n_{\text{O}_2} = 11.88 \text{ mol}$, $n_{\text{C}_3\text{H}_3\text{N}} = 3 \text{ mol}$

Atomic balance approach

- Input = output

$$\text{C: } 3 \times 10 = 3n\text{C}_3\text{H}_6 + 3n\text{C}_3\text{H}_3\text{N}$$

$$\text{H: } 6(10) + 3(12) = 6n\text{C}_3\text{H}_6 + 3n\text{C}_3\text{H}_3\text{N} + 2n\text{H}_2\text{O} + 3n\text{NH}_3$$

$$\text{O: } 2 \times 0.21(78) = 2n\text{O}_2 + n\text{H}_2\text{O}$$

$$\text{N: } 2 \times 0.79(78) + 12 = n\text{NH}_3 + n\text{C}_3\text{H}_3\text{N} + 2n\text{N}_2$$

- $n\text{N}_2$ is inert
- The single pass conversion:

$$f = 0.3 = (10 - n\text{C}_3\text{H}_6) / 10 \quad \text{-----} \quad n\text{C}_3\text{H}_6 = 7 \text{ mol}$$

- Substitute $n\text{C}_3\text{H}_6$ in C atomic balance: $30 = 3 \times 7 + 3n\text{C}_3\text{H}_3\text{N}$, **$n\text{C}_3\text{H}_3\text{N} = 3 \text{ mol}$**
- Substitute $n\text{C}_3\text{H}_3\text{N} = 3 \text{ mol}$ and

$$n\text{N}_2 = 0.79 \times 78 = 61.62 \text{ mol: } 2 \times 0.79(78) + 12 = n\text{NH}_3 + 3 + 2 \times 61.62$$

- Solving for **$n\text{NH}_3$**

$$2 \times 0.79(78) + 12 = n\text{NH}_3 + 3 + 2 \times 61.62 \quad n\text{NH}_3 = \mathbf{9 \text{ mol}}$$

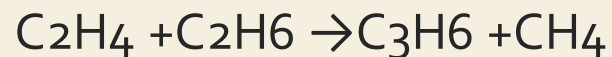
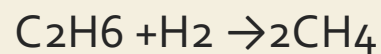
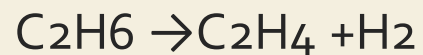
- Solving the rest of equations gives the following results (in mol):
- **$n\text{C}_3\text{H}_6 = 7$, $n\text{NH}_3 = 9$, $n\text{O}_2 = 11.88$, $n\text{C}_3\text{H}_3\text{N} = 3$, $n\text{H}_2\text{O} = 9$, $n\text{N}_2 = 61.62$**

Molecular species balance approach

- Accumulation = (input – output) + (generation – consumption)
- Conversion : $0.3 = (10 - n_{\text{C}_3\text{H}_6})/10$, $n_{\text{C}_3\text{H}_6} = 7 \text{ mol}$
- Accordingly, the amount of C_3H_6 consumed = $10 - 7 = 3 \text{ mol}$
- NH_3 : $0 = 12 - n_{\text{NH}_3} + 0 - 3$ --- $n_{\text{NH}_3} = 9 \text{ mol}$
- O_2 : $0 = 16.38 - n_{\text{O}_2} + 0 - 4.5$ --- $n_{\text{O}_2} = 11.88 \text{ mol}$
- $\text{C}_3\text{H}_3\text{N}$: $0 = 0 - n_{\text{C}_3\text{H}_3\text{N}} + 3 - 0$ ---- $n_{\text{C}_3\text{H}_3\text{N}} = 3 \text{ mol}$
- H_2O : $0 = 0 - n_{\text{H}_2\text{O}} + 9 - 0$ --- $n_{\text{H}_2\text{O}} = 9 \text{ mol}$

Extent of Reaction and Multiple Reactions

- Generally, the synthesis of chemical products does not involve a single reaction but rather multiple reactions. For instance, the goal would be to maximize the production of the desirable product and minimize the production of unwanted by-products. For example, ethylene is produced by the dehydrogenation of ethane:



- Yield and selectivity are used to describe the degree to which a desired reaction predominates over competing side reactions in a multireaction system.

