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2

Energy Balance with Reaction

The large changes in enthalpy and internal energy throughout a chemical reaction require significant heat transfer (heating or cooling) from the reactor in order to eventually maintain the reactor under optimum operating conditions. This chapter demonstrates how to calculate the heat of reaction at a specific temperature and illustrates how to estimate the heat of reaction from the heat of formation. The energy balances for a reacting system using two methods are defined. Problems that involve the application of combined material and energy balances are addressed. Finally, a few applications, specifically, combustion, bioprocesses, and membrane reactors, are discussed at length to practice the concepts further. The following items outline the principal learning objectives of this chapter.

Learning Objectives

1. Calculate the heat of reaction (Section 2.1).
2. Estimate the heat of reaction from heats of formation (Section 2.2).
3. Establish the energy balance for a reacting system (Section 2.3).
4. Write simultaneous material and energy balances for a reacting system (Section 2.4).
5. Write the appropriate balances for combustion processes (Section 2.5).
6. Apply the energy balance to bioprocesses (Section 2.6).
7. Perform material and energy balances for a membrane reactor system (Section 2.7).

2.1 Heat of Reaction

The heat of reaction, $\Delta H_{\mathrm{Rx}}(T, P)$, is the enthalpy change for a process in which stoichiometric quantities of reactants at temperature T and pressure P react completely to form products at the same temperature and pressure. Consider the following reaction:

$$aA + bB \rightarrow cC + dD$$

The standard heat of reaction ($\Delta H\text{Rx}^{o}$) is calculated as the difference between the product and reactant enthalpies when both reactants and products are at standard conditions, that is, at 25°C and 1 atm [1]. The symbol "o" denotes standard conditions. Therefore,

$$\begin{aligned}\Delta H^{o}_{\text{Rx}}[\text{kJ}/\text{mol}] &= H_{\text{products}} - H_{\text{reactants}} \\ &= c\Delta H^{o}_{\text{f,C}} + d\Delta H^{o}_{\text{f,D}} - a\Delta H^{o}_{\text{f,A}} - b\Delta H^{o}_{\text{f,B}} \\ &= \sum \nu_i \Delta H^{o}_{i}\end{aligned}$$

where $\Delta H\text{f}^{o}$ is the standard heat of formation. The reported $\Delta H\text{Rx}$ applies to stoichiometric quantities of each species. Consider the following example:

$A + 2B \rightarrow 3C$, $H\text{Rx}$ (100°C, 1 atm) = −150 kJ/mol

The enthalpy change for the given reaction is

$$\frac{-150\ \text{kJ}}{1\ \text{mol A consumed}} = \frac{-150\ \text{kJ}}{2\ \text{mol B consumed}} = \frac{-150\ \text{kJ}}{3\ \text{mol C generated}}$$

If 150 mol/s of C was generated at 100°C and 1 atm, then

$$\Delta \dot{H} = \left(\frac{-150\ \text{kJ}}{3\ \text{mol C generated}}\right)\left(\frac{150\ \text{mol C generated}}{\text{s}}\right) = -7500\ \text{kJ}/\text{s}$$

If $\Delta H\text{Rx}(T)$ is negative, the reaction is exothermic; that is, energy must be removed from the reactor to prevent the temperature from increasing. If $\Delta H\text{Rx}\ (T)$ is positive, the reaction is endothermic; that is, energy must be added to the reactor to prevent the temperature from decreasing. The heat of reaction ($\Delta H\text{Rx}\ (T,\ P)$) is nearly independent of pressure. The value of the heat of reaction depends on how the stoichiometric equation is written and on the phase of the reactants and products.

2.2 Heats of Formation and Heat of Combustion

The standard heat of reaction ($\Delta H\text{Rx}^{o}$) can be calculated from the standard heat of formation ($\Delta H\text{f}^{o}$). The standard heat of formation is the enthalpy change associated with the formation of 1 mol of the compound at 25°C and 1 atm. The values of $\Delta H\text{f}^{o}$

for many compounds can be obtained from tabulated data (Table A.2). The standard heat of reaction (ΔHRx^{o}) from the heat of formation (ΔHf^{o}, i) of any reaction can be calculated as

$$\Delta H^{o}_{Rx} = \sum_{i} v_i \Delta H^{o}_{f,i}$$

where

vi is the stoichiometric coefficient of reactant or product species i

ΔHf^{o},i is the standard heat of formation of species i

The standard heats of formation of all elemental species are zero (H_2, O_2, N_2).

The standard heat of reaction $(\Delta^{n}_{\infty} H^{o}_{Rx})$ of any reaction involving only oxygen and a combustible species can be calculated as

$$\Delta H^{o}_{Rx} = -\sum_{i} v_i (\Delta H^{o}_{c})_i$$

This is the reverse of determining the heat of reaction from heats of formation, where vi is the stoichiometric coefficient of reactant or product species i. (ΔHc^{o}i) is the standard heat of combustion of species i. If any reactants or products are combustion products (i.e., CO_2, H_2O, SO_2), their heats of combustion are equal to zero. For many substances, it is much easier to measure the standard heat of combustion (ΔHc^{o}) than measuring the standard heat of formation (ΔHf^{o}). Consider the formation of pentane:

$$\mathbf{5C_{(s)} + 6H_{2\,(g)} \rightarrow C_5H_{12\,(l)}} \qquad \Delta H\mathrm{Rx}^{o} = ?$$

Carbon, hydrogen, and pentane can all be burned, and their standard heats of combustion can be determined experimentally. Therefore,

$$\Delta H^{o}_{Rx} = 5\Delta H^{o}_{c,C(s)} + 6\Delta H^{o}_{c,H_2\,(g)} - \Delta H^{o}_{c,C_5H_{12}\,(l)}$$

The standard enthalpy of combustion is the enthalpy change when 1 mol of a reactant completely burns in excess oxygen under standard thermodynamic conditions. The standard heat of combustion of a species i, $\Delta Hc^{o}i$, is the enthalpy change associated with the complete combustion of 1 mol of species i with oxygen at 25° C and 1 atm such that all the carbon forms CO_2 (g), all the hydrogen forms H_2O (l), all the sulfur forms SO_2 (g), and all the nitrogen forms NO_2 (g). The same value of standard heat of reaction can be used to measure the standard heat of formation of pentane:

$$\Delta H^{o}_{Rx} = \Delta H^{o}_{f,C_5H_{12}(l)} - 5\Delta H^{o}_{f,C(s)} - 6\Delta H^{o}_{f,H_2(g)}$$

Since carbon and hydrogen are atoms, the magnitude of their standard heats of formation is zero. Accordingly,

$$\Delta H^{o}_{Rx} = \Delta H^{o}_{f,C_5H_{12}(l)} - 0 - 0$$

Example 2.1 Heat of Reaction from Heats of Formation

Problem

Consider the combustion of liquid ethanol as shown in the following reaction scheme:

$C_2H_5OH_{(l)} + 3O_{2\,(g)} \rightarrow 2CO_{2\,(g)} + 3H_2O_{(l)}$

Use heat of formation and heat of combustion to determine the standard heat of reaction.

Solution

Known quantities: Reaction stoichiometry.

Find: Standard heat of reaction.

Analysis: Values for standard heat of combustion and standard heat of formation are available in the appendix.

$$\Delta H^{o}_{Rx} = 3\Delta H^{o}_{f,\,H_2O\,(l)} + 2\Delta H^{o}_{f,\,CO_2} - 0 - \Delta H^{o}_{f,\,C_2H_5OH\,(l)}$$

Substitute the values of the standard heat of formation:

$$\Delta H^{o}_{Rx}\left(\mathrm{kJ/mol}\right) = 3\left(-285.84\right) + 2\left(-393.51\right) - 0 - \left(-277.63\right) = -1366.9\ \mathrm{kJ/mol}$$

The standard heat of reaction is calculated from the standard heat of combustion as

$$\Delta H^{o}_{Rx} = \Delta H^{o}_{c,\,C_2H_5OH\,(l)} + 3\Delta H^{o}_{c,\,O_2} - 3\Delta H^{o}_{c,\,H_2O\,(l)} - 2\Delta H^{o}_{c,\,CO_2\,(g)}$$

Substitute the values of the standard heat of combustion, knowing that the magnitudes of the standard heat of combustion of oxygen, water, and carbon dioxide are zero:

$$\Delta H^{o}_{Rx}\left(\mathrm{kJ/mol}\right) = -1366.91 + 0 - 0 - 0 = -1366.9\ \mathrm{kJ/mol}$$

Results reveal that both values of standard heat of reactions are identical.

