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3

Simultaneous Material and Energy Balances

Material and energy balances are very important in the chemical industries. Material quantities can be described by material balances. Similarly, energy quantities can be described by energy balances. If there is no accumulation, what goes into a process must come out. Material and energy balances are fundamental to the control of processing, particularly in the control of yields of the products. After completing this chapter, the following learning objectives should be accomplished

Learning Objectives

1. Understand the basic definitions needed in solving material balance problems, for example, conversion, yield, extent of reaction, and standard heat of reaction (Section 3.1).
2. Write an energy balance for a reacting system (Section 3.2).

3.1 Material Balances

There are frequently used definitions that should be known when solving material and energy balance problems involving chemical reactions. As the definitions include conversion, yield, selectivity, and extent of reaction, these are briefly explained in subsequent sections. The general material balance equation takes the form [1, 2]

Accumulation = (in − out) + (generation − consumption)

3.1.1 Conversion

Generally, syntheses of chemical products do not involve a single reaction but rather multiple reactions. The purpose, in this case, is to maximize the production of the desirable product and minimize the production of unwanted by-products. Conversion is the ratio of the moles that react to the moles that are fed to a reactor. Relative to species (i), the fractional conversion can be calculated using the following equation: Fractional conversion of component i

$$f_i = \frac{\{\text{moles of component } i\}_{\text{in}} - \{\text{moles of component } i\}_{\text{out}}}{\{\text{moles of component } i\}_{\text{in}}} \quad \text{.........} (3\text{-}1)$$

$$f_i = \frac{n_{i0} - n_i}{n_{i0}}$$

3.1.2 Yield

The yield of a reaction is the ratio of the desired product formed (in moles) to the total amount that could have been produced if conversion of the limiting reactant was complete (i.e., 100%) and no side reactions occurred [3].

$$\text{Yield} = \frac{\text{moles of desired product formed}}{\begin{array}{c}\text{moles formed if there were no side reactions and}\\ \text{limiting reactant reacted completely}\end{array}} \quad \text{.......} (3\text{-}2)$$

3.1.3 Selectivity

The selectivity of a reaction is the ratio of the desired product formed (in moles) to the undesired product formed (in moles):

$$\text{Selectivity} = \frac{\text{moles of desired product formed}}{\text{moles of undesired product formed}} \quad \text{......} (3\text{-}3)$$

3.1.4 Extent of Reaction (ξ)

The concept of extent of reaction can also be applied to multiple reactions, with each reaction having its own extent. The extent of reaction is the amount in moles (or molar flow rate) that is converted in a given reaction. If a set of reactions take place in a batch or continuous steady state reactor, we can write

$$n_i = n_{i0} + \sum_j \nu_{ij}\xi_j \quad \text{.......} (3\text{-}4)$$

where

vij is the stoichiometric coefficient of substance *i* in reaction *j*

ξj is the extent of reaction for reaction *j*

ni$_0$ is the inlet molar flow rate of component *i*

For a single reaction, the earlier equation reduces to the following equation:

$$\dot{n}_i = \dot{n}_{i0} + \upsilon_i \dot{\xi} \quad \text{....... (3-5)}$$

3.2 Energy Balances

The general energy balance equation for an open system at steady state is as follows [4]:

$$\dot{Q} - \dot{W}_s = \Delta \dot{H} + \Delta KE + \Delta PE \quad \text{....... (3-6)}$$

$$\Delta KE = \frac{1}{2} \dot{m} \left(\upsilon_2^2 - \upsilon_1^2 \right) \quad \text{....... (3-7)}$$

$$\Delta PE = \dot{m} g (z_2 - z_1) \quad \text{....... (3-8)}$$

Methods differ in reference state (and thus in the calculation of $\Delta \dot{H}$).

3.2.1 Heat of Reaction Method

In this method, the reference state is such that the reactants and products are at 25°C and 1 atm:

$$\Delta \dot{H} = \sum_{\text{reactions}} \dot{\xi}_j \Delta H^0_{\text{Rx},j} + \sum_{\text{out}} \dot{n}_i \overline{h}_i - \sum_{\text{in}} \dot{n}_i \overline{h}_i \quad \text{....... (3-9)}$$

$$\overline{h}_i = \int_{T_{\text{ref}}}^{T} C_{p_i} \mathrm{d}T \quad \text{....... (3-10)}$$

$$\Delta H^0_{\text{Rx},j} = \sum_{i}^{n} \upsilon_i \Delta H^0_{\text{f},i} \quad \text{........ (3-11)}$$

3.2.2 Heat of Formation Method

In this method, the reference state is the elemental species that constitutes the reactants and products in the states they occur in nature at 25°C and 1 atm:

$$\Delta \dot{H} = \sum_{\text{out}} \dot{n}_i \overline{h}_i - \sum_{\text{in}} \dot{n}_i \overline{h}_i \quad \text{......... (3-12)}$$

The enthalpy in this case includes the sensible heat and the enthalpy of formation:

$$\Delta \dot{H}_i \Big|_{\text{at } T} = \Delta H_f^0 + \int_{T_{\text{ref}}}^{T} C_{p_i} dT \quad \text{…….} \ (3\text{-}13)$$

3.2.3 Concept of Atomic Balances

Consider the reaction of hydrogen with oxygen to form water:

$$H_2 + O_2 \longrightarrow H_2O$$

We may attempt to do our calculations with this reaction, but there is something Seriously wrong with this equation. It is not balanced; as written, it implies that an atom of oxygen is somehow "lost" in the reaction, but this is in general impossible. Therefore, we must compensate by writing

$H_2 + 1/2\ O_2 \longrightarrow H_2O$

The number of atoms of any given element does not change in any reaction (assuming that it is not a nuclear reaction).

3.2.4 Mathematical Formulation of the Atomic Balance

Now recall the general balance equation:

(In − out) + (generation − consumption) = accumulation

Moles of atoms of any element are conserved; therefore, generation = 0. So we have the following balance on a given element A:

$$\sum \dot{n}_{A,in} - \sum \dot{n}_{A,out} = 0 \quad \text{…….} \ (3\text{-}14)$$

When analyzing a reacting system you must choose either an atomic balance or a molecular species balance but not both. An atomic balance often yields simpler algebra, but also will not directly tell you the extent of reaction, and will not tell you whether the system specifications are actually impossible to achieve for a given set of equilibrium reactions.

3.2.5 Degrees of Freedom Analysis for the Atomic Balance

As before, to do a degrees of freedom analysis, it is necessary to count the number of unknowns and the number of equations one can write, and then subtract them. However, there are a couple of important things to be aware of with these balances: when doing atomic balances, the extent of reaction does not count as an unknown, while with a molecular species balance it does. This is the primary advantage of this method. The extent of reaction does not matter since atoms of elements are conserved regardless of how far the reaction has proceeded. When doing an atomic balance, only reactive species are included, and not inert.

Example 3.1 Natural Gas Burner

Problems

Suppose you have a gas mixture that contains nitrous oxide, oxygen, and methane. The natural gas is burned. The following chemical reaction occurs in it. How many atomic balance equations can you write?

$$CH_4 + 2O_2 \longrightarrow 2H_2O + CO_2$$

Solution

Known quantities: Balanced reaction.

Find: The number of atomic balance equations that could be written.

Analysis: There would be four equations that you can write: three atomic balances (C, H, and O) and a molecular balance on nitrous oxide (inert and not involved in reaction). You would not include the moles of nitrous oxide in the atomic balance on oxygen.

Example 3.2 Equilibrium Reactions

Problem

An amount of 10 kg of compound A is added to 100 kg of 16 wt% aqueous solution of B, which has a density of 0.90 kg/L. A has a molecular weight of 25 kg/kmol and B has a molecular weight of 47 g/mol. If the equilibrium constant, K, for this reaction is 200 at 300 K, how much of compound C could you obtain from this reaction? Adding 10 kg of A to the solution causes the volume to increase by 9 L. The following reaction occurs:

$$\mathbf{A + B \rightleftarrows C + D}$$

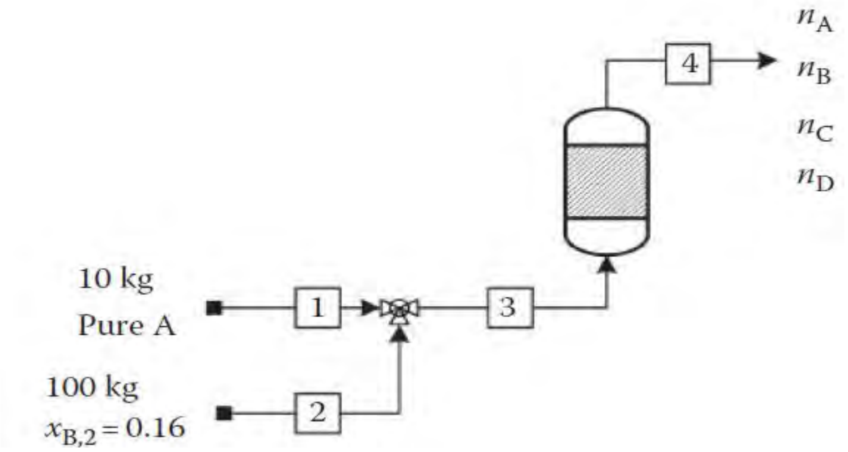
Solution

Known quantities: Mass of components A and B.

Find: Amount of compound C that could be obtained from this reaction.

Analysis: The process flowchart is shown in Example Figure 3.2.1. Since all of the species are dissolved in water, we should write the equilibrium constant in terms of molarities (mol/L):

$$K = 200 = C_C C_D / C_A C_B$$



EXAMPLE FIGURE 3.2.1: Schematic diagram of the equilibrium reaction process.

The number of moles of A we have initially is

$$n_{A0} = 10 \text{ kg A} \times \frac{1 \text{ kmol}}{25 \text{ kg}} = 0.4 \text{ kmol}$$

The number of moles of B we have initially is

$$n_{B0} = 100 \text{ kg solution} \times \frac{0.16 \text{ kg B}}{\text{kg solution}} \frac{1 \text{ kmol}}{47 \text{ kg}} = 0.34 \text{ kmol}$$

Now, the volume contributed by 100 kg of 16% B solution is

$$V_B = \frac{m}{\rho} = \frac{100 \text{ kg}}{0.90 \frac{\text{kg}}{\text{L}}} = 111 \text{ L}$$

After adding 9 L of A to the volume, the new volume is

$$\boldsymbol{V_{final} = 111 + 9 \text{ L} = 120 \text{ L}}$$

There is no C or D in the solution initially:

$C_{C0} = C_{D0} = 0$

Plugging all the known values into the equilibrium equation for liquids, the following equation is obtained:

$$200 = \frac{\left(\frac{\xi}{120}\right)\left(\frac{\xi}{120}\right)}{\left(\frac{0.40 - \xi}{120}\right)\left(\frac{0.34 - \xi}{120}\right)}$$

Simplifying,

$$200 = \frac{\xi^2}{(0.40-\xi)(0.34-\xi)}$$

Rearranging,

$$200(0.40-\xi)(0.34-\xi) = \xi^2$$

$$27.2 - 148\xi + 200\xi^2 = \xi^2$$

$$27.2 - 148\xi + 199\xi^2 = 0$$

This equation can be solved using trial and error or any available software package:

$\xi = 0.411$ kmol

n_C =_ = 0.411 kmol

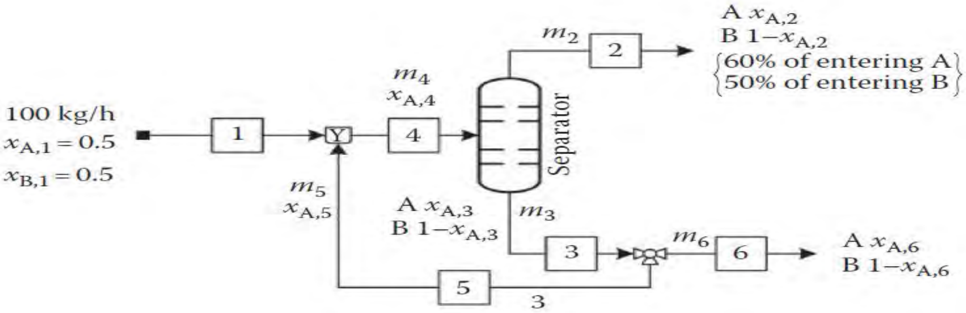
A total of 411 mol of component C can be produced by this reaction.