Yield

Yield has various definitions:

Yield = moles of desired product formed/ moles formed if there were no side reactions and limiting reactant reacted completely

Yield = moles of desired product formed/ moles of reactant fed

Yield = moles of desired product formed/ moles of reactant consumed

Selectivity

- The selectivity of a component is the number of moles of desired component to the number of moles of undesired component.

**Selectivity = moles of desired product formed/
moles of undesired product formed**

Multiple Reactions

- The concept of extent of reaction can also be applied to multiple reactions, with each reaction having its own extent. If a set of reactions takes place in a batch or continuous, steady-state reactor, we can write the following equation for species i :

$$n_i = n_i^0 + \sum_j \nu_{ij} \xi_j$$

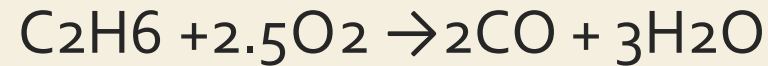
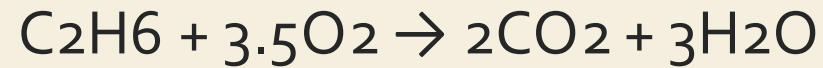
where

ν_{ij} is the stoichiometric coefficient of substance i in reaction j

ξ_j is the extent of reaction for reaction j

Ethane Combustion Problem

- The following reactions take place in a reactor, where CO is the undesired product:



- The feed to reactor consists of 100 mol C₂H₆ and 500 mol O₂. The product stream was analyzed and found to contain 20 mol C₂H₆, 120 mol CO₂, 40 mol CO, 240 mol O₂, and 240 mol H₂O. The reactor conversion is 80%.
- Calculate the yield and selectivity.

Solution

- Use the three definitions for yield and selectivity:

Yield = moles of desired product formed/ moles formed if there were no side reactions and limiting reactant reacted completely

$$= 120 \text{ mol CO}_2 / 200 \text{ mol CO}_2 \text{ should be formed} = 0.6$$

Yield = moles of desired product formed/ moles of reactant fed

$$= 120 \text{ mol CO}_2 / 100 \text{ mol C}_2\text{H}_6 = 1.2$$

Yield = moles of desired product formed/ moles of reactant consumed

$$= 120 \text{ mol CO}_2 / (100 - 20) = 1.5$$

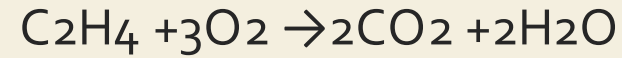
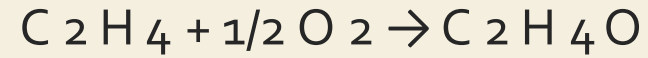
Selectivity

- Selectivity is the number of moles of desired product (carbon dioxide) to the number of moles of undesired product formed:

$$\text{Selectivity} = 120 \text{ mol CO}_2 / 40 \text{ mol CO} = 3$$

Oxidation Reaction Problem

- Ethylene is oxidized to ethylene oxide (desired) and carbon dioxide (undesired).
- The following reactions are taking place:



Solution

- Assign an extent of reaction for each reaction; ξ_1 for the first reaction and ξ_2 for the second reaction. 1
- The first reaction: $\text{C}_2\text{H}_4 + 2 \text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{O} \quad \xi_1$
The second reaction: $\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \quad \xi_2$
- Mole balance using the extent of reaction approach:

$$\text{C}_2\text{H}_4 : \quad n_{\text{C}_2\text{H}_4} = n_{\text{C}_2\text{H}_4}^0 - \xi_1 - \xi_2$$

$$\text{O}_2 : \quad n_{\text{O}_2} = n_{\text{O}_2}^0 - \frac{1}{2}\xi_1 - 3\xi_2$$