Example 2.2

Problem

If 240 mol/s of CO_2 is produced in the following reaction where reactants and products are all at 25C, and no CO_2 is present in the feed stream,

$$\mathbf{2C_4H_{10\,(g)} + 13O_{2\,(g)} \rightarrow 8CO_{2\,(g)} + 10H_2O_{(l)}}$$

what is the standard rate of change in enthalpy?

Solution

Known quantities: Molar flow rate of effluent CO_2 and reaction temperature.

Find: Standard rate of change in enthalpy.

Analysis: The standard heat of reaction from the heat of formation is as follows:

$$\Delta H^\circ_{Rx}\ (25°C, 1\ \text{atm}) = \sum \nu_i \Delta H^\circ_{f,i}$$

The heat of reaction is given by

$$\Delta H^\circ_{Rx}\ (25°C, 1\ \text{atm}) = 10\Delta H^\circ_{f,H_2O\,(l)} + 8\Delta H^\circ_{f,CO_2} - 2\Delta H^\circ_{f,C_4H_{10}} - 13\Delta H^\circ_{f,O_2}$$

$$\Delta H^\circ_{Rx}\ (25°C, 1\ \text{atm}) = 10(-285.84) + 8(-393.5) - 2(-124.7) - 13(0)$$

$$\Delta H^\circ_{Rx}\ (25°C, 1\ \text{atm}) = -5757\ \text{kJ/mol}$$

The extent of reaction is calculated using the mole balance of CO2; note that no carbon dioxide is present in the feed stream before the reaction takes place:

$$n_{CO_2} = 0 + 8\xi = 240 = 0 + 8\xi$$

$$\xi = \frac{240}{8} = 30\ \text{mol/s}$$

The change in enthalpy transfer rate is

$$\Delta \dot{H} = \xi \times \Delta H^\circ_{Rx} = 30 \times -5757\ \text{kJ/mol} = -1.727 \times 10^5\ \text{kJ/s}$$

Example 9.3 Butane Combustion

The reaction stoichiometry and standard heat of the reaction on *n*-butane vapor is shown here:

$$C_4H_{10}(g) + \frac{13}{2}O_2\ (g) \rightarrow 4CO_2\ (g) + 5H_2O\ (l),\ \Delta H^\circ_{Rx} = -2900\ \text{kJ/mol}$$

Assume that 40 mol/s of CO2 is produced in this reaction and the reactants and products are all at 25° C. The fresh feed to the reactor contains 20 mol/s of CO2. Calculate the rate of change in enthalpy ΔHRx^o (kJ/s).

Solution

Known quantities: Inlet and exit CO2 molar flow rate and reaction temperature.

Find: The rate of change in enthalpy.

Analysis: Since inlet and exit streams’ temperature is equal, the change in the sensible heat is irrelevant. Accordingly, the rate of change in enthalpy is only due to heat of reaction and is calculated as

$$\Delta\dot{H} = \dot{\xi}\Delta H^{o}_{Rx}(T, P) \text{ at } 25^{\circ}\text{C}, \ \Delta\dot{H} = \dot{\xi}\Delta H^{o}_{Rx},$$

where *ΔHRx*^{o} is the standard heat of reaction.

The extent of reaction is calculated using the mole balance of CO2:

$$\dot{n}_{CO_2} = \dot{n}_{CO_2,\text{feed}} + 4\dot{\xi}$$

Substitute the values of inlet and exit molar flow rates of carbon dioxide:

$$40 = 20 + 4\dot{\xi}$$

The extent of reaction is $\dot{\xi} = \dfrac{40 - 20}{4} = \dfrac{20}{4} = 5 \text{ mol/s}$

The standard rate of change in enthalpy, $\Delta\dot{J}$ is

$$\Delta\dot{H} = \dot{\xi}\Delta H^{o}_{Rx} = \left(5\,\frac{\text{mol}}{\text{s}}\right)\left(\frac{-2900\text{ kJ}}{\text{mol}}\right) = -1.45 \times 10^{4}\text{ kJ/s}$$

2.2.1 Extent of Reaction

If n_{Ar} is the moles of A generated or consumed by a reaction at a temperature *T* and pressure *P*, and v_A is the stoichiometric coefficient of the reactant or product, the associated enthalpy change is

$$\Delta\dot{H} = \dot{\xi}\Delta H_{Rx}(T, P)$$

The extent of reaction, *ξ*, is a measure of how far a reaction has proceeded:

$$(\dot{n}_i)_{\text{out}} = (\dot{n}_i)_{\text{in}} + \nu_i\dot{\xi}$$

Rearranging, the extent of reaction is expressed as

$$\dot{\xi} = \frac{(\dot{n}_i)_{\text{out}} - (\dot{n}_i)_{\text{in}}}{\nu_i}$$

1.2.2 Reactions in Closed Processes

If the reaction is taking place in a closed system of constant volume, the change in the internal energy of reaction, Δ *U*Rx, is given as

$$\Delta U_{\mathrm{Rx}} = \Delta H_{\mathrm{Rx}} - (\Delta n)RT$$

The change in the number of moles is equivalent to the change in the number of stoichiometric coefficients between the product and the reactant.

Substituting $\Delta n = \sum v_i,$

$$\Delta U_{\mathrm{Rx}} = \Delta H_{\mathrm{Rx}} - RT\sum v_i$$

where *vi* is the stoichiometric coefficient of the gaseous reactant or product component (+for product, −for reactant).

Example 2.4 Heat of Reaction from Internal Energy

Calculate the standard heat of the reaction of the following reaction:

$$C_2H_4\ (g) + 2Cl_2\ (g) \rightarrow C_2HCl_3\ (l) + H_2\ (g) + HCl\ (g)$$

The internal energy of reaction at standard conditions (25C, 1 atm) is
Δ *U*Rx = −418 kJ/mol.

Solution

Known quantities: Internal energy of reaction.

Find: The standard heat of reaction.

Analysis: Use the following equation for closed system:

$$\Delta U_{\mathrm{Rx}}(T) = \Delta H_{\mathrm{Rx}}(T) - RT\sum v_i$$

Substitute known quantities:

$$-418\ \mathrm{kJ/mol} = \Delta H^{\mathrm{o}}_{\mathrm{Rx}} - \frac{8.314\ \mathrm{J}}{\mathrm{mol\ K}}\frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}} \times 298.15\ \mathrm{K} \times (1 + 1 + 0 - 2 - 1)$$

$$\Delta H^{\mathrm{o}}_{\mathrm{Rx}} = -420.5\ \mathrm{kJ/mol}$$

Note that *vi* is the stoichiometric coefficient (+for product, −for reactant) of the gaseous reactant or product component only (not liquids or solids components). If a set of reactions can be manipulated through a series of algebraic operations to yield the desired reaction, then the desired heat of reaction can be obtained by performing the same algebraic operations on the heats of reaction of the manipulated set of reactions (Hess law).

Example 2.5 Standard Heat of Reaction

Calculate the heat of combustion for C_2H_6 from the following reactions:

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta H^{o}_{Rx1} = -1409.5\ \mathrm{kJ/mol}$$

$$C_2H_4 + H_2 \rightarrow C_2H_6, \quad \Delta H^{o}_{Rx2} = -136.7\ \mathrm{kJ/mol}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H^{o}_{Rx3} = -285.5\ \mathrm{kJ/mol}$$

Solution

Known quantities: Standard heat of reaction.

Find: Standard heat of reaction for the combustion of ethane.

Analysis: Use Hess’ law.

The reaction for combustion of ethane is as follows:

$$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O \quad \Delta H^{o}_{Rx1} = ?$$

The first reaction minus the second reaction based on one mole reacted

$$\begin{array}{ll} C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O, & -1409.5\ \mathrm{kJ} \\ \underline{C_2H_6 \rightarrow C_2H_4 + H_2,} & \underline{+136.7\ \mathrm{kJ}} \\ C_2H_6 + 3O_2 \rightarrow 2CO_2 + 2H_2O + H_2 & -1272.8\ \mathrm{kJ} \end{array}$$

Accordingly, the heat of combustion of C_2H_6 is −1558.3 kJ.