3.2.6 Implementing Recycle on the Separation Process

Recycle may improve reaction conversion enough to eliminate the need for a second reactor to achieve an economical conversion. Recycle reduces the amount of waste that a company generates. Not only it is the most environmentally sound way to go about but it also saves the company money in disposal costs. Using recycle, it is possible to recover expensive catalysts and reagents. Catalysts are not cheap, and if we do not try to recycle them into the reactor, they may be lost in the product stream. This not only gives us a contaminated product but also wastes a lot of catalyst

Example 3.3 Separation of Binary Liquid Mixture
Problem

Fresh feed stream (100 kg/h) contains equal mass fractions of A and B joining a recycle stream and fed to a separator. The top product stream of the separator contains 60% of A and 50% of the B that is fed to the separator and not that of the fresh feed stream. The recycle system is set up in which half of the separator bottom product stream is recycled and recombined with the fresh feed. Calculate the compositions of A in all streams.



Solution

Known quantities: Fresh feed stream flow rate and composition.

Find: Exit stream molar flow rates.

Analysis: The process flow sheet is shown in Example Figure 3.3.1. The number of degrees of freedom (NDF) of each process:

	Mixing	Separator	Splitter	Overall
Number of unknowns	4	6	6	4
Number of independent equations	2	2	1	2
Number of auxiliary relations	0	2	1	0
NDF	2	2	4	2

Since none of the units got zero degree of freedom, by contrast, the whole process is solvable because the number of independent equations plus auxiliary relations (7 + 3) equals the total number of unknowns (10 unknowns) in the process:

System: Overall

Overall mass balance: $100\ \frac{\text{kg}}{\text{h}} = \dot{m}_2 + \dot{m}_6$

Overall mass balance on A: $50\ \frac{\text{kg}}{\text{h}} = \dot{m}_2 \times x_{A,2} + \dot{m}_6 \times x_{A,6}$

We have four unknowns and two equations at this point. First, combine this information with the splitting ratio and constant composition at the splitter.

Splitting ratio: $m_6 = \frac{m_3}{2}$

Constant composition: $x_{A,6} = x_{A,3}$

Plugging these into the overall balances, we have $100 = \dot{m}_2 + \frac{\dot{m}_3}{2}$

Component balance (A): $50 = x_{A,2}\dot{m}_2 + x_{A,3}\frac{\dot{m}_3}{2}$

Relations: Translating words in the relations into algebraic equations.

If 60% of A entering the separator goes into stream 2, then 40% of A entering the separator goes into stream 3, and then

$$x_{A,2}\dot{m}_2 = 0.6x_{A,4}\dot{m}_4$$

$$x_{A,3}\dot{m}_3 = 0.4x_{A,4}\dot{m}_4$$

If 50% of B entering the separator goes into stream 2, then 50% of B entering the separator goes into stream 3, and then

$$(1 - x_{A,2})\dot{m}_2 = 0.5(1 - x_{A,4})\dot{m}_4$$

$$(1 - x_{A,3})\dot{m}_3 = 0.5(1 - x_{A,4})\dot{m}_4$$

Plugging in all of these into the existing balances, we finally obtain two equations in two unknowns:

System: Overall

Component balances:

$$A: \quad 50 = 0.6x_{A,4}\dot{m}_4 + \frac{0.4}{2}x_{A,4}\dot{m}_4 \Rightarrow x_{A,4}\dot{m}_4 = 62.5$$

$$B: \quad 50 = 0.5(1 - x_{A,4})\dot{m}_4 + \frac{0.5}{2}(1 - x_{A,4})\dot{m}_4 \Rightarrow 50 = 0.75\dot{m}_4 - 0.75x_{A,4}\dot{m}_4$$

Substitute $x_{A,4}\dot{m}_4 = 62.5$ in B component balance equation:

$$50 = 0.75\dot{m}_4 - 0.75(62.5)$$

Solving these equations gives

$$\dot{m}_4 = 129.17\,\frac{\text{kg}}{\text{h}}, \quad x_{A,4} = 0.484$$

System: Mixer

Total balance

$$100 + \dot{m}_5 = \dot{m}_4 = 129.17 \Rightarrow \dot{m}_5 = 29.17\ \text{kg/h}$$

System: Splitter

The recycle stream ($\dot{m}_5$) is half of the separator bottom product stream ($\dot{m}_3$): $\dot{m}_3 = 2\dot{m}_5 = 2 \times 29.17 = 58.34\ \text{kg/h}$

System: Overall

$$100 = \dot{m}_2 + 29.165 \Rightarrow \dot{m}_2 = 70.835\ \text{kg/h}$$

Relations:

$$x_{A,2}\dot{m}_2 = 0.6x_{A,4}\dot{m}_4$$

$$x_{A,2} \times 70.835 = 0.6 \times 0.484 \times 129.17 \Rightarrow x_{A,2} = 0.530$$

$$x_{A,3}\dot{m}_3 = 0.4x_{A,4}\dot{m}_4$$

$$x_{A,3} \times 58.34 = 0.4 \times 0.484 \times 129.17 \Rightarrow x_{A,3} = 0.429$$

Example 3.4 Methane Oxidization
Problem

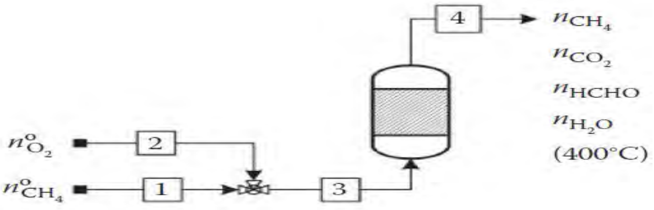
Methane and oxygen at 25°C are fed to a continuous reactor in stoichiometric amounts according to the following reaction to produce formaldehyde:

$$CH_4\ (g) + O_2\ (g) \longrightarrow HCHO\ (g) + H_2O\ (g)$$

In a side reaction, methane is oxidized to carbon dioxide and water:

$$CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (g)$$

The product gases emerge at 400°C, and the number of moles of CO_2 in the effluent gases is 0.15, and there is no remaining O2 found in the effluent gases stream. Determine the composition of effluent gas per mole of CH4 fed to the reactor. Determine the amount of heat removed from the reactor per mole of CH4 fed to the reactor.



EXAMPLE FIGURE3.4.1: Schematic diagram of the methane oxidation process.

Solution
Known quantities: Inlet component molar flow rate and compositions.
Find: The amount of heat removed from the reactor per mole of CH_4 fed to the reactor.
Analysis: The process flow sheet is shown in Example Figure 3.4.1.

Material balance

Material balance using the extent of reaction method is given by

$$n_{CH_4} = 1 - \xi_1 - \xi_2$$

There is no remaining O_2:

$$n_{O_2} = 0 = 1 - \xi_1 - 2\xi_2$$

$$n_{HCHO} = \xi_1$$

The number of moles of CO_2 in the effluent stream is 0.15 mol:

$$n_{CO_2} = \xi_2 = 0.15$$

$$n_{H_2O} = \xi_1 + 2\xi_2$$

Hence, $1 - \dot{\xi}_1 - 2\dot{\xi}_2 = 0$ and $n_{CO_2} = \dot{\xi}_2 = 0.15$
Substituting $\dot{\xi}_2 = 0.15$ in the earlier equation and solving for $\dot{\xi}_1$, we get $\dot{\xi}_1 = 0.7$

Substitute values of $\dot{\xi}_2 = 0.15$ and $\dot{\xi}_1 = 0.7$ in the mole balance equations:

$$\dot{n}_{CH_4} = 0.15\ \text{mol/s},\quad \dot{n}_{HCHO} = 0.7\ \text{mol/s},\quad \dot{n}_{CO_2} = 0.15\ \text{mol/s},$$

$$\dot{n}_{H_2O} = 1\ \text{mol/s}$$

The amount of heat removed from the reactor per mole of CH_4 fed to the reactor. The heat capacities are taken from tabulated values as a function of temperature.

Energy balance

Reference temperature = 25°C

The standard heats of reaction for both reactions at 25°C are calculated from the standard heats of formation.

The heats of formation are

$$\Delta H^0_{f,CH_4} = -74.85\ \text{kJ/mol}$$

$$\Delta H^0_{f,O_2} = 0$$

$$\Delta H_{f,HCHO} = -115.9\ \text{kJ/mol}$$

$$\Delta H^0_{f,H_2O} = -241.83\ \text{kJ/mol}$$

$$\Delta H^0_{f,CO_2} = -393.5\ \text{kJ/mol}$$

The standard heats of reaction are

$$\Delta H^0_{Rx,1} = \Delta H^0_{f,H_2O}(g) + \Delta H^0_{f,HCHO}(g) - \Delta H^0_{f,CH_4}(g) - \Delta H^0_{f,O_2}(g)$$

$$\Delta H^0_{Rx,1} = -115.9 - 241.83 - (-74.85) - (0) = -282.88\ \frac{\text{kJ}}{\text{mol}}$$

$$\Delta H^0_{Rx,2} = 2\Delta H^0_{f,H_2O}(g) + \Delta H^0_{f,CO_2}(g) - \Delta H^0_{f,CH_4}(g) - 2\Delta H^0_{f,O_2}(g)$$

$$\Delta H^0_{Rx,2} = 2(-241.83) + (-393.5) - (-74.85) - 2(0) = -802.31\frac{\text{kJ}}{\text{mol}}$$

The sensible heat is calculated using specific heat:

$$C_P\left(\frac{\text{J}}{\text{mol °C}}\right) = a + bT + cT^2 + dT^3$$

The specific heat can be found from Table A.3:

$HCHO$: $a = 34.28,\quad b = 4.268\times10^{-2},\quad c = 0.0,\quad d = -8694\times10^{-9}$

CH_4: $a = 34.31,\quad b = 5.469\times10^{-2},\quad c = 0.3661\times10^{-5},\quad d = -11\times10^{-9}$

CO_2: $a = 36.11,\quad b = 4.233\times10^{-2},\quad c = -2.887\times10^{-5},\quad d = 7.464\times10^{-9}$

H_2O: $a = 33.46,\quad b = 0.688\times10^{-2},\quad c = 0.7604\times10^{-5},\quad d = -3.593\times10^{-9}$

Calculation of enthalpies of outlet and inlet streams relative to the reference temperature (i.e., 25°C) is shown in the following.