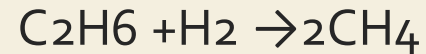
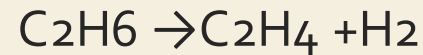
$$\text{C}_2\text{H}_4\text{O} : \quad n_{\text{C}_2\text{H}_4\text{O}} = 0 + \xi_1$$

$$\text{CO}_2 : \quad n_{\text{CO}_2} = 0 + 2\xi_2$$

$$\text{H}_2\text{O} : \quad n_{\text{H}_2\text{O}} = 0 + 2\xi_2$$

Production of Ethylene Problem

- The feed stream contains 85 mol% ethane (C_2H_6), and the balance is inert. The fractional conversion of ethane is 0.5, and the fractional yield of ethylene (C_2H_4) is 0.40. Calculate the molar composition of the product gas and the selectivity of ethylene for methane production.
- The following two multiple reactions take place in a continuous reactor at steady state:



Solution

- Assign an extent of reaction for each reaction, namely, ξ_1 for the first reaction and ξ_2 for the second reaction. For simplicity, you may assign symbols for the components involved in the reaction.
- Basis: 100 mol of feed.
The primary reaction: $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \quad \xi_1$
The secondary reaction: $\text{C}_2\text{H}_6 + \text{H}_2 \rightarrow 2\text{CH}_4 \quad \xi_2$
- Component mole balance equations using the extent of reaction method approach:

$$\text{C}_2\text{H}_6 : \quad n_{\text{C}_2\text{H}_6} = 85 - \xi_1 - \xi_2$$

$$\text{C}_2\text{H}_4 : \quad n_{\text{C}_2\text{H}_4} = 0.0 + \xi_1$$

$$\text{H}_2 : \quad n_{\text{H}_2} = 0.0 + \xi_1 - \xi_2$$

$$\text{CH}_4 : \quad n_{\text{CH}_4} = 0.0 + 2\xi_2$$

Solution

- The fractional conversion of ethane, C_2H_6 , is

$$f_{C_2H_6} = 0.5 = (85 - n_{C_2H_6}) / 85$$

Moles of unreacted ethane in the exit stream: $n_{C_2H_6} = 42.25 \text{ mol}$

- The yield of ethylene (C_2H_4) equals the number of moles of the desired component produced to the number of moles produced of the same component, if there were no side reactions and the reactant is completely used up:

$$0.40 = n_{C_2H_4} / 85$$

The number of moles of ethylene in the exit stream is, $n_{C_2H_4} = 34 \text{ mol}$

Solution

- Substitute $n_{C_2H_4}$ in Equation to determine ξ_1 : $34 = 0.0 + \xi_1$
- The extent of reaction for the first reaction is $\xi_1 = 34$ mol Substitute ξ_1 and $n_{C_2H_6}$ in Equation to determine ξ_2 : $42.5 = 85 - 34 - \xi_2$
- The extent of reaction for the second reaction is $\xi_2 = 8.5$ mol Substituting ξ_1 and ξ_2 in Equation gives

$$n_{H_2} = 0.0 + \xi_1 - \xi_2 \quad n_{H_2} = 0.0 + 34 - 8.5$$

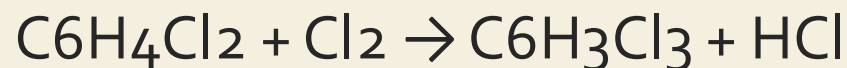
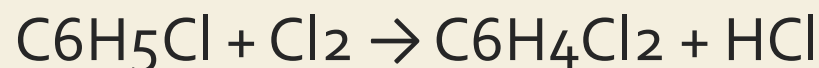
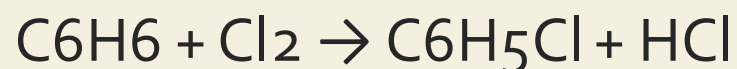
- The number of moles of hydrogen in the exit stream is $n_{H_2} = 25.5$ mol Substituting ξ_2 in Equation to find out n_{CH_4} :

$$n_{CH_4} = 0.0 + 2 \times 8.5$$

The number of moles of methane in the exit stream is $n_{CH_4} = 17$ mol

Molecular Species Approach for Multiple Reactions

- When using the molecular species approach for multiple reactions, we have to choose a single chemical species in each equation that appears in that reaction only. We can then use the number of moles of that species to keep track of how much of that reaction occurs. Consider the following multiple reactions:



- We have to choose a single unique chemical species in each reaction that does not appear in other reactions.
- There is a unique chemical compound to the first and the last reactions only. However, reaction 2 has no species that are unique to it.
- The amount of reaction that occurs in the first reaction can be determined by computing how much benzene (C₆H₆) reacts.
- All other species consumed or produced via the first reaction can be expressed in terms of this quantity and the stoichiometric coefficients.

$$\mathfrak{R}_{\text{C}_6\text{H}_6} = \dot{n}_{\text{C}_6\text{H}_6}^o - \dot{n}_{\text{C}_6\text{H}_6}$$

- The amount of reaction that occurs in the third reaction can be determined by computing how much trichlorobenzene ($\text{C}_6\text{H}_3\text{Cl}_3$) is generated. All other species consumed or produced via the third reaction can be expressed in terms of this quantity and the stoichiometric coefficients.

$$\mathfrak{R}_{\text{C}_6\text{H}_3\text{Cl}_3} = \dot{n}_{\text{C}_6\text{H}_3\text{Cl}_3}$$

- The amount of the second reaction that occurs is the total amount of HCl minus that is formed by the first and last reactions. Thus the amount of the second reaction that occurs is

$$\mathfrak{R}_{\text{HCl}} = \left(\dot{n}_{\text{HCl}} - \dot{n}_{\text{HCl}}^{\circ} \right) - \left(\dot{n}_{\text{C}_6\text{H}_6}^{\circ} - \dot{n}_{\text{C}_6\text{H}_6} \right) - \dot{n}_{\text{C}_6\text{H}_3\text{Cl}_3}$$

- Material balances on the remaining chemical species:
- Material balance on Cl:

$$\dot{n}_{\text{Cl}_2} = \dot{n}_{\text{Cl}_2}^{\circ} - \left(\dot{n}_{\text{C}_6\text{H}_6}^{\circ} - \dot{n}_{\text{C}_6\text{H}_6} \right) - \left(\dot{n}_{\text{HCl}} + \dot{n}_{\text{C}_6\text{H}_6} - \dot{n}_{\text{C}_6\text{H}_3\text{Cl}_3} - \dot{n}_{\text{C}_6\text{H}_6}^{\circ} \right) - \left(\dot{n}_{\text{C}_6\text{H}_3\text{Cl}_3} \right)$$

- Material balance on C₆H₅Cl:

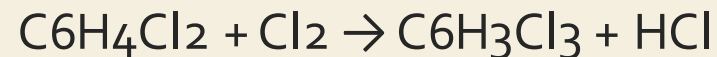
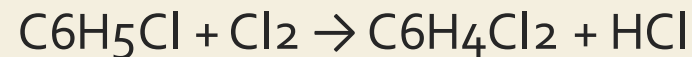
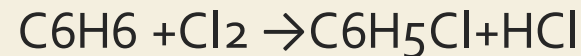
$$\dot{n}_{\text{C}_6\text{H}_5\text{Cl}} = \dot{n}_{\text{C}_6\text{H}_5\text{Cl}}^{\circ} + \left(\dot{n}_{\text{C}_6\text{H}_6}^{\circ} - \dot{n}_{\text{C}_6\text{H}_6} \right) - \left(\dot{n}_{\text{HCl}} + \dot{n}_{\text{C}_6\text{H}_6} - \dot{n}_{\text{C}_6\text{H}_3\text{Cl}_3} - \dot{n}_{\text{C}_6\text{H}_6}^{\circ} \right)$$