Example 2.6 Dehydrogenation of Ethane

Calculate the standard heat of reaction from the dehydrogenation of ethane using the standard heats of combustion:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

Solution

$$\Delta H^{o}_{Rx} = \Delta H^{o}_{c,\,C_2H_6} - \Delta H^{o}_{c,\,C_2H_4} - \Delta H^{o}_{c,\,H_2}$$

Substituting the values of standard heat of combustion (from the appendix) yields

_HRx^{o} (kJ/mol) = −1559.9 − (−1410.99) − (−285.84) = 136.93 kJ/mol

2.3 Energy Balance for Reactive Processes

For energy balances with reaction, we have two methods for solving these types of problems: the heat of reaction method (extent of reaction) and the heat of formation method (element balance). These two methods differ in the choice of the reference state [2, 3].

2.3.1 Heat of Reaction Method

The heat of reaction method is ideal when there is a single reaction for which ΔHRx^{o} is known. This method requires calculation of the extent of reaction, • ξ . The extent of reaction can be obtained by performing material balance for any reactant or product for which the feed and product flow rates are known. The reference state is such that all reactant and product species are at 25^{o} C and 1 atm in the states for which the heat of reaction is known (Figure 2.1).

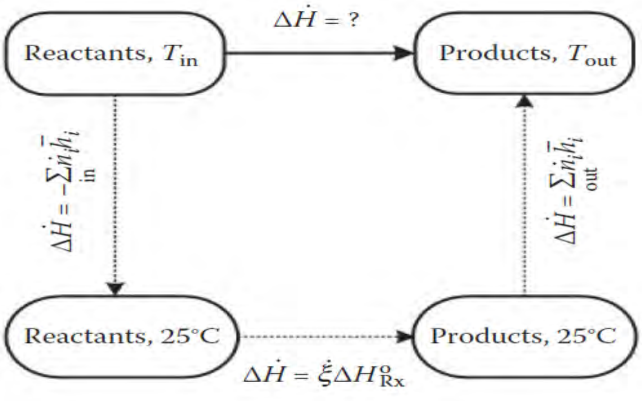


FIGURE 2.1 Rate of change in enthalpy for a reactive process.

For a single reaction at a reference state of 25°C and 1 atm while reactant and product are at different inlet and exit temperatures [4],

$$\Delta \dot{H} = \dot{\xi} \Delta H^{\circ}_{\mathrm{Rx}} + \sum_{\mathrm{out}} \dot{n}_i \overline{h}_i - \sum_{\mathrm{in}} \dot{n}_i \overline{h}_i$$

where *hi*(J/mol) is the specific molar enthalpy of a definite component. For multiple reactions, where the reference state is 25° C and 1 atm and the inlet and exit streams are at temperatures other than the reference states,

$$\Delta \dot{H} = \sum_{\mathrm{reactions}} \dot{\xi}_j \Delta H^{\circ}_{\mathrm{Rx},j} + \sum_{\mathrm{out}} \dot{n}_i \overline{h}_i - \sum_{\mathrm{in}} \dot{n}_i \overline{h}_i$$

A reference temperature other than 25° C can be considered in this case, and the heat of reaction should be calculated at the new reference state:

$$\Delta \dot{H} = \sum_{\mathrm{reactions}} \dot{\xi}_j \Delta H_{\mathrm{Rx},j} + \sum_{\mathrm{out}} \dot{n}_i \overline{h}_i - \sum_{\mathrm{in}} \dot{n}_i \overline{h}_i$$

The heat of reaction at any temperature

$$\Delta H_{\mathrm{Rx}} = \Delta H^{\circ}_{\mathrm{Rx}}\,(25^{\circ}\mathrm{C}) + \int_{25^{\circ}\mathrm{C}} \Delta C_{\mathrm{p}} \mathrm{d}T$$

$$\text{where } \Delta C_{\mathrm{p}} = \sum v_i C_{\mathrm{p},i}$$

2.3.2 Heat of Formation or Element Balance Method

In the heat of formation method, the heats of reaction terms ($\Delta H\mathrm{rxn}^{\circ}$) are not required as they are implicitly included when heats of formation of the reactants are subtracted from the products [5]. For single and multiple reactions,

$$\Delta \dot{H} = \sum_{\mathrm{out}} \dot{n}_i \overline{h}_i - \sum_{\mathrm{in}} \dot{n}_i \overline{h}_i$$

where *hi* accounts for the change in molar enthalpy with *T* and phase $+ \Delta Hf^{\circ}$ (Figure 2.2). In this case we find the enthalpy of all of the compounds relative to the elements at 25° C. No heat of reaction needs to be calculated at all. We then plug these enthalpies directly into the energy balance expression. In the absence of kinetic and potential energy, the energy balance equation is

$$Q - W = \Delta\dot{H} = \sum_{\text{out}} \dot{n}_i \bar{h}_i - \sum_{\text{in}} \dot{n}_i \bar{h}_i$$

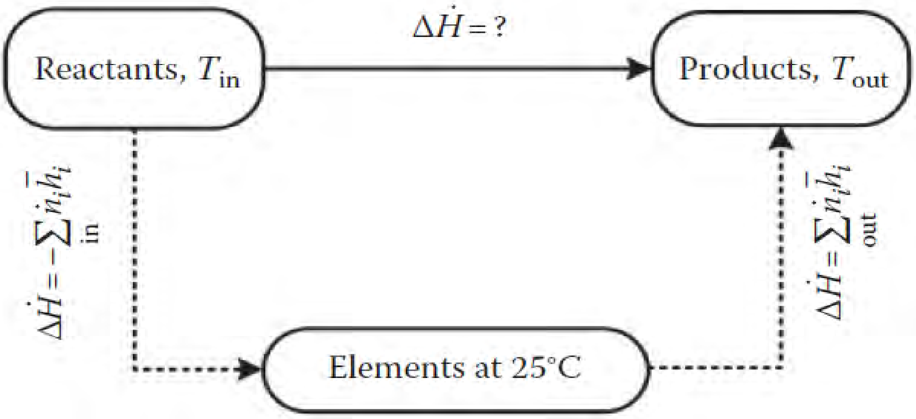


FIGURE 2.2
Heat of formation or element balance method.

where the specific molar enthalpy of component *i* in the inlet streams is

$$\bar{h}_{i,\text{in}} = \int_{25}^{T_{\text{in}}} C_{\text{p},i} \, dT + \Delta H^{\circ}_{\text{f},i}$$

Specific molar enthalpy of component *i* in the exit streams is

$$\bar{h}_{i,\text{out}} = \int_{25}^{T_{\text{out}}} C_{\text{p},i} \, dT + \Delta H^{\circ}_{\text{f},i}$$

2.4 Simultaneous Material and Energy Balances

Material balances could be written on either compound that requires the extent of reaction or their elements, which requires only balances without generation terms for each element. Similarly, we can also write down energy balances using either compounds or elements. From material balances with reaction that we had discussed, there are three methods of analyzing these types of reactive processes: atomic species balances, extents of reaction, and component balances. For energy balances with reaction, we have two methods for solving these types of problems: the heat of reaction method and the heat of formation method or element balance method.

Example 2.7 Gas Phase Reaction

Gas phase reaction is taking place in a continuous reactor. Stoichiometric proportions of CO_2 and H2 are fed to the reactor at 400° C. The reaction proceeds to 80% completion. Given 1 mol of carbon dioxide, estimate the heat that must be provided or removed, if the gas exit steams are to be kept at 500° C. Perform the energy balance using the heat of reaction method at two reference temperatures (500° C and 25° C) and the heat of formation method.

Solution

Known quantities: Inlet and exit temperatures, percent conversion, inlet flow rate of carbon dioxide and hydrogen.

Find: The amount of heat added or removed.

Analysis: The schematic diagram is shown in Example Figure 2.7.1.

Basis: 1 mol of CO_2 and 4 mol of H_2. The process flow diagram is shown in Example Figure 2.7.1.