Enthalpy of outlet stream components:

$$\overline{h}_{HCHO} = \int_{25}^{400} C_P\,dT = \int (34.28 + 4.268\times10^{-2}T + 0T^2 - 8694\times10^{-9}T^3)\,dT$$

$$\overline{h}_{HCHO} = \int_{25}^{400} C_P\,dT = \left[34.28T + 4.268\times10^{-2}\frac{T^2}{2} - 3(8694\times10^{-9})\frac{T^4}{4}\right]_{25}^{400}$$

$$\overline{h}_{HCHO} = \frac{\text{kJ}}{1000\ \text{J}}\left[34.28(400-25) + 4.268\times10^{-2}\frac{(400^2-25^2)}{2} - 8694\times10^{-9}\times\frac{(400^4-25^4)}{4}\right]$$

Note that $(400^2 - 25^2) \neq (400 - 25)^2$

The results are

$$\bar{h}_{HCHO} = 16.2\,\frac{kJ}{mol},\quad \bar{h}_{CH_4} = 17.23\,\frac{kJ}{mol},\quad \bar{h}_{CO_2} = 16.35\,\frac{kJ}{mol},$$

$$\bar{h}_{H_2O} = 13.23\,\frac{kJ}{mol}$$

The general energy balance equation is

$$Q = \sum_{out} \dot{n}_i \hat{H}_i - \sum_{in} \dot{n}_i \hat{H}_i + \xi_1 \Delta H^0_{rxn1} + \xi_2 \Delta H^0_{rxn2}$$

Substituting known quantities,

$$\dot{Q} = \left\{\dot{n}_{CH_4}\left(\bar{h}_{CH_4}\right) + \dot{n}_{CO_2}\left(\bar{h}_{CO_2}\right) + \dot{n}_{HCHO}\left(\bar{h}_{HCHO}\right) + \dot{n}_{H_2O}\left(\bar{h}_{H_2O}\right)\right\}_{400°C}$$

$$-\left\{\dot{n}_{CH_4}\left(\bar{h}_{CH_4}\right) + \dot{n}_{O_2}\left(\bar{h}_{O_2}\right)\right\}_{25°C} + \dot{\xi}_1 \Delta H^0_{Rx,1} + \dot{\xi}_2 \Delta H^0_{Rx,2}$$

The enthalpy of inlet stream components is zero because inlet temperature is at reference temperature; therefore, the enthalpy of inlet components relative to reference temperature of 25°C is zero:

$$\dot{Q} = \{0.15(17.23) + 0.15(16.35) + 0.7(16.2) + 1(13.23)\}_{out} - \{0 + 0\}_{in}$$

$$+ 0.7(-282.88) + 0.15(-802.31)$$

$$= -288.76\ kJ/s$$

Example 3.5 Adiabatic Saturation Temperature

Problem

Air at a temperature of 50°C and 10% relative humidity is to be humidified adiabatically (constant wet-bulb temperature line) to 40% relative humidity. Use the psychrometric chart to estimate the adiabatic saturation temperature of the air, the rate at which water must be added to humidify 15 kg/min of the entering air and the final temperature of air.

Solution

Known quantities: Inlet air temperature and relative humidity.

Find: The adiabatic saturation temperature of the air.

Analysis: Refer to a psychrometric chart:

$$\text{at } T_{db} = 50°\text{C and } h_r = 10\% \Rightarrow T_{as} = T_{wb} = 23.5°\text{C}$$

$$h_a = 0.0077 \frac{\text{kg H}_2\text{O}}{\text{kg DA}}$$

The state of the exit air lies on the line *T*wb = 23.5°C. From the intersection of this line and the 40% relative humidity curve, the absolute humidity of exit air is determined to be

*h*a = 0.014 kg H2O/kg dry air

The rate at which water must be added to humidify 15 kg/min of the entering air is

$$\frac{15 \text{ kg air}}{\text{min}} \left| \frac{1 \text{ kg DA}}{1.0077 \text{ kg air}} \right| \frac{0.014 - 0.0077}{\text{kg DA}} \right| = 0.0938 \frac{\text{kg H}_2\text{O}}{\text{min}}$$

From the intersection of the 40% relative humidity curve and the *T*wb = 23.6°C line, the dry-bulb temperature of exit gas is found to be around 35°C.

Example 3.6 Partial Condensation of Cyclopentane

Problem

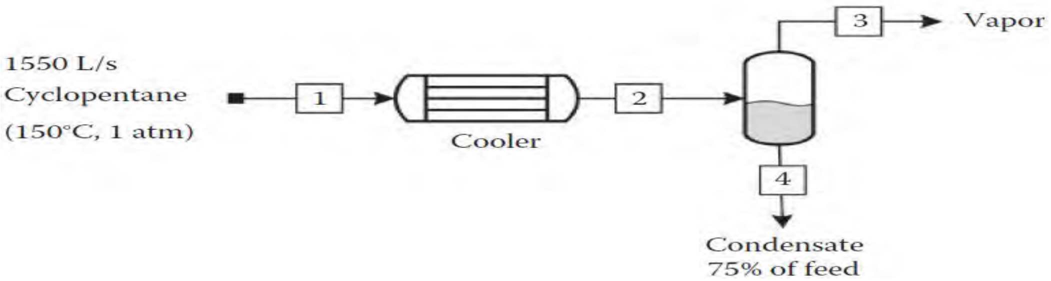
A stream of pure cyclopentane vapor is flowing at a rate of 1550 L/s, at a temperature of 150°C, and at a pressure of 1 atm it enters a cooler. Seventy-five percent of the feed is condensed and exits the cooler at 1 atm. What is the temperature of the exiting streams from the cooler?

Solution

Known quantities: Inlet stream volumetric flow, inlet temperature, and pressure.

Find: Temperature of the exiting streams from the cooler.

Analysis: The process flow diagram is shown in Example Figure 3.6.1. The exit stream temperature must be 49.3°C for cyclopentane, because the boiling point of cyclopentane at 1 atm pressure is 49.3°C. Taking the reference temperature at 49.3°C and cyclopentane in liquid state



EXAMPLE FIGURE 3.6.1: Partial condensation of cyclopentane.

(i.e., *T*ref = 49.3°C, liquid state), the number of moles of inlet cyclopentane in vapor phase, using the ideal gas law, is

$$n = \frac{PV}{RT} = \frac{1\ \text{atm} \times 1550\ \text{L/s}}{0.08206\ \dfrac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times (150 + 273.15)\text{K}} = 44.64\ \frac{\text{mol}}{\text{s}}$$

The inlet specific molar enthalpy of vapor cyclopentane at 150°C relative to reference temperature (49.3°C, liquid) is shown in the following equation:

$$\bar{h}_{\text{in}} = \Delta\bar{h}_{\text{vap}} + \int_{49.3^\circ\text{C}}^{150^\circ\text{C}} C_{\text{p,v}}\, dT$$

Heat capacity of cyclopentane vapor (*C*pv) as a function of temperature is shown here:

$$C_{\text{p}_\text{v}}\left(\frac{\text{J}}{\text{mol K}}\right) = 73.39 + 0.3928T - 2.554 \times 10^{-4}T^2$$

The change in specific molar enthalpy of cyclopentane vapor is

$$\Delta\bar{h}_{\text{v}} = \int_{49.3^\circ\text{C}}^{150^\circ\text{C}} C_{\text{p}}\, dT = \left[aT + \frac{b}{2}T^2 + \frac{c}{3}T^3\right]_{49.3^\circ\text{C}}^{150} = 11{,}060\ \frac{\text{J}}{\text{mol}}$$

The heat of vaporization of cyclopentane at 1 atm and its boiling point 49.3°C is

$$\Delta\bar{h}_{\text{vap}} = 27.30\ \frac{\text{kJ}}{\text{mol}}$$

Substituting heat of vaporization and sensible heat,

$$\bar{h}_{\text{in}} = \Delta\bar{h}_{\text{v}} + \int_{49.3}^{150} C_{\text{p}_\text{v}}\, dT = 27.3 + 11.06 = 38.36\ \text{kJ/mol}$$

The resultant enthalpies can be summarized in the following table. Enthalpies Relative to Reference Conditions (*T*ref = 49.3°C, liquid state, 1 atm)

Substance	$\dot{n}_{\text{in}}$ (mol/s)	$\bar{h}_{\text{in}}$ (kJ/mol)	$\dot{n}_{\text{out}}$ (mol/s)	$\bar{h}_{\text{out}}$ (kJ/mol)
Cyclopentane (*v*)	44.64	38.36	11.14	27.3
Cyclopentane (*l*)	—	—	33.5	0

Total energy balance: $Q = \sum_{\text{out}} n_i\bar{h}_i - \sum_{\text{in}} n_i\bar{h}_i$

$$Q = \left(11.14\ \frac{\text{mol}}{\text{s}}\right)\left(27.30\ \frac{\text{kJ}}{\text{mol}}\right) - 44.64\ \frac{\text{mol}}{\text{s}}(38.36)\ \frac{\text{kJ}}{\text{mol}} = -1408\ \frac{\text{kJ}}{\text{s}}$$

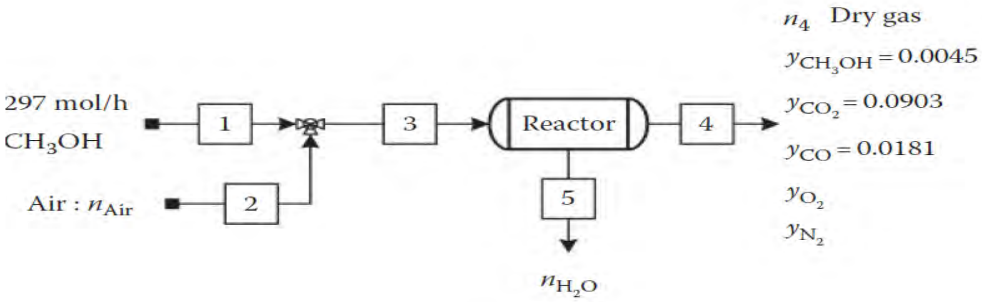
Example 3.7 Methanol Combustion Process

Problem

Methanol (CH_3OH) is fed at a rate of 297 mol/h and burned with excess air. The product gas is analyzed, and the following dry-basis mole percentages are determined: CH_3OH = 0.45%, CO_2 = 9.03% and CO = 1.81%. Calculate the fractional conversion of methanol, the percentage excess air fed, and the mole fraction of water in the product gas. The equations of the chemical reactions taking place in the heater are

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

$$CH_3OH + O_2 \rightarrow CO + 3H_2O$$



EXAMPLE FIGURE 3.7.1: Schematic of the methanol combustion process.