- Material balance on C₆H₄Cl₂:

$$\dot{n}_{\text{C}_6\text{H}_4\text{Cl}_2} = \dot{n}_{\text{C}_6\text{H}_4\text{Cl}_2}^{\circ} + \left(\dot{n}_{\text{HCl}} + \dot{n}_{\text{C}_6\text{H}_6} - \dot{n}_{\text{C}_6\text{H}_3\text{Cl}_3} - \dot{n}_{\text{C}_6\text{H}_6}^{\circ} \right) - \left(\dot{n}_{\text{C}_6\text{H}_3\text{Cl}_3} \right)$$

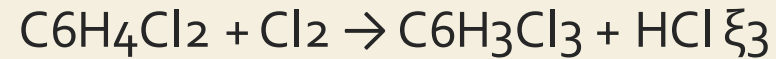
Multiple Reactions Problem

- 10 mol/h of benzene (C₆H₆) and 20 mol/h of chlorine (Cl₂) are fed to a reactor. The exit stream was analyzed and found to contain 1 mol/h of Cl₂, 2 mol/h of C₆H₅Cl, and 4 mol/h of C₆H₄Cl₂.
- Solve the problem using the extent of reaction method, atomic species balance, and molecular species approach.
- Calculate the percent conversion of benzene.
- The chlorination of benzene occurs via the following reactions:



Extent of reaction approach

- Basis: 1 h of operation.
- Extent of reaction approach
Let ξ_1 , ξ_2 , and ξ_3 be the extent of the first, second, and third reactions, respectively.



- The number of moles of each species in the reactor exist stream may written as

$$\text{C}_6\text{H}_6 : n_{\text{C}_6\text{H}_6} = n_{\text{C}_6\text{H}_6}^0 - \xi_1$$

$$\text{Cl}_2 : n_{\text{Cl}_2} = n_{\text{Cl}_2}^0 - \xi_1 - \xi_2 - \xi_3$$

$$\text{C}_6\text{H}_5\text{Cl} : n_{\text{C}_6\text{H}_5\text{Cl}} = n_{\text{C}_6\text{H}_5\text{Cl}}^0 + \xi_1 - \xi_2$$

$$\text{HCl} : n_{\text{HCl}} = n_{\text{HCl}}^0 + \xi_1 + \xi_2 + \xi_3$$

$$\text{C}_6\text{H}_4\text{Cl}_2 : n_{\text{C}_6\text{H}_4\text{Cl}_2} = n_{\text{C}_6\text{H}_4\text{Cl}_2}^0 + \xi_2 - \xi_3$$

$$\text{C}_6\text{H}_3\text{Cl}_3 : n_{\text{C}_6\text{H}_3\text{Cl}_3} = n_{\text{C}_6\text{H}_3\text{Cl}_3}^0 + \xi_3$$

$$n_{\text{C}_6\text{H}_6} = 10 - \xi_1$$

$$1 = 20 - \xi_1 - \xi_2 - \xi_3$$

$$2 = 0 + \xi_1 - \xi_2$$

$$n_{\text{HCl}} = 0 + \xi_1 + \xi_2 + \xi_3$$

$$4 = 0 + \xi_2 - \xi_3$$

$$n_{\text{C}_2\text{H}_3\text{Cl}_3} = 0 + \xi_3$$

Solving the third equation for ξ_1 and the fifth for ξ_3 as follows:

$$\xi_1 = 2 + \xi_2$$

$$\xi_3 = \xi_2 - 4$$

Substitute ξ_1 and ξ_3 into the second equation to get

$$0 = 19 - (2 + \xi_2) - \xi_2 - (\xi_2 - 4)$$

- Solving this equation gives $\xi_2 = 7 \text{ mol}$
Substituting ξ_2 into these preceding equations gives

$$\xi_1 = 9 \text{ mol and } \xi_3 = 3 \text{ mol.}$$

- Substituting these values into the species balances gives

$$n_{\text{C}_6\text{H}_6} = 1 \text{ mol, } n_{\text{HCl}} = 19 \text{ mol, } n_{\text{C}_6\text{H}_3\text{Cl}_3} = 3 \text{ mol}$$