Material balance (Extent of reaction method)

$$CO_2 + 4H_2 \rightarrow 2H_2O + CH_4 \quad \xi$$

Component balance is calculated using the extent of reaction method as follows:

$$CO_2\text{: } n_{CO_2} = 1 - \xi$$

$$H_2\text{: } n_{H_2} = 4 - 4\xi$$

$$CH_4\text{: } n_{CH_4} = 0 + \xi$$

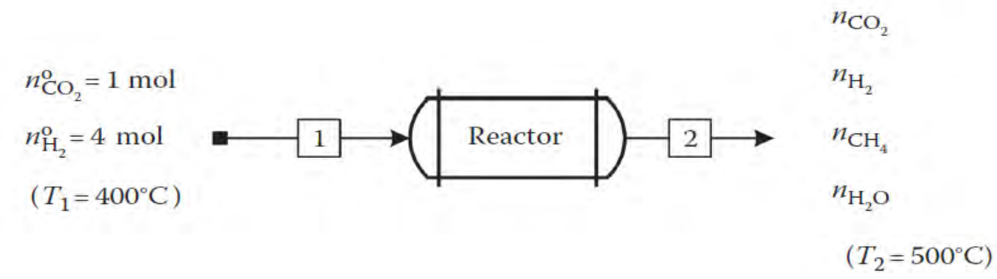
$$H_2O\text{: } n_{H_2O} = 0 + 2\xi$$

From the fractional conversion of CO2,

$$f = \frac{n^{o}_{CO_2} - n_{CO_2}}{n^{o}_{CO_2}}$$

$$0.8 = \frac{1.0 - n_{CO_2}}{1.0}$$

$$n_{CO_2} = 1.0 - 0.8 = 0.2 \text{ mol}$$



EXAMPLE FIGURE 2.7.1 Process flow diagram of gas phase reaction.

Accordingly, the number of moles of carbon dioxide leaving the reactor is nCO_2= 0.2mol.

The extent of reaction, ξ, is calculated by substituting nCO_2= 0.2mol in the CO_2 mole balance equation: $0.2 = 1 - \xi$.

Solving for the extent of reaction, $\xi = 0.8$.

To calculate moles of exit components, substitute values of the extent of reaction in the mole component balance equations given earlier. The following results are obtained:

$$nH_2 = 0.8, nCH_4 = 0.8, nH_2O = 1.6$$

Energy balance (Heat of reaction method)

The energy balance is performed at two reference temperatures; exit stream temperature (500° C) and at the standard heat of reaction temperature (25° C). First, prepare the following data table using the polynomial form of the specific heat capacity:

$Cp(J/mol°C) = a + bT + cT^2$

The standard heats of formation at 25° C can be obtained from Table A.2 (Appendix A.1). Components of heat capacity (Appendix A.2) and heats of formation (Table A.2):

Components	v_i	a	b	c	ΔH_f^o
CO_2	−1	36.11	0.04233	-2.887×10^{-5}	−393.5
H_2	−4	28.84	0.0000765	0.3288×10^{-5}	00.00
H_2O	2	33.46	0.006880	0.7604×10^{-5}	−241.83
CH_4	1	34.31	0.054690	0.3661×10^{-5}	−74.85
Δ		−50.24	0.025810	3.4600×10^{-5}	−165.00

Note: $\Delta = CH_4 + 2H_2O - 4H_2 - CO_2$

The ΔHf^o in the last column is for the heats of formation. The Δ in the last row is the difference between the product and reactants based on the stoichiometric coefficient; for example, the Δa is calculated as

$$\Delta a = \sum v_i a = -1 \times 36.11 - 4 \times 28.84 + 2 \times 33.46 + 34.31 = -50.24$$

The same method is used for calculating the values of Δb, Δc, and ΔHf^o.

Reference temperature = 500° C

In this approach, we perform the energy balance using the heat of reaction method at the reference temperature of 500° C: Tref = 500° C. This requires knowledge of the heat of reaction at 500° C. The energy balance for this process includes the sensible heat to change the temperature of everything in the inlet stream from 500° C to 400° C and the heat of reaction at 500° C times the extent of reaction. Recall that the heat of reaction was expressed in kilojoules per mole, where the mole basis was per molar extent of reaction:

$$Q = \xi \Delta H_{\mathrm{Rx}}\,(T_{\mathrm{ref}}) + H_{\mathrm{out}} - H_{\mathrm{in}}$$

For multiple input and exit components,

$$Q = \int_{500°C}^{500°C} \sum_{\mathrm{out}} n_i C_{\mathrm{p}_i}\, \mathrm{d}T - \int_{500°C}^{400°C} \sum_{\mathrm{in}} n_i^o C_{\mathrm{p}_i}\, \mathrm{d}T + \xi\, \Delta H_{\mathrm{Rx}}\Big|_{500°C}$$

Substituting the proper values,

$$Q = 0 + \int_{400°C}^{500°C} \sum_i n_i^o C_{\mathrm{p}_i} \mathrm{d}T + \xi\, \Delta H_{\mathrm{Rx}}\Big|_{500°C}$$

The heat of reaction at 500° C is then

$$\Delta H_{\mathrm{Rx}}\big|_{500^\circ\mathrm{C}} = \Delta H^{\circ}_{\mathrm{Rx}} + \int_{25^\circ\mathrm{C}}^{500^\circ\mathrm{C}} \Delta C_{\mathrm{p}}\,\mathrm{d}T = \Delta H^{\circ}_{\mathrm{Rx}} + \int_{25}^{500} \left(\Delta a + \Delta bT + \Delta cT^{2}\right)\mathrm{d}T$$

The ΔCp for the reaction is immediately obtained from the Δ row for use in integration from one temperature to another:

$$\Delta H_{\mathrm{Rx}}\big|_{500^\circ\mathrm{C}} = -165\ \mathrm{kJ/mol} + [(-50.24)(500-25) + \frac{1}{2}(0.02581)(500^{2}-25^{2}) + \frac{1}{3}(3.46\times10^{-5})(500^{3}-25^{3})]\,\frac{\mathrm{J}}{\mathrm{mol}}\,\frac{\mathrm{kJ}}{1000\ \mathrm{J}} = -184.6\ \mathrm{kJ/mol}$$

The heat of reaction at 500°C is

$$\Delta H_{\mathrm{Rx}}\big|_{500^\circ\mathrm{C}} = -184.6\ \mathrm{kJ/mol}$$

Now the sensible heat term (first terms shown in the earlier equation) includes only the moles of those compounds in the inlet stream. This gives

$$H_{\mathrm{in}} = \int_{500^\circ\mathrm{C}}^{400^\circ\mathrm{C}} \sum_{i} n_i^{\circ} C_{\mathrm{p}\,i}\,\mathrm{d}T = (1)\int_{500}^{400} C_{\mathrm{p\,CO_2}}\,\mathrm{d}T + (4)\int_{500}^{400} C_{\mathrm{p\,H_2}}\,\mathrm{d}T = 1(-5) + 4(-2.95)\ \mathrm{kJ} = -16.80\ \mathrm{kJ}$$

$$H_{\mathrm{out}} = \int_{500^\circ\mathrm{C}}^{500^\circ\mathrm{C}} \sum_{i} \dot{n}_i C_{\mathrm{p}\,i}\,\mathrm{d}T = 0$$

So finally, substitute estimated inlet, exit enthalpies and heat of reaction in the general energy balance equation shown here:

$$Q = \xi \Delta H_{\mathrm{Rx}}\,(T_{\mathrm{ref}}) + H_{\mathrm{out}} - H_{\mathrm{in}}$$

$$Q = (0.8\ \mathrm{mol})\ (-184.6\ \mathrm{kJ/mol}) + 0 - (-16.80\ \mathrm{kJ}) = -131\ \mathrm{kJ}$$

Reference temperature = 25° C

The energy balance for this process at this reference temperature includes the sensible heat to change the temperature of everything in the inlet stream from 25° C to 400° C and also to change everything in the product stream from 25° C to 500° C. Again, the heat of reaction at 25° C must be multiplied by the extent of reaction. The heat of the process at 25° C is

$$Q = H_{\text{out}} - H_{\text{in}} + \xi\Delta H^{\circ}_{\text{Rx}} = \int_{25^\circ\text{C}}^{500^\circ\text{C}} \sum_{\text{out}} n_i C_{p_i}\, dT - \int_{25^\circ\text{C}}^{400^\circ\text{C}} \sum_{\text{in}} n_i^{\circ} C_{p_i}\, dT + \xi\Delta H^{\circ}_{\text{Rx}}$$