Solution

Known quantities: Methanol volumetric flow rate, dry gas composition.

Find: The fractional conversion of methanol, the percentage excess air fed, and the mole fraction of water in the product gas.

Analysis: The labeled flowchart is shown in Example Figure 3.7.1. Degrees of Freedom Analysis (Atomic Balance)

Number of unknowns	4
Atomic balance equations (C, H, O)	3
Number of relations	1
NDF	0

Atomic balance

Basis: 297 mol/h of inlet methanol

C balance:

$$n_{\text{dry gas}} = \frac{297\ \text{mol/h}}{0.1129} = 2631\ \text{mol/h}$$

$$297\ \frac{\text{mol}}{\text{h}} = (0.0045 + 0.0903 + 0.0181)n_{\text{dry gas}}$$

H balance:

$$297\ \text{mol}\frac{\text{CH}_3\text{OH}}{\text{h}}\times\frac{4\ \text{mol H}}{\text{mol CH}_3\text{OH}}$$

$$= 2n_{\text{H}_2\text{O}} + 0.0045\ \text{mol CH}_3\text{OH}\frac{4\ \text{mol H}}{\text{mol CH}_3\text{OH}}n_{\text{dry gas}}$$

$$n_{\text{H}_2\text{O}} = 570.3\ \text{mol/s}$$

$$\text{Total moles out} = 570.3 + 2631 = 3201\ \text{mol}$$

$$\text{Fraction of water in the product stream} = \frac{570.3}{3201} = 0.178$$

$$\text{Fractional conversion of methanol} = x = \frac{297 - 0.0045\times 2631}{297} = 0.96$$

Calculation of the amount of excess air:

O balance:

$$2(0.21\times n_{\text{Air}}) + 297 = (0.0045 + 2\times 0.0903 + 0.0181 + 2\times y_{\text{O}_2})\times 2631 + 569.2$$

N balance:

$$2(0.79\times n_{\text{Air}}) = 2\times(1 - 0.0045 - 0.0903 - 0.0181 - y_{\text{O}_2})\times 2631$$

Solving for air, oxygen, and nitrogen,

$$n_{\text{Air}} = 2733.41\ \text{mol/s},\quad y_{\text{N}_2} = 0.822,\quad y_{\text{O}_2} = 0.065$$

To calculate the percent excess air, first calculate the theoretical oxygen using the complete combustion reaction:

$$\text{Theoretical oxygen} = \frac{297\ \text{mol CH}_3\text{OH}}{\text{h}}\left|\frac{\frac{3}{2}\text{mol O}_2\ \text{conusmed}}{1\ \text{mol CH}_3\text{OH}}\right. = 445.5\ \frac{\text{mol}}{\text{h}}$$

$$\text{Theoretical air} = \frac{\dot{n}_{\text{O}_2}}{0.21} = \frac{445.5\ \text{mol O}_2/\text{h}}{0.21} = 2121.43\ \text{mol/h}$$

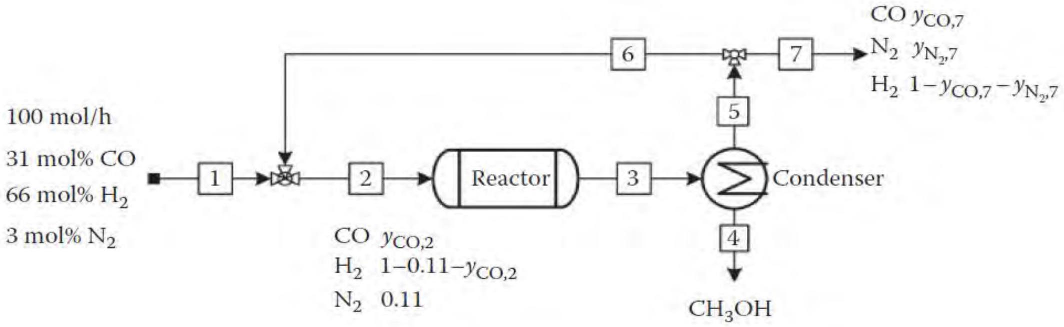
$$\%\ \text{Excess air} = \frac{\text{Total inlet air} - \text{Theoretical air}}{\text{Theoretical air}} = \frac{2733.41 - 2121.43}{2121.43}$$

$$\times 100\% = 28.85$$

Example 3.8 Methanol Synthesis

Problem

A fresh feed stream is flowing at 100 mol/h, containing 31% carbon monoxide (CO), 66 mol% hydrogen (H_2), and 3 mol% nitrogen. The fresh feed stream joins a recycle stream, and the combined stream is fed to a catalytic reactor for methanol synthesis. This stream is mixed with a recycle stream in a ratio of 4 mol recycle to 1 mol of fresh feed to enter the reactor, and the stream entering the reactor contains 11 mol% N2. The reactor effluent goes to a condenser, from which two streams emerge: a liquid stream containing pure liquid CH3OH and a gas stream containing all the CO, H_2, and N_2. The gas stream from the condenser is split into a purge stream, and the remainder is recycled to mix with the fresh feed to enter the reactor. Calculate the production rate of methanol (mol/h), the molar flow rate and composition of the purge gas, and the overall conversion of CO.



EXAMPLE FIGURE 3.8.1: Schematic diagram of the methanol production process.

Solution

Known quantities: Fresh feed stream flow rate and composition.

Find: The production rate of methanol (mol/h), the molar flow rate and composition of the purge gas, and the overall conversion of CO.

Analysis: The process flowchart is shown in Example Figure 3.8.1.

Basis: 100 mol/h of fresh feed

Degrees of Freedom Analysis

Degrees of Freedom Analysis	Overall Process	Mixing Point
Number of unknowns	5 ($\dot{n}_4, \dot{n}_7, y_{CO,7}, y_{N_2,7}, \xi$)	5($\dot{n}_2, y_{CO,2}, \dot{n}_6, y_{N_2,6}, y_{CO,6}$)
Number of equations	4	4
Number of relations	—	1
NDF	1	0

System: Mixing point balances

From the relation recycle stream = 4 times of the fresh feed stream,

$n6$ = 400 mol/h

$$n_2 = 500 \text{ mol/h}$$

N_2 balance:

$$3 + y_{N_2,6} \times 400 = 0.11 \times 500$$

$$y_{N_2,6} = 0.13$$

System: Overall balance

N_2 balance:

$$3 = y_{N_2,7} \times n_7$$

Since the composition of recycle stream and purge stream are the same,

$$y_{N_2,7} = y_{N_2,6} = 0.13$$

The flow rate of purge is

$$n_7 = 23 \text{ mol/h}$$

Atomic C balance:

$$31 \text{ mol CO} \times 1 = n_4 \text{ mol } CH_3OH + y_{CO,7} \times 23$$

Simplify

$$n_4 = 31 - 23 \times y_{CO,7}$$

Substituting $n_4 = 31 - 23 \times y_{CO,7}$ in the earlier equation yields

$$132 = (31 - 23y_{CO,7}) \times 4 + 40.02 - 46y_{CO,7}$$

$$-32.02 = -138 \times y_{CO,7}$$

$$y_{CO,7} = 0.23$$

$$y_{H_2,7} = 0.87 - 0.23 = 0.64 \frac{\text{mol } H_2}{\text{mol}}$$

$$n_4 = 25.71 \text{ mol } CH_3OH$$

$$\text{Overall conversion} = \frac{31 \text{ mol} - 0.23 \times 23}{31} = 0.83$$

Overall, 83% conversion of CO is achieved.

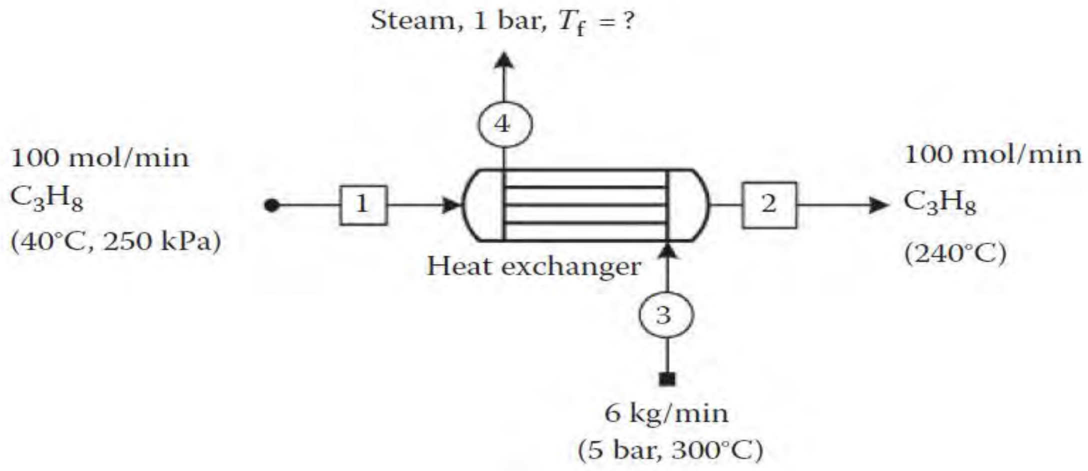
Atomic H balance:

$$2 \times 66 \text{ mol } H_2 = \left(n_4 \text{ mol } CH_3OH \frac{4 \text{ mol H}}{\text{mol } CH_3OH} \right) + \left((1 - 0.13 - y_{CO,7}) \frac{2 \text{ mol H}}{\text{mol } H_2O} \times 23 \right)$$

Example 3.9 Heating of Propane Gas

Problem

Propane gas at 40° C and 250 kPa enters a continuous adiabatic heat exchanger where no heat is lost from the outside of the unit while heat is transferred between streams. The stream exits at 240° C. The flow rate of propane is 100 mol/min, and superheated steam at 5 bar absolute pressure and 300° C enters the heat exchanger with a flow rate of 6 kg/min. The steam exits the heat exchanger at 1 bar absolute pressure. Calculate the temperature of the exit steam.



EXAMPLE FIGURE 3.9.1: Heating of propane.

Solution

Known quantities: Propane gas temperature, pressure flow rate.

Find: Temperature of the exit steam.