- The conversion of benzene is
- $f_{\text{C}_6\text{H}_6} = (10 \text{ mol} - 1 \text{ mol}) / 10 \text{ mol} = 0.90$
- Selectivity is defined as

Selectivity = moles of desired product formed / moles of undesired product formed

The desired product is $\text{C}_6\text{H}_5\text{Cl}$, and the undesired product is $\text{C}_6\text{H}_3\text{Cl}_3$.

Accordingly, Selectivity = $2/3 = 0.667$

Atomic species approach

- An alternative solution is the atomic species approach. We can now write the atomic species balances for C, H, and Cl.

$$\text{C: } 6(10) = 6\dot{n}_{\text{C}_6\text{H}_6} + 6(2) + 6(4) + 6\dot{n}_{\text{C}_6\text{H}_3\text{Cl}_3}$$

$$\text{H: } 6(10) = 6\dot{n}_{\text{C}_6\text{H}_6} + 5(2) + 4(4) + 3\dot{n}_{\text{C}_6\text{H}_3\text{Cl}_3} + \dot{n}_{\text{HCl}}$$

$$\text{Cl: } 2(20) = 2(1) + 1(2) + 2(4) + 3\dot{n}_{\text{C}_6\text{H}_3\text{Cl}_3} + \dot{n}_{\text{HCl}}$$

Simplifying these three equations gives

$$6\dot{n}_{\text{C}_6\text{H}_6} + 6\dot{n}_{\text{C}_6\text{H}_3\text{Cl}_3} = 24$$

$$6\dot{n}_{\text{C}_6\text{H}_6} + 3\dot{n}_{\text{C}_6\text{H}_3\text{Cl}_3} + \dot{n}_{\text{HCl}} = 34$$

$$3\dot{n}_{\text{C}_6\text{H}_3\text{Cl}_3} + \dot{n}_{\text{HCl}} = 28$$

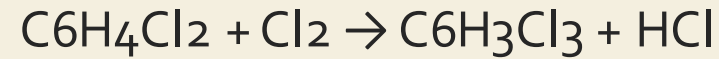
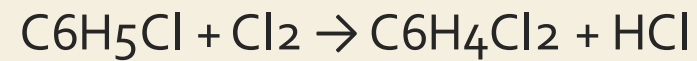
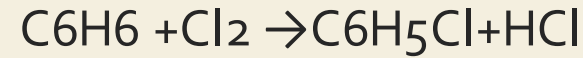
- There are now three equations in three unknowns. Subtract the last from

$$6n = 6, \text{ hence } n = 1 \text{ mol C}_6\text{H}$$

- Substitute this value into the first equation to get $n \text{ C}_6\text{H}_3\text{Cl}_3 = 3 \text{ mol}$, and further substitute this value into the last equation to get $n \text{ HCl} = 19 \text{ mol}$.
- Since these are the same numbers as those obtained via the extent of reaction method, the conversion and selectivity values will be 90% and 0.667, respectively.

Molecular species approach

- The third alternative solution is the molecular species approach. The three chemical reactions that occur are as follows:



- In using the molecular species approach, we pick a single chemical species in each reaction that is unique to that reaction.

Degrees of Freedom Analysis for Reactive Processes

$$NDF = \left\{ \begin{array}{c} \text{number of} \\ \text{unknowns} \end{array} \right\} + \left\{ \begin{array}{c} \text{number of} \\ \text{independent} \\ \text{chemical} \\ \text{reactions} \end{array} \right\} - \left\{ \begin{array}{c} \text{number of} \\ \text{independent molecular} \\ \text{species balances} \end{array} \right\} - \left\{ \begin{array}{c} \text{number of} \\ \text{other equations} \\ \text{relating} \\ \text{variables} \end{array} \right\}$$