The enthalpy of inlet stream relative to reference temperature (25° C) is

$$H_{\text{in}} = \int_{25^\circ\text{C}}^{400^\circ\text{C}} \sum_{i} n_i^{\circ} C_{p_i} dT = (1\ \text{mol}) \int_{25^\circ\text{C}}^{400^\circ\text{C}} C_{p\text{CO}_2} dT$$

$$+ (4\ \text{mol}) \int_{25^\circ\text{C}}^{400^\circ\text{C}} C_{p\text{H}_2} dT = 16.35 + 43.54 = 59.89\ \text{kJ}$$

The heat of reaction term at 25° C is found from the Δ term in the table for the heats of formation. Likewise, we have already found in method 1 that $\xi = 0.8$ mol. Thus, the reaction term is

$$\xi\Delta H^{\circ}_{\text{Rx}} = (0.8\ \text{mol})(-165\ \text{kJ/mol}) = -132\ \text{kJ}$$

We can now calculate the sensible heat term for heating everything in the outlet stream from 25° C to 500° C. The enthalpy change of the outlet stream with respect to reference temperature (25° C) is

$$H_{\text{out}} = \int_{25^\circ\text{C}}^{500^\circ\text{C}} \sum_{i} n_i C_{p_i}\, dT = (0.2\ \text{mol}) \int_{25}^{500} C_{p\,\text{CO}_2} dT + (0.8\ \text{mol}) \int_{25}^{500} C_{p\,\text{H}_2}\, dT$$

$$+ (0.8\ \text{mol}) \int_{25}^{500} C_{p\,\text{CH}_4}\, dT + (1.6\ \text{mol}) \int_{25}^{500} C_{p\,\text{H}_2\text{O}}\, dT$$

Integration of the earlier equation after substitution of components heat capacity yields

$$H_{\text{out}} = \int_{25^\circ\text{C}}^{500^\circ\text{C}} \sum_{i} n_i C_{p_i}\, dT = (4.27 + 11.06 + 18.48 + 27.22)\ \text{kJ} = 61.03\ \text{kJ}$$

Finally, we obtain

$$Q = H_{\text{out}} - H_{\text{in}} + \xi\Delta H^{\circ}_{\text{Rx}} = \sum_{\text{out}} n_i \bar{h}_i - \sum_{\text{in}} n_i^{\circ} \bar{h}_i + \xi\Delta H^{\circ}_{\text{Rx}}$$

$$= 61.03 - 59.89 - 132 = -131\ \text{kJ}$$

The heat transferred from the system is 131 kJ.

Heat of formation method (Element balance)

In this case, no heat of reaction needs to be calculated at all. We write the energy balance as follows:

$$Q = \sum_{\text{out}} n_i \bar{h}_i - \sum_{\text{in}} n_i \bar{h}_i$$

Next, we compute the enthalpy of each component in each stream relative to their elements. The compound is formed from its elements at 25°C (this is the heat of formation), and then we raise the temperature of the compound up to the temperature of the stream.

The specific enthalpy of outlet compounds

$$CH_4 : \bar{h}_{CH_4} = \Delta H_f^o(25) + \int_{25°C}^{500°C} C_{p,CH_4}\, dT = -74.85 + 23.10 = -51.75 \text{ kJ/mol}$$

$$H_2O : \bar{h}_{H_2O} = \Delta H_f^o(25) + \int_{25°C}^{500°C} C_{p,H_2O}\, dT = -241.83 + 17.01 = -224.8 \text{ kJ/mol}$$

$$CO_2 : \bar{h}_{CO_2} = \Delta H_f^o(25) + \int_{25°C}^{500°C} C_{p,CO_2}\, dT = -393.5 + 21.34 = -372.2 \text{ kJ/mol}$$

$$H_2 : \bar{h}_{H_2} = 0 + \int_{25°C}^{500°C} C_{p\,H2}\, dT = 13.83 \text{ kJ/mol}$$

Thus, the sum of all of the outlet specific enthalpies is

$$H_{\text{out}} = \sum_{\text{out}} n_i h_i = (0.2)(-372.2) + (0.8)(13.83) + (0.8)(-51.75) + (1.6)(-224.8) = -464.5 \text{ kJ}$$

The specific enthalpies of inlet compounds

$$CO_2 : h_{CO_2}^o = \Delta H_f^o + \int_{25°C}^{400°C} C_{p,CO_2} dT = -393.5 + 16.35 = -377.2 \text{ kJ/mol}$$

$$H_2 : h_{H_2}^o = 0 + \int_{25°C}^{400°C} C_{p\,H_2} dT = 10.89 \text{ kJ/mol}$$

Thus, the sum of all of the inlet enthalpies is

$$H_{\text{in}} = \sum_{\text{in}} n_i h_i = (1)(-377.2) + (4)(10.89) = -333.6 \text{ kJ}$$

Finally, from the energy balance we obtain

$$Q = H_{\text{out}} - H_{\text{in}} = -464.5 \text{ kJ} + 333.6 \text{ kJ} = -131 \text{ kJ}$$

The heat calculated using the three methods are equal.

Example 2.8 Oxidation of Ammonia

Hundred moles per minute of ammonia (NH_3) and 200 mol/min of oxygen (O_2) at 25° C are fed into a continuous reactor in which ammonia is completely consumed. The product gas emerges at 300° C. Calculate the rate at which heat must be transferred to or from the reactor to maintain the reactor temperature at 300° C. The standard heat of reaction for the gas phase oxidation of ammonia is

$$NH_3\,(g) + 1.25O_2\,(g) \rightarrow NO\,(g) + 1.5H_2O \quad \Delta H^{o}_{\text{Rx}} = -225 \text{ kJ/mol}$$

Solution

Known quantities: Inlet molar flow rates, inlet temperature, exit temperature.

Find: Rate of heat transferred from or to the reactor.

Analysis: Use the first law of thermodynamics for an open system.

Basis: 100 mol/min of NH3

Reference: 25° C and 1 atm

Using the first law of thermodynamics for an open system,

$$Q - W_s = \Delta \dot{H} + \Delta KE + \Delta PE$$

Since there is no shaft work in the process, no moving parts, no change in elevation between inlet and exit stream, and no change in velocity of inlet and exit streams, the general energy balance equation is reduced to

$$Q = \Delta \dot{H}$$

Using the extent of reaction or heat of reaction method,

$$Q = \Delta \dot{H} = \dot{\xi} \Delta H^{o}_{\text{Rx}} + \sum_{\text{out}} \dot{n}_i h_i - \sum_{\text{in}} \dot{n}_i h_i$$

Material balance (Extent of reaction method)

$$\dot{n}_{NH_3} = 100 - \xi$$

$$\dot{n}_{O_2} = 200 - 1.25\xi$$

$$\dot{n}_{NO} = 0.0 + \xi$$

$$\dot{n}_{H_2O} = 0.0 + 1.5\xi$$

Because of complete conversion of ammonia ($f = 1$), no ammonia exits in the reactor exit stream; $n \cdot NH_3 = 0$

$$0.0 = 100 - \xi \Rightarrow \xi = 100 \text{ mol}$$

Substituting the values of the extent of reaction in the material balance equation will give the following molar flow rate of exit stream components:

$\dot{n}_{NH_3} = 0.0$ mol/min, $\dot{n}_{O_2} = 75$ mol/min, $\dot{n}_{NO} = 100$ mol/min, $\dot{n}_{H_2O} =$ 150 mol/min

Energy balance (Heat of reaction method)

Reference temperature: 25° C

$$Q = \Delta\dot{H} = \xi\Delta H^o_{Rx} + \sum_{out} \dot{n}_i\bar{h}_i - \sum_{in} \dot{n}_i\bar{h}_i$$