Analysis: The process flow sheet is shown in Example Figure 3.9.1. For a heat capacity of propane,

$$a = 68.032, \quad b = 0.2259, \quad c = -1.311 \times 10^{-4}, \quad d = 3.171 \times 10^{-8}$$

Substituting values of *a*, *b*, *c*, and *d* and integrating,

$$\Delta \bar{h}_{C_3H_8} = \int_{40^\circ C}^{240^\circ C} C_p \left(\frac{J}{\text{mol } ^\circ C} \right) dT = \int_{40^\circ C}^{240^\circ C} (a + bT + cT^2 + dT^3)\, dT$$

$$\Delta \bar{h}_{C_3H_8} = 0.68\left[T_2 - T_1\right] + \frac{0.2259}{2}\left[T_2^2 - T_1^2\right] + \frac{-1.311 \times 10^{-4}}{3}\left[T_2^3 - T_1^3\right] + \frac{3.171 \times 10^{-8}}{4}\left[T_2^4 - T_1^4\right]$$

Substituting the given values of inlet and exit temperatures,

$$= 0.68[240 - 40] + \frac{0.2259}{2}[240^2 - 40^2] + \frac{-1.311 \times 10^{-4}}{3}[240^3 - 40^3$$

$$+ \frac{3.171 \times 10^{-8}}{4}[240^4 - 40^4]$$

The change in specific molar enthalpy $\overline{h}(\mathrm{J/mol})$ is

$$\Delta \overline{h}_{C_3H_8} = 13{,}606.4 + 6325.2 - 13 + 26.3 = 19{,}360\ \frac{\mathrm{J}}{\mathrm{mol}}$$

The amount of heat transferred from the steam to heat propane is

$$\dot{n}\Delta\overline{h} = 100\ \frac{\mathrm{mol}}{\mathrm{min}} \times 19.36\ \frac{\mathrm{kJ}}{\mathrm{mol}} = 1936\ \frac{\mathrm{kJ}}{\mathrm{min}}$$

The change in mass specific enthalpy of steam, $h(\mathrm{J/g})$, is

$$\dot{m}\Delta h = 6\ \frac{\mathrm{kg}}{\mathrm{min}}\left[h_{\mathrm{out}} - 3065\right]\frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\dot{Q} = 0 = 1936\ \frac{\mathrm{kJ}}{\mathrm{min}} + 6\ \frac{\mathrm{kg}}{\mathrm{min}}\left[h_{\mathrm{out}} - 3065\right]\frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\frac{1936}{6}\ \frac{\mathrm{kJ}}{\mathrm{kg}} + 3065\ \frac{\mathrm{kJ}}{\mathrm{kg}} = h_4$$

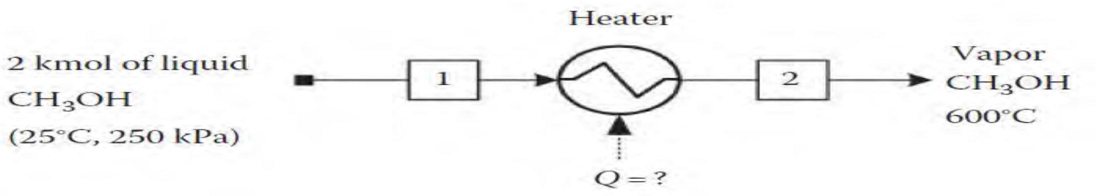
Using the superheated steam table calculate the temperature at 1 bar absolute pressure and enthalpy, *h*4 = 2742.3 kJ/kg. Since the value of the calculated enthalpy at 1 bar does not exist in the steam table, interpolation is required to get the value of the exit temperature:

$$\frac{2776 - 2676}{150 - 100} = \frac{2776 - 2742.3}{150 - T_f} \Rightarrow T_f = 133^\circ\mathrm{C}$$

Example 3.10 Heating of Liquid Methanol

Problem

Liquid methanol at 25° C is heated and vaporized for use in a chemical reaction. How much heat is required to heat and vaporize 2 kmol/h of methanol to 600° C.



EXAMPLE FIGURE 3.10.1: Schematic of heating liquid methanol.

Solution

Known quantities: Inlet liquid methanol temperature and flow rate.

Find: Heat required to heat and vaporize 2 kmol of methanol to 600° C.

Analysis: The inlet and exit conditions of the heater are shown in Example Figure 3.10.1. Consider Tref = 25° C and methanol in liquid phase as reference conditions. The normal boiling point of methanol is 64.7° C. Accordingly, the change of methanol enthalpy is the sum of change in the enthalpy of the liquid methanol, heat of vaporization, and the change in enthalpy of vapor methanol from its boiling point to its final temperature. The enthalpy change for methanol liquid is

$$\Delta\bar{h}_{CH_3OH} = \int_{25°C}^{64.7°C} C_{P CH_3OH,l}\, dT = 0.07586[64.7 - 25]$$

$$+\frac{16.83\times10^{-5}}{2}[64.7^2 - 25^2] = 3.312 \text{ kJ/mol}$$

The enthalpy change for methanol vapor is

$$\Delta\bar{h}_{CH_3OH} = \int_{64.7°C}^{600°C} C_{p_v}\, dT = 0.68[600-64.7]+\frac{0.2259}{2}[600^2-64.7^2]$$

$$+\frac{-1.31\times10^{-4}}{3}[600^3-64.7^3]-\frac{3.71\times10^{-8}}{4}[600^4-64.7^4$$

$$= 68.21 \text{ kJ/mol}$$

The methanol latent heat of vaporization is

$$\Delta\bar{h}_{vapor} = 36.14\,\frac{\text{kJ}}{\text{mol}}$$

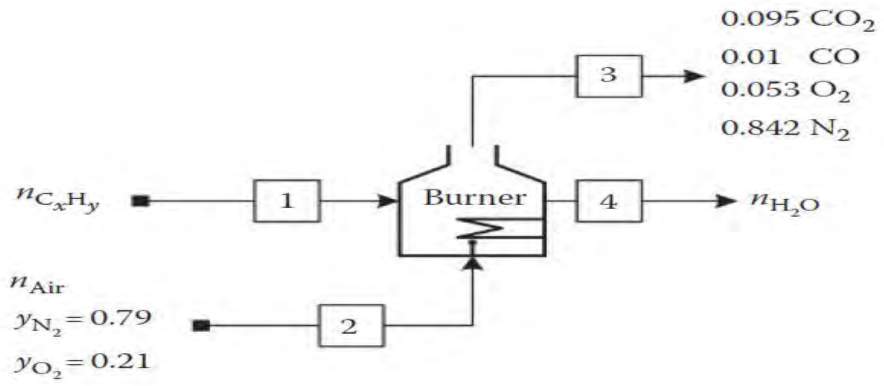
The change in enthalpy of the methanol heated from 25°C to 600°C is

$$Q = 2000\,\frac{\text{mol}}{\text{h}}\times[3.312 + 68.21 + 36.14]\frac{\text{kJ}}{\text{mol}} = 2{,}15{,}324\,\frac{\text{kJ}}{\text{h}}$$

Example 3.11 Turbine Power Plant

Problem

A hydrocarbon fuel whose composition is unknown but may be represented by the expression *CxHy* is burned with excess air. An analysis of the product gas gives the following results in mol% on a moisture-free basis: 9.51% CO2, 1.0% CO, 5.3% O2, and 84.2% N2. Given 100 mol/h of flue gas dry gas, determine the molar ratio of hydrogen to carbon in the fuel, *r*, where *r* = *y*/*x*, and the percentage of excess air used in the combustion.



EXAMPLE FIGURE 3.11.1: Schematic diagram of burning hydrocarbon.

Solution

Known quantities: Dry gas mole fraction.

Find: The ratio of hydrogen to carbon in the used fluid.

Analysis: The number of independent chemical reactions in the process is two since the flue gases contain CO, which means that there is a side reaction and the combustion is not complete.

Basis: 100 mol of flue gases (dry basis).

$$C_xH_y + \frac{(2x + y/2)}{2}O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

$$C_xH_y + \frac{(x + y/2)}{2}O_2 \rightarrow xCO + \frac{y}{2}H_2O$$

The flowchart of this process is shown in Example Figure 3.11.1.

Degrees of Freedom Analysis

Degrees of Freedom Analysis	Overall Process (Atomic Balance)
Number of unknowns	5 ($n_{C_xH_y}$, n_{H_2O}, x, y, n_2)
Number of independent equations	4
Number of relations	—
NDF	1

Atomic balance:

C atomic balance: $x\ n$ CxHy = 9.5 + 1.0

H atomic balance: $y\ n\ n$ CxHy = 2† × † H2O

N atomic balance: 2(0.79nAir) = 2(84.2 mol)

$n$air = 106.6 mol

O atomic balance: 2 × (106.6 × 0.21) = (2 × 9.5) + 1.0 + (2 × 5.3) + nH2O

nH2O = 14.17

The molar ratio of hydrogen to carbon in the fuel $r = y/x$, and the percentage of excess air used in the combustion can thus be calculated from the following equations:

C atomic balance: $x\ n$ × CxHy = 9.5 + 1.0

H atomic balance: $y\ n$ × CxHy = 2 × 14.17

Divide H atomic balance equation by C atomic balance

$$\frac{y \times \cancel{C_xH_y}}{x \times \cancel{C_xH_y}} = \frac{2 \times 14.17}{9.5 + 1.0}$$

$$r = \frac{y}{x} = \frac{28.34}{10.5}$$

For complete combustion, the following reaction is taking place:

$$C_xH_y + \left(\frac{y}{4} + x\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

For 106.6 mol air fed, 10.5 mol of CO2 produced, $x = 10.5$, $y = 28.34$. The percentage of excess air used in the combustion:

Moles of CxHy can be found from the equation of C atomic balance:

$$10.5 \times n_{C_xH_y} = 9.5 + 1.0$$

$$n_{C_xH_y} = \frac{10.5}{10.5} = 1\ \text{mol}$$

Per one mole of C_xH_y fed to the burner,

$$\text{Theoretical } O_2 = 1\ \text{mol } C_xH_y \frac{\left(\frac{y}{4} + x\right)O_2}{\text{mol } C_xH_y} = \frac{28.34}{4} + 10.5 = 17.59\ \text{mol } O_2$$

$$\text{Theortical } N_2 = 17.59\ \text{mol } O_2 \times \frac{0.79\ \text{mol } N_2}{0.21\ \text{mol } O_2} = 66.15\ \text{mol } N_2$$

The associated theoretical nitrogen is thus calculated.

$$\text{Theoretical air} = \text{moles of theoretical oxygen} + \text{nitrogen}$$
$$= 17.59 + 66.15 = 83.74 \text{ mol}$$

$$\text{Excess air: } 106.6 - 83.74 = 27.86 \text{ mol}$$

$$\% \text{ excess air} = \frac{22.8}{83.7} \times 100\% = 27\% \text{ excess air}$$

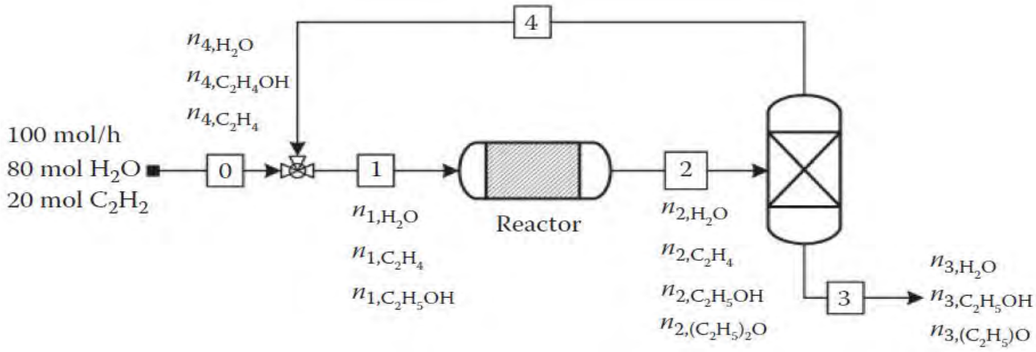
Example 3.12 Ethanol Production
Problem

Fresh feed containing 20.0% C2H4 and 80.0% H2O is fed to a continuous reactor. The reaction products are fed to a condenser that has two product streams: a vapor stream that contains C_2H_4, C_2H_5OH, and water vapor; and a liquid stream that contains the remaining ethanol, ethylene oxide, and water. The vapor stream from the condenser is recycled and mixed with the fresh feed to be fed to the reactor. The overall process yield is 80% of ethanol produced. In the reactor, ethanol (C_2H_5OH) is produced by steam (H_2O) reformation with ethylene (C_2H_4). An undesirable side reaction, ethylene oxide is formed:

$$C_2H_4 + H_2O \rightarrow C_2H_5OH$$

$$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$$

If the ratio of water in the recycle stream to water in the product stream is 1:10, and the ratio of the ethylene in the recycle to ethylene in the fresh feed is 4:1. The mole fraction of ethanol in the reactor exit stream is 0.157. Determine the recycle flow rate and the single-pass conversion of ethylene in the reactor.