In atomic balance case, the degrees of freedom analysis

$$NDF = \left\{ \begin{array}{c} \text{number of} \\ \text{unknowns} \end{array} \right\} - \left\{ \begin{array}{c} \text{number of} \\ \text{independent} \\ \text{atomic} \\ \text{species} \\ \text{balances} \end{array} \right\} - \left\{ \begin{array}{c} \text{number of} \\ \text{molecular} \\ \text{balances on} \\ \text{independent} \\ \text{nonreactive} \\ \text{species} \end{array} \right\} - \left\{ \begin{array}{c} \text{number} \\ \text{of other} \\ \text{relations} \\ \text{relating} \\ \text{variables} \end{array} \right\}$$

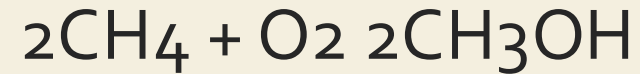
A set of chemical reactions are independent, if the stoichiometric equation of any one of them cannot be obtained by a linear combination (via addition, subtraction, or multiplication) of the stoichiometric equations of others.

Chemical Equilibrium

- More often than not, reactions do not proceed instantly. Predicting the speed at which a reaction occurs is very important.
- Reactions do not necessarily happen independently. Very often, the reverse “half” reaction of the reaction we are interested in also takes place.
- Chemical equilibrium is reached when the rates of the forward and reverse reactions are equal to each other (i.e., compositions no longer change with time). While we will not calculate reaction rates, we need to know what affects them because this will affect the equilibrium.
- **Things that we must consider that affect reaction rates and, hence, equilibrium are temperature and concentration.**

Equilibrium Reaction

- Consider the reaction of methane with oxygen:

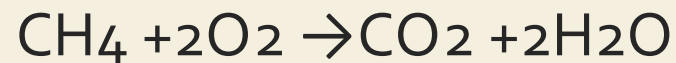
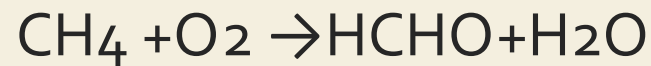


At equilibrium, the compositions of the components satisfy the relation:

$$K(T) = \frac{y_{\text{CH}_3\text{OH}}^2}{y_{\text{CH}_4}^2 y_{\text{O}_2}}$$

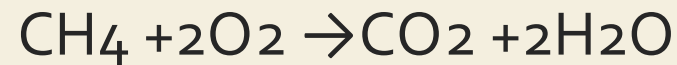
Methane Oxidation Process Problem

- The feed to a plug flow reactor contains equimolar amounts of methane and oxygen. Assume a basis of 100 mol feed/s. The fractional conversion of methane is 0.9, and the fraction yield of formaldehyde is 0.855. Calculate the molar composition of the reactor output stream and the selectivity of formaldehyde production relative to carbon dioxide production. Methane (CH₄) and oxygen react in the presence of a catalyst to form formaldehyde (HCHO). In a parallel reaction, methane is oxidized to carbon dioxide and water:



Methane Oxidation Process Problem

- The feed to a plug flow reactor contains equimolar amounts of methane and oxygen. Assume a basis of 100 mol feed/s. The fractional conversion of methane is 0.9, and the fraction yield of formaldehyde is 0.855. Calculate the molar composition of the reactor output stream and the selectivity of formaldehyde production relative to carbon dioxide production. Methane (CH₄) and oxygen react in the presence of a catalyst to form formaldehyde (HCHO). In a parallel reaction, methane is oxidized to carbon dioxide and water:



Answers

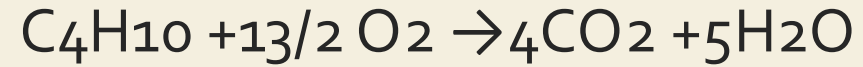
- $n_{\text{CH}_4} = 5 \text{ mol}$
- $n_{\text{HCHO}} = 42.75 \text{ mol}$
- $n_{\text{O}_2} = 5 \text{ mol}$
- $n_{\text{CO}_2} = 2.75 \text{ mol}$
- $n_{\text{H}_2\text{O}} = 47.25 \text{ mol}$