Heat capacities of components involved in the process Cpi (J/mol.C) are

$$C_{PO_2} = 29.1 + 0.01158T - 0.6076 \times 10^{-5}T^2$$

$$C_{PNO} = 29.5 + 0.008188T - 0.2925 \times 10^{-5}T^2$$

$$C_{PH_2O} = 33.46 + 0.00688T + 0.7604 \times 10^{-5}T^2$$

Substitute known values:

$$Q = \Delta\dot{H} = 100(-225\ \text{kJ/mol}) + \frac{\text{kJ}}{1000\ \text{J}}$$

$$\times \left[75 \int_{25^\circ\text{C}}^{300^\circ\text{C}} C_{\text{p}\,\text{O}_2} dT + 100 \int_{25}^{300} C_{\text{p}\,\text{NO}} dT + 150 \int_{25}^{300} C_{\text{p}\,\text{H}_2\text{O}} dT \right]_{\text{out}}$$

$$- \frac{\text{kJ}}{1000\ \text{J}} \left[100 \int_{25}^{25} C_{\text{p}\,\text{NH}_3} dT + 200 \int_{25}^{25} C_{\text{p}\,\text{O}_2} dT \right]_{\text{in}}$$

The change in sensible heat is in the units of J/mol, so it should be divided by 1000 to convert to the units of kJ/mol to be added to heat of reaction. Accordingly, the heat transfer rate is

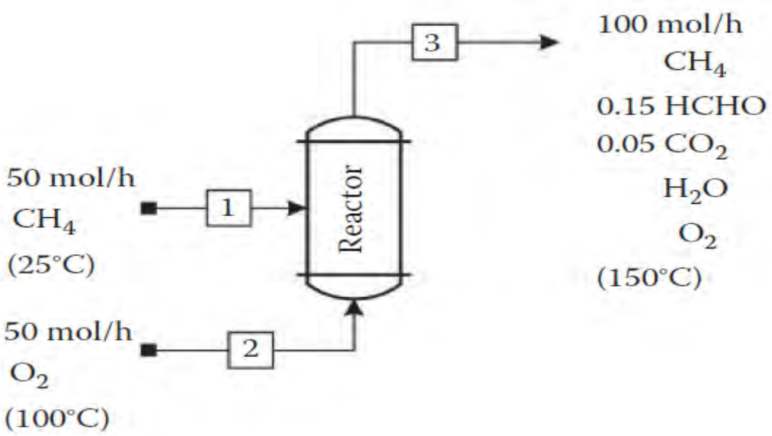
$$Q = \Delta\dot{H} = 100\ \text{mol} \left[\frac{-225\ \text{kJ}}{\text{mol}} \right] + [75(8.47) + 100(8.45) + 150(9.57)] - 0$$

$$= -19{,}600\ \text{kJ/min}$$

The heat released from the reaction process is −19,600 kJ/min (−326 kW).

Example 2.9 Production of Formaldehyde

Formaldehyde is produced in a continuous reactor by oxidizing methane with pure oxygen (Example Figure 2.9.1). Feed streams of 50 mol/h of methane and 50 mol/h of pure oxygen are fed to a continuous reactor. The exit stream molar flow rate is 100 mol/h. The mole fractions of formaldehyde and carbon dioxide are 0.15 and 0.05, respectively. Calculate the rate of heat that must be added to or removed from the reactor to maintain the reactor temperature at 150° C.



EXAMPLE FIGURE 2.9.1 Process flow sheet of the methane oxidation process.

Solution

Known quantities: Inlet and exit streams temperature and molar composition of formaldehyde and carbon dioxide.

Find: Heat transfer rate from or to the system.

Analysis: Use the extent of reaction method for both material and energy balance.

Basis: 100 mol/h of the exit gas stream

Material balance:

Since carbon dioxide appears in the exit gas stream, the following reactions take place in the reactor:

$$CH_4(g) + O_2 \rightarrow HCHO\,(g) + H_2O \quad \xi_1$$

$$CH_4(g) + 2O_2 \rightarrow CO_2 + 2H_2O \quad \xi_2$$

To calculate the extent of reaction of the first reaction, select a component that is available only in the first reaction, which is formaldehyde in this case:

$$n_{HCHO} = n^{o}_{CHHO} + \xi_1$$

$$0.15 \times 100\ \mathrm{mol/h} = 0 + \xi_1 \Rightarrow \xi_1 = 15\ \mathrm{mol/h}$$

The extent of the second reaction is obtained by selecting a component that is only available in the second reaction, which is in this case carbon dioxide:

$$n_{CO_2} = n^{o}_{CO_2} + \xi_2$$

Substitute inlet and exit molar flow rate of carbon dioxide:

$$0.05 \times 100\ \mathrm{mol/h} = 0 + \xi_2 \Rightarrow \xi_2 = 5\ \mathrm{mol/h}$$

Knowing the extent of the first and second reactions, the component molar flow rate can be found easily by performing the extent of reaction balance for each component:

$$n_{CH_4} = 50 - \xi_1 - \xi_2 = 50 - 15 - 5 = 30\ \mathrm{mol/h}$$

$$n_{H_2O} = 0 + \xi_1 + 2\xi_2 = 15 + 2 \times 5 = 25\ \mathrm{mol/h}$$

$$n_{O_2} = 50 - \xi_1 - 2\xi_2 = 50 - 15 - 2 \times 5 = 25\ \mathrm{mol/h}$$

Energy balance:

Reference state: 25° C

The standard heat of reaction for both reactions is calculated from standard heats of formation as follows:

The standard heat of the first reaction, Δ *H*R x°1, is given by

$$\Delta H^{o}_{Rx1} = \Delta H^{o}_{f,H_2O(v)} + \Delta H^{o}_{f,HCHO(g)} - \Delta H^{o}_{f,CH_4(g)}$$

$$\Delta H^{o}_{Rx1} = (-241.83) + (-115.9) - (-74.85) = -282.88 \text{ kJ/mol}$$

The standard heat of the second reaction, Δ *H*R x°$_2$, is given by

$$\Delta H^{o}_{Rx2} = 2\Delta H^{o}_{f,H_2O(v)} + \Delta H^{o}_{f,CO_2(g)} - \Delta H^{o}_{f,CH_4(g)}$$

Overall energy balance of the reactor, no work, no moving parts, no change in elevation, hence, work, kinetic and potential energy, are neglected:

$$Q = \Delta \dot{H}$$

The rate of change in enthalpy, *ΔH*•, is given by

$$\Delta \dot{H} = \sum_{\text{reactions}} \dot{\xi}_j \Delta H^{o}_{Rx,j} + \sum_{\text{out}} \dot{n}_i \bar{h}_i - \sum_{\text{in}} \dot{n}_i \bar{h}_i$$

Heat capacities of all components involved in the process, *C* p*i* (J/molϒC), are as follows:

$$C_{PCH_4} = 34.31 + 0.05469T + 0.3661 \times 10^{-5} T^2$$

$$C_{PHCHO} = 34.28 + 0.04268T$$

$$C_{PCO_2} = 36.11 + 0.04233T - 2.887 \times 10^{-5} T^2$$

$$C_{PH_2O} = 33.46 + 0.00688T + 0.7604 \times 10^{-5} T^2$$

$$C_{PO_2} = 29.1 + 0.01158T - 0.6076 \times 10^{-5} T^2$$

In more detail, the energy balance equation is as follows:

$$Q = \dot{\xi}_1 \Delta H^{o}_{Rx1} + \dot{\xi}_2 \Delta H^{o}_{Rx2} + \left\{ \dot{n}_{CH_4} \bar{h}_{CH_4} + \dot{n}_{HCHO} \bar{h}_{HCHO} + \dot{n}_{CO_2} \bar{h}_{CO_2} + \dot{n}_{H_2O} \bar{h}_{H_2O} + \dot{n}_{O_2} \bar{h}_{O_2} \right\}_{out} - \left\{ \dot{n}_{CH_4} \bar{h}_{CH_4} + \dot{n}_{O_2} \bar{h}_{O_2} \right\}_{in}$$

Substitute known quantities:

$$Q = \Delta\dot{H} = \dot{\xi}_1 \Delta H^{o}_{Rx1} + \dot{\xi}_2 \Delta H^{o}_{Rx2} + \left\{ 30 \int_{25^\circ C}^{150^\circ C} C_{p\,CH_4}\, dT \right.$$

$$+15 \int_{25}^{150} C_{p\,HCHO(g)}\, dT + 5 \int_{25}^{150} C_{p\,CO_2}\, dT + 25 \int_{25}^{150} C_{p\,H_2O}\, dT$$

$$\left. + 25 \int_{25}^{150} C_{p\,O_2}\, dT \right\} - \left\{ 50 \int_{25}^{25} C_{p\,CH_4}\, dT + 50 \int_{25}^{100} C_{p\,O_2}\, dT \right\}$$

Substituting the expressions of the heat capacities and integrating,

$$Q = \{15(-282.88) + 5(-802.31)\} + \{30(4.9) + 15(4.75) + 5(4.75)$$

$$+ 25(4.27) + 25(3.758)\} - \{50(0) + 50(2.235)\} = -7923 \text{ kJ/h}$$

The rate of heat transfer is –7923 kJ/h (–2.2 kW).