EXAMPLE FIGURE 3.12.1: Schematic of the ethanol production process.

Solution

Known quantities: Fresh feed containing 20.0% C_2H_4 and 80.0% H_2O is fed to a continuous reactor.

Find: The recycle flow rate and the single-pass conversion of ethylene in the reactor.

Analysis: The flowchart of the process is shown in Example Figure 3.12.1. Degrees of Freedom Analysis

Degrees of Freedom Analysis	Overall Process
Number of unknowns	3 (n_{3,H_2O}, n_{3,C_2H_4OH}, $n_{3,(C_2H_5)_2O}$)
Number of reactions	1
Number of atomic balances	3
Number of relations	1 (overall conversion)
NDF	0

System: Overall process

$$\text{Overall yield} : 0.8 = \frac{n_{C_2H_4OH}}{20}$$

$$n_{3,C_2H_4OH} = 16 \text{ mol}$$

$$\text{C atomic balance: } 20 \times 2 = 4 n_{3(C_2H_4)_2O} + 16 \times 2$$

$$n_{3,(C_2H_4)_2O} = 2 \text{ mol}$$

$$\text{O atomic balance: } 80 = 2 + 16 + n_{3H_2O}$$

$$n_{3,H_2O} = 62 \text{ mol}$$

Relation: The ratio of water vapor in the recycle stream (4) to liquid water in the product stream (3) is 1/10:

$$\frac{n_{4,H_2O}}{n_{3,H_2O}} = \frac{1}{10}$$

$$n_{4,H_2O} = \frac{1}{10} n_{3,H_2O} = \frac{1}{10} \times 62$$

$$n_{4,H_2O} = 6.2 \text{ mol}$$

Mixing point balance: water in the recycle stream + water in the fresh stream

$$n_{1,H_2O} = 80 + 6.2 = 86.2 \text{ mol}$$

Water balance around the condenser:

$$n_{2,H_2O} = 62 + 6.2 = 68.2 \text{ mol}$$

$$\frac{\text{Ethylene in recycle}}{\text{Ethylene in fresh feed}} = \frac{n_{4,C_2H_4}}{20} = \frac{4}{1}$$

$$n_{4,C_2H_4} = 80 \text{ mol}$$

Also 80 mol C_2H_4 enters the condenser. The exit of the reactor contains the following:

$$80 \text{ mol } C_2H_4$$

$$2 \text{ mol} (C_2H_5)_2O$$

68.2 mol H_2O

$$y_{C_2H_5OH} = 0.157$$

$$f_{C_2H_4} = \frac{n_{1,C_2H_4} - n_{2,C_2H_4}}{n_{1,C_2H_4}}$$

$$\%\ \text{Conversion} = \frac{100 - 80}{100} = 20\%$$

Total moles of reactor effluent stream

$$80 + 2 + 68.2 = (1 - 0.157)n_2$$

Solving for n_2,

$$n_2 = \frac{150.2}{0.843} = 178.10 \text{ mol}$$

Total moles of ethanol present in the reactor effluent

$$n_{2,CH_3OH} = 0.157 \times 178.10 = 27.96 \text{ mol}$$

The flow rate of recycle stream is $27.96 - 16 = 11.96$ mol of ethanol:

$$\text{Recycle} = 80 \text{ mol } C_2H_4 + 6.2 \text{ mol } H_2O + 11.9 \text{ mol ethanol} = 98.1 \text{ mol}$$

Example 3.13 Methanol Combustion

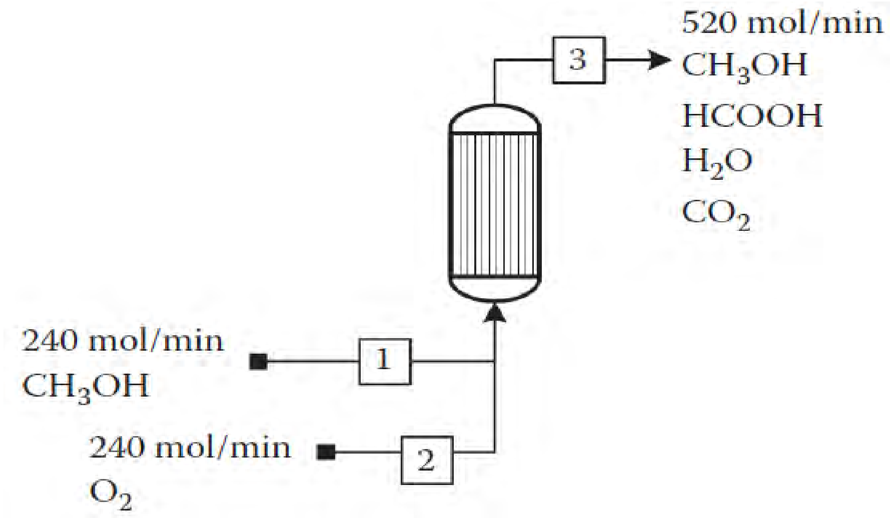
Problem

Methanol (CH3OH) at 240 mol/min and oxygen (O2) at a rate of 240 mol/ min are fed to an isothermal reactor operating at 25° C. The reactor operates at steady state. Two reactions take place:

$$CH_3OH + O_2 \rightarrow HCOOH + H_2O$$

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

The flow rate out of the reactor is 520 mol/min. No oxygen was found in the reactor product stream. Determine the heat that must be withdrawn to keep the reactor at constant temperature. Determine the fractional conversion of methanol. Determine the selectivity for the conversion of methanol to formic acid.



EXAMPLE FIGURE 10.13.1: Process flow sheet of the methanol combustion process.

Solution
Known quantities: Inlet and product stream flow rates.
Find: The fractional conversion of methanol, selectivity for the methanol.
Analysis: The process flowchart is shown in Example Figure3.13.1.
Material balance
Using the extent of reaction method,

$$CH_3OH: \quad n_{CH_3OH} = 240 - \xi_1 - \xi_2$$

$$HCOOH: \quad n_{HCOOH} = 0 + \xi_1$$

$$H_2O: \quad n_{H_2O} = 0 + \xi_1 + 2\xi_2$$

$$CO_2: \quad n_{CO_2} = 0 + \xi_2$$

$$O_2: \quad n_{O_2} = 240 - \xi_1 - \frac{3}{2}\xi_2$$

$$n_3 = 480 + \frac{1}{2}\xi_2$$

The total molar flow rate out of the reactor

$$\dot{n}_3 = 480 + \frac{1}{2}\dot{\xi}_2 = 520$$

$$\text{Solving}: \dot{\xi}_2 = 80 \text{ gmol/min}$$

O_2 mole balance: (note that no oxygen is found in the reactor effluent stream)

$$\dot{n}_{3,O_2} = 240 - \dot{\xi}_1 - \frac{3}{2}\dot{\xi}_2 = 240 - \xi_1 - 120 = 0$$

Solving for the extent of reaction 1,

$$\dot{\xi}_1 = 120 \text{ gmol/min}$$

Energy balance

Since the reactor is isothermal (25°C), the heat released is the heat of reaction:

$$Q = \Delta H^0_{\mathrm{Rx}}$$

The standard heat of reaction

$$Q = \Delta H^0_{\mathrm{Rx}} = \xi_1 \Delta H^0_{\mathrm{Rx},1} + \xi_2 \Delta H^0_{\mathrm{Rx},2}$$

The standard heat of reaction from the heat of formations

$$\Delta H^0_{\mathrm{Rx},1} = \Delta H^0_{\mathrm{f,H_2O}} + \Delta H^0_{\mathrm{f,HCOOH}} - \Delta H^0_{\mathrm{f,O_2}} - \Delta H^0_{\mathrm{f,CH_3OH}}$$

Substitute standard heat of formation found in Table A.2:

$$\Delta H^0_{\mathrm{Rx},1} = -241.83 + (-115.9) - 0 - (-238.6) = -119.13 \text{ kJ/mol}$$

The standard heat of reaction for the second reaction

$$\Delta H^0_{\mathrm{Rx},2} = 2\Delta H^0_{\mathrm{f,H_2O}} + \Delta H^0_{\mathrm{f,CO_2}} - \frac{3}{2}\Delta H^0_{\mathrm{f,O_2}} - \Delta H^0_{\mathrm{f,CH_3OH}}$$

Substitute the values of standard heat of formation for the second reaction:

$$\Delta H^0_{\mathrm{Rx},2} = 2(-241.83) + (-393.5) - \frac{3}{2}(0) - (-238.6) = -638.56 \text{ kJ/mol}$$

The heat evolved from the reactor, Q, is given by

$$Q = \xi_1 \Delta H^0_{\mathrm{Rx},1} + \xi_2 \Delta H^0_{\mathrm{Rx},2}$$

Substitute the values of heat of reaction and extent of reaction:

$$Q = 120(-119.13) + 80(-638.56) = -65{,}380.4 \text{ kJ/min}$$

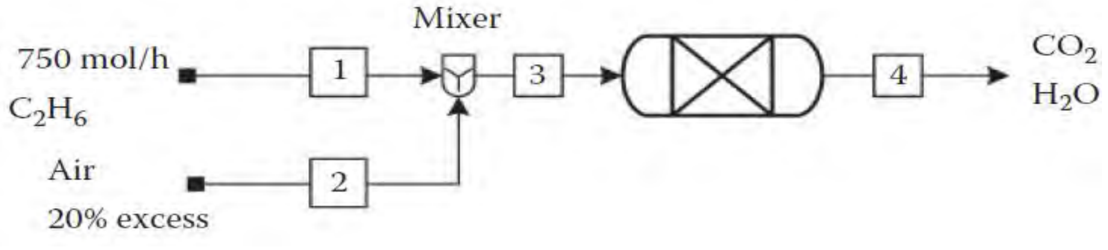
Fractional conversion of methanol: $\dfrac{\dot{\xi}_1 + \dot{\xi}_2}{\dot{n}_{1,\mathrm{CH_3OH}}} = \dfrac{120 + 80}{240} = 0.833$

Fractional selectivity to formic acid: $\dfrac{\dot{\xi}_1}{\dot{\xi}_1 + \dot{\xi}_2} = \dfrac{120}{120 + 80} = 0.60$

Example 3.14 Ethane Combustion

Problem

Ethane (C2H6) at a molar flow rate of 750 mol/h is mixed with 20% excess air and fed to a burner where the mixture is completely combusted isothermally at 25° C, using cold water. What is the air flow rate to the burner (mol/h) and what is the amount of heat released to the cold water?