Combustion Reactions

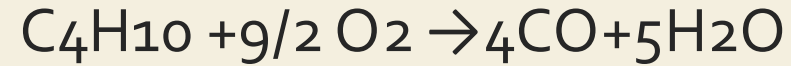
- Combustion is the rapid reaction of a fuel with oxygen to produce energy. Combustion is a very important industrial chemical reaction. Fuels include coal (C, H, S, and others), fuel oil (high Mw hydrocarbons and some S), gaseous fuel (natural gas—mostly methane), or liquefied petroleum gas (propane and/or butane). Maximum energy is produced when fuel is completely burned (oxidized). The product gas is called stack gas or flue gas.
- Complete combustion results in all C oxidized to CO_2 , all H oxidized to H_2O , and all S oxidized to SO_2 .
- In incomplete combustion, C is oxidized to CO and CO_2 .

Combustion Reactions

- Complete combustion of butane:



- Side reaction; incomplete combustion of butane:

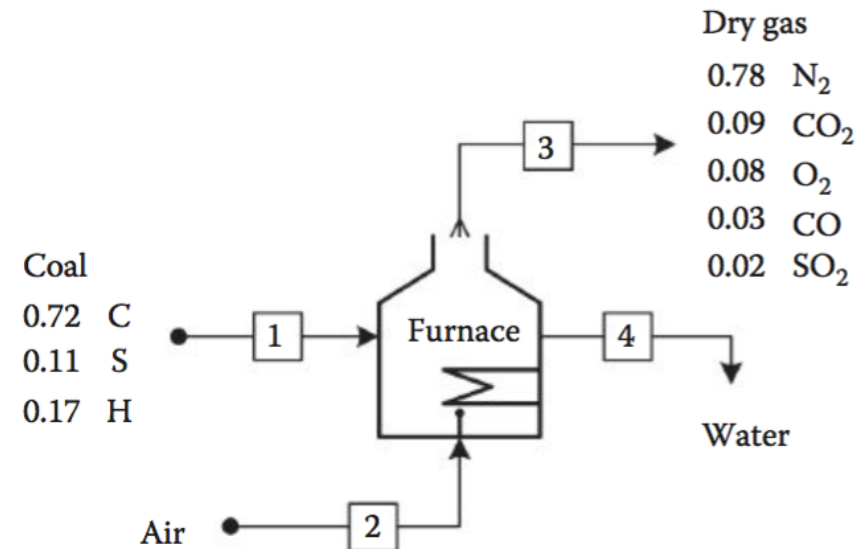
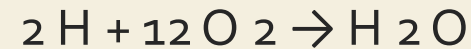
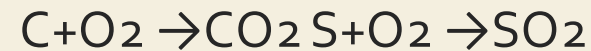


Theoretical and Excess Air

- For obvious economic reasons, air (79% N₂, 21% O₂) is the source of oxygen in combustion reactions. Combustion reactions are always conducted with excess air, thus ensuring good conversion of the expensive fuel.
- Theoretical oxygen is the moles or molar flow rate of O₂ required for complete combustion of all the fuel. Theoretical air is the quantity of air that contains the theoretical oxygen.
- Theoretical air = $1/0.21 \times \text{theoretical O}_2$
- Excess air is the amount of air fed to the reactor that exceeds the theoretical air.
- Percent excess air = $\frac{((\text{moles air})_{\text{fed}} - (\text{moles air})_{\text{theoretical}})}{(\text{moles air})_{\text{theoretical}}} \times 100\%$

Combustion process of coal

- Calculate the flow rate of all streams and their compositions. Assuming all the coal is consumed, **calculate the percent excess air and the ratio of water vapor and dry gas.** Note that the feed composition is given in mole fraction. The following reactions are taking place:



Answers

- 43% excess air
- 0.014 mol H₂O/mol dry gas