Example 2.10 Methane Combustion

Problem

Methane and oxygen are fed in stoichiometric proportions to a continuous reactor at 25 ° C and 1 atm. The reaction proceeds to completion and the effluent stream is found to be at 200° C. Calculate the heat transfer rate from the reactor. On the basis of 1 mol of methane set up an energy balance using the elements balance approach. The combustion reaction of methane is as follows:

Solution

Known quantities: Inlet temperature and pressure, stoichiometric proportions of feed.

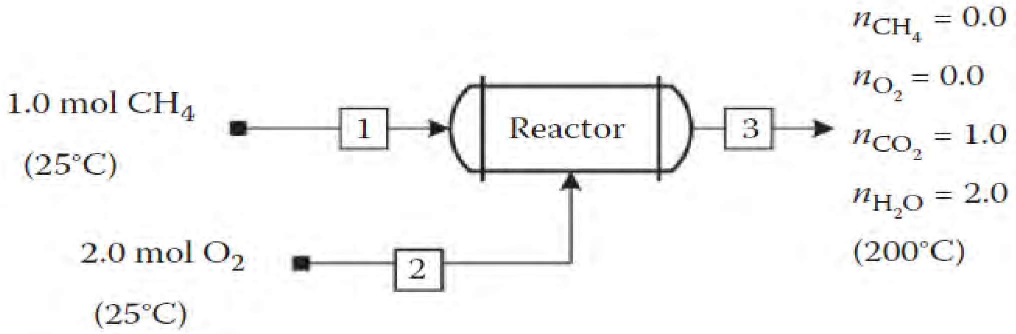
Find: Heat transfer rate from the reactor, Q.

Analysis: Start by calculating the enthalpy at the stream condition for each individual compound in each stream relatively to the elements at 25° C. We then plug these enthalpies into the normal energy balance expression.

Material balance:

Basis: 1 mol/s of methane and 2 mol/s of oxygen

Since the reaction goes to completion and the feed enters the reactor in stoichiometric proportions, the exit molar flow rate of methane and oxygen are zero. Based on the balance reaction stoichiometry for 1 mol of carbon dioxide reacted, 1 mol of carbon dioxide and 2 mol of water are produced.



EXAMPLE FIGURE 2.10.1: Schematic of a methane combustion reactor.

The schematic diagram of the combustion process is shown in Example Figure 2.10.1.

***Energy balance*:**

The specific molar flow rate and molar enthalpies of inlet and exit components are arranged in the following table:

Species	n_{in}	h_{in}	n_{out}	h_{out}
CH_4	1	$\bar{h}_{CH_4}(T_1)$	0	—
O_2	2	$\bar{h}_{O_2}(T_2)$	0	—
CO_2	0	—	1	$\bar{h}_{CO_2}(T_3)$
H_2O	0	—	2	$\bar{h}_{H_2O}(T_3)$

From the following data

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

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

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

$$C_{PCO_2}(\text{J/mol °C}) = 36.11 + 0.04233T - 2.887 \times 10^{-5}T^2$$

$$C_{PH_2O}(\text{J/mol °C}) = 33.46 + 0.00688T + 0.7604 \times 10^{-5}T^2$$

The general energy balance equation is

$$Q = \sum_{\text{out, } 200^\circ\text{C}} \dot{n}_i \overline{h}_i - \sum_{\text{in, } 25^\circ\text{C}} \dot{n}_i^\circ \overline{h}_i = \left[\dot{n}_{CO_2}\overline{h}_{CO_2} + \dot{n}_{H_2O}\overline{h}_{H_2O}\right]_{\text{out}}$$

$$-\left[\dot{n}_{CH_4}\overline{h}_{CH_4} + \dot{n}_{O_2}\overline{h}_{O_2}\right]_{\text{in}}$$

Specific molar enthalpy of inlet streams at $T1 = 25^\circ$ C is

$$CH_4\text{: } \overline{h}_{CH_4}(T_1) = \Delta H^\circ_{f,CH_4} + \int_{25^\circ\text{C}}^{25^\circ\text{C}} C_{p\,CH_4}\,dT = -74.85\text{ kJ/mol} + 0 = -74.85\text{ kJ/mol}$$

Specific molar enthalpy of inlet oxygen at $T2 = 25^\circ$ C is

$$O_2\text{: } \overline{h}_{O_2}(T_2) = 0 + \int_{25^\circ\text{C}}^{25^\circ\text{C}} C_{p\,O_2}\,dT = 0 + 0 = 0$$

Specific molar enthalpies of the exit streams at $T3 = 200^\circ$ C are

$$CO_2\text{: } \overline{h}_{CO_2}(T_3) = \Delta H^\circ_{f,CO_2} + \frac{1\text{ kJ}}{1000\text{ J}} \int_{25^\circ\text{C}}^{200^\circ\text{C}} C_{p\,CO_2}\,dT = -393.5 + 7.08$$

$$= -386.42\text{ kJ/mol}$$

$$H_2O\text{: } \overline{h}_{H_2O}(T_3) = \Delta H^\circ_{f,H_2O} + \frac{1\text{ kJ}}{1000\text{ J}} \int_{25^\circ\text{C}}^{200^\circ\text{C}} C_{p\,H_2O}\,dT = -241.83 + 6.01$$

$$= -235.82\text{ kJ/mol}$$

Using the values calculated by the procedures shown earlier, we simply plug the values of specific enthalpies into the general energy balance equation using the element balance approach:

$$Q = \sum_{\text{out}} \dot{n}_i \overline{h}_i - \sum_{\text{in}} \dot{n}_i \overline{h}_i$$

Substitute the calculated values of specific enthalpies:

$$Q = \left[\dot{n}_{CO_2}\overline{h}_{CO_2} + \dot{n}_{H_2O}\overline{h}_{H_2O}\right]_{\text{out}} - \left[\dot{n}_{CH_4}\overline{h}_{CH_4} + \dot{n}_{O_2}\overline{h}_{O_2}\right]_{\text{in}}$$

$$Q = \left[1(-386.42) + 2(-235.82)\right] - \left[1(0) + 1(-74.85)\right] = -783.21\text{ kJ/s}$$

2.4.1 Unknown Process Exit Temperature

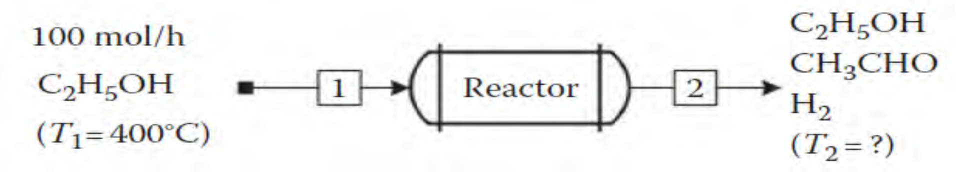
Another set of problems involves the calculation of outlet temperature when the inlet conditions and heat input or output are specified. These types of problems require that the enthalpies be evaluated in terms of the unknown outlet temperature. The resulting enthalpy expressions are then substituted into the general energy balance equation and solved for the outlet temperature. The following example explains this case.

Example 2.11 Dehydrogenation of Ethanol

Problem

Dehydrogenation of ethanol to form acetaldehyde is carried out in an adiabatic reactor. Hundred moles per hour of ethanol at 400° C is fed to a continuous reactor. The reactor conversion is 30%. The gas average heat capacities of C_2H_5OH, CH_3CHO, and H2 are 78, 96, and 29 (J/mol K), respectively. Calculate the reactor exit stream temperature. The following reaction takes place in gas phase:

$$C_2H_5OH \longrightarrow CH_3CHO + H_2$$



EXAMPLE FIGURE 2.11.1: Ethanol dehydration process, reactor system.

Solution

Known quantities: Inlet ethanol molar flow rate, temperature, and percent conversion.

Find: The product stream temperature.