EXAMPLE FIGURE 3.14.1: Ethane combustion process flow sheet.

Solution

Known quantities: Ethane molar flow rate and percent excess air.

Find: The air flow rate to the burner (mol/h) and the amount of heat released to the cooling water.

Analysis: The process flowchart is shown in Example Figure 3.14.1.

Balanced reaction is $C_2H_6+\frac{7}{2}O_2 \rightarrow 2CO_2+3H_2O$

Air flow at 20% above the stoichiometric requirement is calculated as

$$\text{Theoretical air} = \left(\frac{750\text{ mol ethane}}{\text{h}}\right)\left(\frac{3.5\text{ mol }O_2}{\text{mol ethane}}\right) \times \left(\frac{1\text{ mol air}}{0.21\text{ mol }O_2}\right) = 12,500\text{ mol/h}$$

Excess air:

Excess air = 0.2(Theoretical air) = 0.2(12,500 mol/h) = 2500 mol/h

Total air = Theoretical + excess = 12,500 + 2500 = 15,000 mol/h

The heat released to the coolant is given by

$$Q = \dot{\xi} \times \Delta\hat{H}^0_{\text{rxn}}$$

$$\Delta H^0_{\text{Rx}} = 3\Delta H^0_{f,H_2O} + 2\Delta H^0_{f,CO_2} - \Delta H^0_{f,C_2H_6} - \frac{7}{2}\Delta H^0_{f,O_2}$$

$$\Delta H^0_{\text{Rx}} = 3(-241.83) + 2(-393.5) - (-84.67) - 0 = -1427.8\text{ kJ/mol}$$

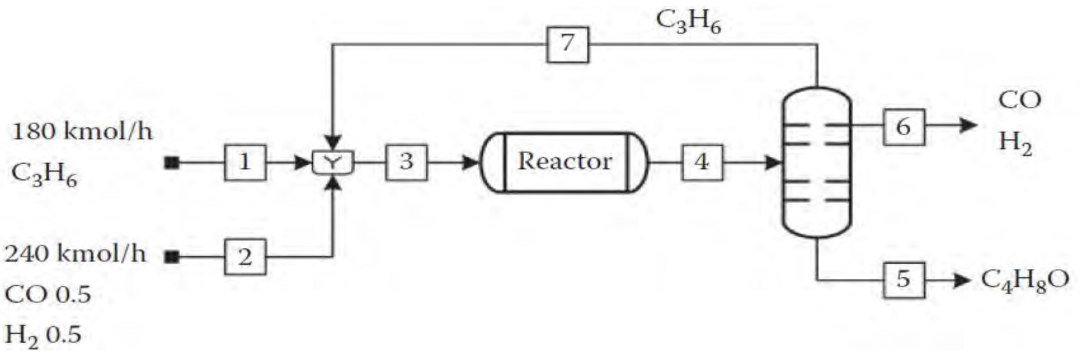
$$Q = 750\text{ mol/h }(-1427.8\text{ kJ/mol}) = -1.24 \times 10^6\text{ kJ/h}$$

Example 3.15 Chemical Reactors with Recycle

Problem

180 kmol/h of propylene (C_3H_6) is mixed with 240 kmol/h of a mixture containing 50% CO and 50% H_2 and with a recycle stream containing only unreacted propylene and then fed to a reactor. A single-pass conversion of propylene of 30% is achieved. Butanol (C4H8O), used to make laundry detergents, is made by the reaction of propylene (C_3H_6) with CO and H_2:

$$C_3H_6 + CO + H_2 \rightarrow C_4H_8O$$



EXAMPLE FIGURE 3.15.1: Process flow sheet for butanol production.

The desired product butanol (B) is removed in one stream, unreacted CO and H_2 are removed in a second stream, and unreacted C_3H_6 is recovered and recycled. Calculate production rate of butanol (kmol/h) and the flow rate of the recycle stream (kmol/h).

Solution

Known quantities: Inlet stream molar flow rate and compositions.

Find: Production rate of butanol (kmol/h) and the flow rate of the recycle stream (kmol/h).

Analysis: The process flow sheet is shown in Example Figure 3.15.1. First choose the entire process as the system. Since no propylene leaves the process, the overall conversion is 100% (fractional conversion = 1.0).

Basis: 180 kmol/h of propylene feed.

Therefore

$$1 = \frac{\dot{\xi}}{180} \quad \text{or} \quad \dot{\xi} = 180 \text{ kgmol/h}$$

The balance on butanol is simply $\dot{n}_{5,C_4H_8O} = \dot{\xi} = 180$ kg mol/h.
Butanol (C_4H_8O) production rate is 180 kmol/h.

Now choose the reactor as the system. The fractional single-pass conversion = 0.3. The extent of reaction is the same as that for overall process because the reactor is the only unit where reaction takes place in the process. Therefore,

$$0.3 = \frac{\dot{\xi}}{\dot{n}_{3,C_3H_6}} = \frac{180}{\dot{n}_{3,C_3H_6}}$$

Solving for the molar flow rate of propylene fed to the reactor,

$$\dot{n}_{3,C_3H_6} = 600 \text{ kmol/h}$$

From a balance around the mixer, we can find that the recycle rate must be

$$600 - 180 = 420 \text{ kgmol/h}$$

Homework Problems

3.1 An adiabatic pot is used to cool and condense 10 kg of hot ethanol (150° C, 1.2 atm) by mixing it with cold ethanol (5° C, 1.2 atm). If the final ethanol product is to be at 25° C and 1.2 atm, the heat capacity of liquid and vapor ethanol is 112 and 65.6 J/mol ° C. Boiling point of ethanol is 78.3° C. The latent heat of vaporization of ethanol is 36,600 J/mol. How much cold ethanol (kg) must be added? (220 kg)

3.2 A quantity of 100 mol/h acetylene (C_2H_2) is mixed with 2000 mol/h air (79 mol% N_2, 21 mol% O_2) and the mixture (at 298 K and 1 atm) fed to a reactor, where complete combustion takes place. The reactor is equipped with cooling tubes. The combustion mixture leaving the reactor is at 1000 K and 1 atm. Draw and label the process flowchart. How much heat (kJ/h) was removed in the reactor? (−82,370 kJ/h)

Suppose the coolant supply was suddenly shut off. What reactor outlet temperature would be reached?

$$C_{PCO_2} = 37 \text{ J/mol °C}, \quad C_{PH_2O} = 33.6 \text{ J/mol °C},$$
$$C_{PO_2} = 29.3 \text{ J/mol °C}, \quad C_{PN_2} = 29.3 \text{ J/mol °C}$$

Assume these values to be constant and independent of temperature.

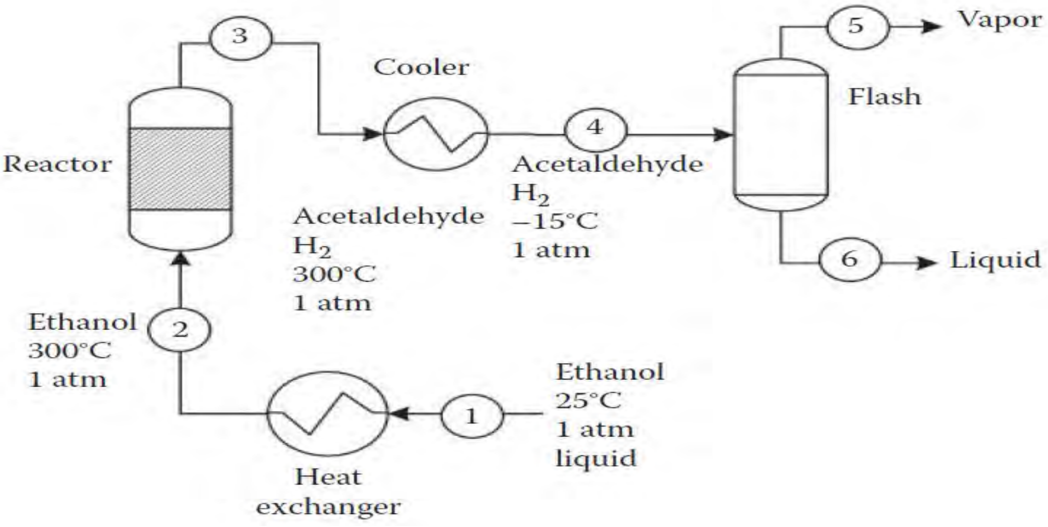
3.3 Ethanol (C2H5OH) is dehydrogenated in a catalytic reactor to acetaldehyde (CH_3CHO), with hydrogen (H_2) as a by-product. In an existing process, 100 mol/min liquid ethanol at 25° C and 1 atm pressure is first heated to 300° C in a heat exchanger, and then fed to the reactor. One hundred percent of the ethanol is converted to products, and the product stream leaves the reactor at 300° C and 1 atm (760 mmHg). The product stream leaving the reactor is cooled to −15° C, and sent to a flash drum, where vapor and liquid streams are separated (Problem Figure 3.3.1).

How much heat must be supplied to the first heat exchanger? (6400 kJ/min)

How much heat must be supplied to or removed from (state which one) the reactor in order to maintain a constant temperature of 300° C? (7100 kJ/min)

What are the flow rates of the vapor and liquid streams leaving the flash drum? (126 mol/min, 74 mol/min

Species	T_b °C	$\Delta H_{vap}(T_b)$ kJ/gmol	C_p(liquid) kJ/gmol °C	C_p(gas) kJ/gmol °C	ΔH_f^0(25 °C) kJ/gmol
H_2	−252.76	0.904	—	0.029	0 (g)
CH_3CHO	20.2	25.1	0.089	0.055	−166.2 (g)
C_2H_5OH	78.5	38.58	0.158	0.077	−277.63 (L) −235.31 (g)



PROBLEM FIGURE 3.3.1: Ethanol (C_2H_5OH) dehydrogenation process.

Antoine equation:

$$\text{Ethanol}: \quad \log_{10} P_{sat}(\text{mmHg}) = 8.04494 - \frac{1554.3}{222.65 + T(°\text{C})}$$

$$\text{Acetaldehyde}: \quad \log_{10} P_{sat}(\text{mmHg}) = 6.81089 - \frac{992}{230 + T\ (°\text{C})}$$

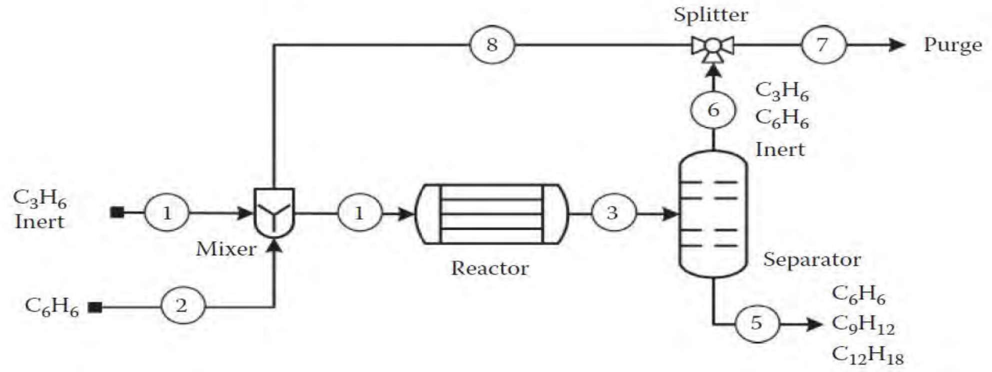
3.4 A gas contains the following compounds: CH_4, C_2H_6, O2, CO_2, CO, H_2O, and H2. What is the maximum number of independent chemical reactions that can be written involving these compounds? (Four independent equations)

3.5 Cumene (C9H12) is synthesized from propylene (C_3H6) and benzene (C_6H_6). Unfortunately, a side reaction also occurs, in which diisopropylbenzene
(C12H18) is generated by reaction of propylene with cumene. The two balanced reactions are

$$C_3H_6 + C_6H_6 \rightarrow C_9H_{12}$$

$$C_3H_6 + C_9H_{12} \rightarrow C_{12}H_{18}$$

A block flow diagram for the cumene manufacturing process is shown in Problem Figure 3.5.1. A quantity of 100 kmol/h of a gas containing 95 mol% Propylene and 5 mol% Inert is mixed with 80 kmol/h benzene plus a recycle stream. The mixer outlet is fed to a reactor. The fractional conversions achieved in the reactor based on the reactor feed stream are: the fractional conversion of benzene is 0.9 and the fractional conversion of propylene is 0.7. The reactor outlet is sent to a separator, where all of the propylene, all of the Inert, and 10% of the benzene are recovered in stream 6, and the remaining benzene and all of the cumene and di-isopropyl benzene are recovered as bottom product. Stream 6 is sent to a splitter. Eighty-five percent of the splitter feed is recycled to the mixer and the remainder is purged. Calculate
the following:



PROBLEM FIGURE 3.5.1: Cumene (C_9H_{12}) synthesis process.

(a) Flow rates of propylene and benzene (kmol/h) in stream 3. (80.7 kmol/h)

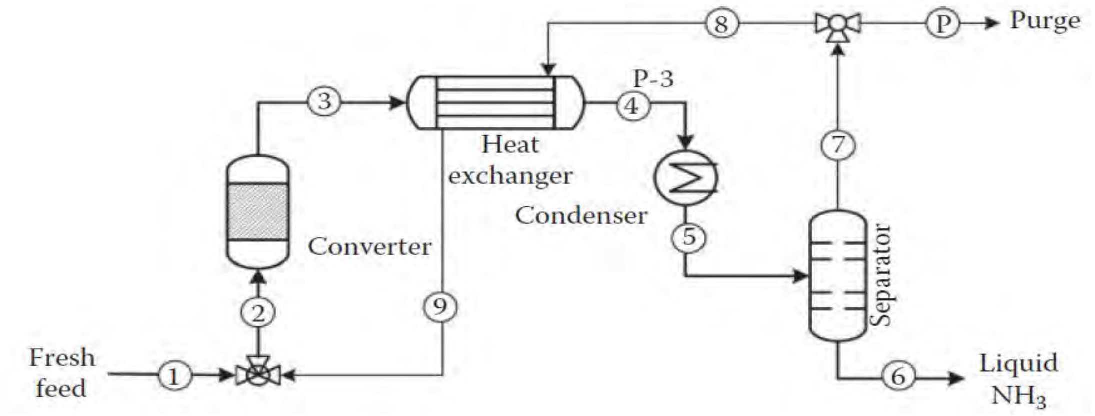
(b) Mol% Inert in purge stream. (46%)

(c) Selectivity for converting benzene to cumene achieved by the overall process. (0.77)

3.6 Ammonia is synthesized through the reaction of nitrogen with hydrogen as follows: $N_2 + 3H_2 \longrightarrow 2NH_3$

Problem Figure 10.6.1 shows a process flow sheet for the ammonia synthesis process. In this process, the fresh feed consists of argon (1 mol%) and stoichiometric amounts of N_2 and H_2. The reactor feed has a molar flow rate of 100 mol/min and a composition of 15 mol% argon, 21.25 mol% N_2, and 63.75 mol% H_2. The reactor feed temperature is 400° C. The fractional conversion of N_2 to NH_3 in the reactor is

0.15 mol N_2 reacted/mol N_2 feed to the reactor. The hot reactor effluent gas is used to heat the recycle gas from the separator in a combined reactor effluent/recycle heat exchanger. After passing through this heat exchanger, the reactor effluent gas passes through a condenser where the NH_3 product is condensed. The liquid NH_3 is separated from the non-condensable recycle gases. A purge stream is taken off the separator off-gas to maintain the level of argon at 15 mol% feed to the reactor. In this particular process, the converter is operated adiabatically and the heat of reaction at 400° C was found to be −53.109 kJ/mol at the pressure of the reactor. The following table gives the heat capacities at the pressure of the reactor. Note that the given heat capacities are assumed to be constant over the temperature range found in the reactor:



PROBLEM FIGURE 3.6.1: Ammonia synthesis process.

Compound	C_p (J/mol °C)
NH_3	49.4
H_2	29.5
N_2	31.0
Argon	20.8

Determine the flow rates in moles per minute and compositions in mole percent of

(a) Fresh feed stream. (12.5 mol/min)

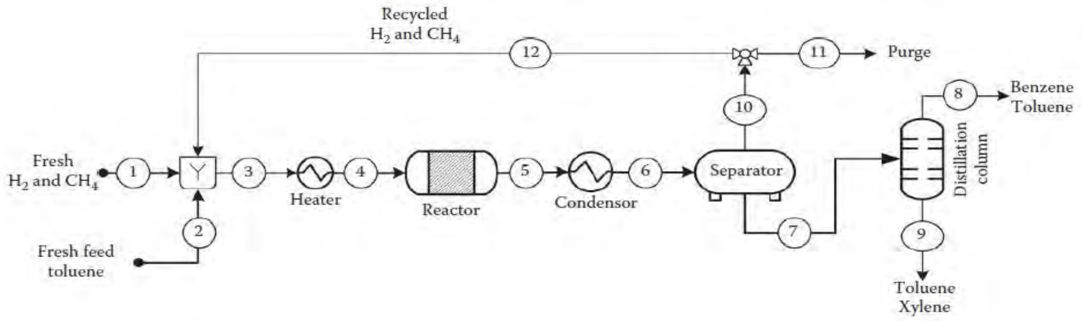
(b) Separator purge gas stream. (0.74 mol/min)

(c) Recycle gas stream. (87.5 mol/min)

(d) Estimate the temperature of the effluent gases from the converter. (460.776° C)

(e) If the recycle gas stream enters the heat exchanger at 50° C and leaves the exchanger at 400° C, determine the outlet temperature of the reactor effluent stream from the heat exchanger. Assume no condensation of ammonia in the heat exchanger. (147.271° C)

3.7 Toluene (225 kmol/h) is fed to a reactor to produce benzene. In this process (Problem Figure 3.7.1), toluene reacts with a fractional conversion of 0.80, resulting in benzene and xylene yields of 0.505 and 0.495, respectively:



PROBLEM FIGURE 3.7.1: Process flow sheet of benzene production process.

$$2C_7H_8 \rightarrow C_6H_6 + C_8H_{10}$$

Toluene also may dealkylate in the reactor to form benzene and methane:

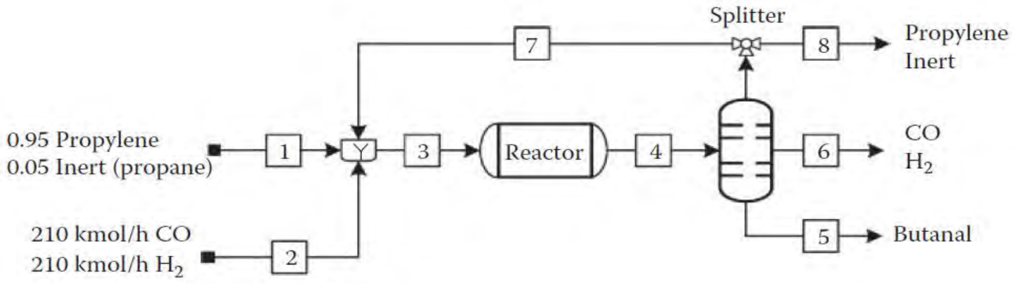
$$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$$

Yields are defined as moles of product/moles of toluene reacted. In this process, the reactor effluent is condensed and separated. The separator liquid is sent to a benzene distillation column where benzene with a purity of 99.5 mol% (balance toluene) is removed as the overhead product. The bottom products contain benzene, unreacted toluene, and xylene. A purge stream containing 90% hydrogen and 10% methane is taken off the separator gas stream. The rest of this separator gas stream is combined with a fresh hydrogen stream containing hydrogen and methane with concentrations of 95.0 and 5.0 mol%, respectively. These combined hydrogen streams are added to the fresh toluene feed and sent to the reactor heater. If the liquid toluene fresh feed stream, fresh hydrogen stream, and recycled streams are all at 25° C and 15 bar absolute, determine the heat requirements for the reactor heater to provide the reactor with a combined feed at 400° C and 15 bar absolute in the vapor phase.

3.8 The dehydrogenation of propane is carried out in a continuous reactor. Pure propane is fed to the reactor at 1300° C and at a rate of 100 mol/s. Heat is supplied at a rate of 1.34 kW. If the product temperature is 1000° C, calculate the extent of reaction. ($\xi = 26$)

3.9 A fresh feed stream contains 5% inert (propane) and 95% propylene. The fresh feed of propylene and inert (propane) is mixed with 210 mol/h carbon dioxide and same amount of hydrogen. At your reactor conditions, propane (I) is an inert, and it is too expensive to separate propane from propylene, so you decide to install a purge stream. The single-pass conversion of propylene in the reactor is 0.3. The production rate of butanol is 180 kmol/h. An overall conversion of 0.90 can be achieved. The purge stream is necessary to avoid inert accumulation in the process. Calculate the flow rate of the contaminated propylene stream to the process (Problem Figure 3.9.1). (210.5 kmol/h)

3.10 Steam flowing at a mass flow rate of 1500 kg/h, a pressure of 20 bar, and 350° C is fed to a turbine that operates adiabatically and at steady state. The steam leaves the turbine at 1.0 bar and 150° C and is cooled in a heat exchanger to a saturated liquid. Draw and label the process flow diagram. How much work (kJ/h) is extracted in the turbine? (541,650 kW) How much heat (kJ/h) is removed in the heat exchanger? (−3.54 × 106 kJ/h)



PROBLEM FIGURE 3.9.1: Butanal production process.

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