Analysis: The exit temperature is unknown, so a simultaneous material and energy balance is required. The schematic diagram of the dehydrogenation process is shown in Example Figure 2.11.1.

Basis: One hour of operation, accordingly all calculated flow rates are on per one hour basis.

Material balance

Using the extent of reaction method,

$$n_{C_2H_5OH} = 100 - \xi$$

$$n_{CH_3CHO} = 0 + \xi$$

$$n_{H_2} = 0 + \xi$$

A 30% conversion of methanol is achieved:

$$0.3 = \frac{100 - n_{C_2H_5OH}}{100} \Rightarrow n_{C_2H_5OH} = 70 \text{ mol}$$

Substitute known values (nC_2H_5OH) in the ethanol mole balance equation:

$$70 = 100 - \xi \Rightarrow \xi = 30 \text{ mol}$$

Substitute the extent of reaction in the material balance equations to get the following results:

nC_2H5OH = 70 mol, nCH3CHO = 30 mol, nH2 = 30 mol

Energy balance:

Reference temperature: 25° C

Using the heat of reaction approach, the general energy balance equation is

$$\Delta\dot{H} = \xi\Delta H^{o}_{Rx} + \sum_{out} n_i\bar{h}_i - \sum_{in} n_i\bar{h}_i$$

The standard heat of reaction is calculated from the heats of formation as follows:

$$\Delta H^{o}_{Rx} = \Delta H^{o}_{f,H_2} + \Delta H^{o}_{f,CH_3CHO} - \Delta H^{o}_{f,C_2H_5OH}$$

Substituting tabulated standard heat of formation values (from the appendix) yields

$$\Delta H^{o}_{Rx} = 0 + (-166.2) - (-235.31) = 69.11 \text{ kJ/mol}$$

Open system, adiabatic process, no change in potential and kinetic energy, ccordingly the general energy balance is simplified to the following form:

$Q = \Delta H \cdot = 0.$

The change in enthalpy is a function of heat of reaction and sensible heat as follows:

$$0 = \xi\Delta H^{o}_{Rx} + \left\{n_{C_2H_5OH}\bar{h}_{C_2H_5OH} + n_{CH_3CHO}\bar{h}_{CH_3CHO} + n_{H_2}\bar{h}_{H_2}\right\}_{out,\,T_2=?}$$

$$-\left\{n_{C_2H_5OH}\bar{h}_{C_2H_5OH}\right\}_{in,\,400\,°C}$$

Substituting specific molar enthalpies in terms of heat capacities,

$$0 = \xi\ \Delta H^{\circ}_{\mathrm{Rx}} + \left\{ n_{\mathrm{C_2H_5OH}} \int_{25}^{T_2} C_{\mathrm{PC_2H_5OH}}\, \mathrm{d}T + n_{\mathrm{CH_3CHO}} \int_{25}^{T_2} C_{\mathrm{PCH_3CHO}}\, \mathrm{d}T + n_{\mathrm{H_2}} \int_{25}^{T_2} C_{\mathrm{pH_2}}\, \mathrm{d}T \right\}$$

$$- \left\{ n_{\mathrm{C_2H_5OH}} \int_{25^\circ\mathrm{C}}^{400^\circ\mathrm{C}} C_{\mathrm{PC_2H_5OH}}\, \mathrm{d}T \right\}$$

Substitute the values of the molar flow rates of inlet and exit components and heat capacities of each component:

$$0 = 30 \times 69.11\ \mathrm{kJ/mol} + \{70 \times 78(T_2 - 25) + 30 \times 96(T_2 - 25)$$

$$+ 30 \times 29(T_2 - 25)\} - \{100 \times 78(400 - 25)\}$$

Rearranging by taking ($T2 - 25$) as common factor,

$$0 = 30 \times 69.11 \frac{\mathrm{kJ}}{\mathrm{mol}} \frac{1000\ \mathrm{J}}{\mathrm{kJ}} + (T_2 - 25)\{70 \times 78 + 30 \times 96 + 30 \times 29\}$$

$$- \{100 \times 78(400 - 25)\}$$

Simplifying and rearranging leads to the following value of reactor exit temperature:

$$T_2 = \frac{851{,}700}{9210} + 25 = 117.5^\circ\mathrm{C}$$

Example 9.12 Methanol Dehydrogenation

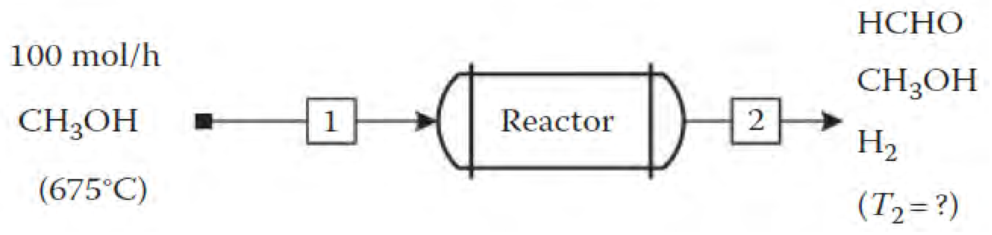
Problem

Hundred moles per hour of methanol at 675° C and 1 bar is fed to an adiabatic reactor, where 25% of it is dehydrogenated to formaldehyde. Calculate the temperature of the gases leaving the reactor, assuming constant average heat capacities of 17, 12, and 7 cal/mol ° C for methanol, formaldehyde, and hydrogen, respectively. The dehydrogenation of methanol proceeds according to the following reaction:

$$\mathrm{CH_3OH\,(g)} \rightarrow \mathrm{HCHO\,(g)} + \mathrm{H_2\,(g)}$$

The heats of formation in kcal/mol are as follows:

$$\Delta H^{\circ}_{\mathrm{f,\,HCHO}} = -27.7\ \mathrm{kcal/mol}, \quad \Delta H^{\circ}_{\mathrm{f\,,CH_3OH}} = -48.08\ \mathrm{kcal/mol}$$



EXAMPLE FIGURE 2.12.1: Formaldehyde production in an adiabatic reactor.

Solution

Known quantities: Inlet temperature, pressure, and molar flow rate are known.

Find: Exit stream temperature.

Analysis: The process flow sheet is shown in Example Figure 2.12.1. In the solution of this example, use the extent of reaction method.

Material balance

Basis: 100 mol/h of methanol

The extent of reaction method is used to calculate exit number of moles:

$$\text{HCHO: } \dot{n}_{\text{HCHO}} = 0 + \xi$$

$$\text{CH}_3\text{OH: } \dot{n}_{\text{CH}_3\text{OH}} = 100 - \xi$$

$$\text{H}_2\text{: } \dot{n}_{\text{H}_2} = 0 + \xi$$

The single-pass conversion of methanol

$$f = 0.25 = \frac{100 - \dot{n}_{\text{CH}_3\text{OH}}}{100}, \quad \dot{n}_{\text{CH}_3\text{OH}} = 75\ \text{mol/h}$$

Substitute $n \cdot \text{CH3OH} = 75\text{mol/h}$ in the methanol balance equation and calculate the extent of reaction: $\xi = 25$ mol/h. Substitute the extent of reaction in the formaldehyde and hydrogen mole balance equation to get the following results:

$$\dot{n}_{\text{HCHO}} = 25\ \text{mol/h}, \quad \dot{n}_{\text{CH}_3\text{OH}} = 75\ \text{mol/h}, \quad \dot{n}_{\text{H}_2} = 25\ \text{mol/h}$$

Energy balance

The system is open so the first law of thermodynamics for open systems is used as follows:

$$Q - W_s = \Delta\dot{H} + \Delta KE + \Delta PE$$

Neglecting kinetic and potential energies, no shaft work is done, and the reactor is adiabatic. The energy balance equation is simplified to the following form:

$$0 - 0 = \Delta\dot{H} + 0 + 0$$

The enthalpy consists of enthalpy of reaction and the sensible heat:

$$0 = \Delta H = \xi\Delta H_{\text{Rx}}(T_{\text{ref}}) + \sum_{\text{product}} n_i \int_{T_{\text{ref}}}^{T_{\text{out}}} C_{pi}\,\mathrm{d}T - \sum_{\text{reactant}} n_i \int_{T_{\text{ref}}}^{T_{\text{in}}} C_{pi}\,\mathrm{d}T$$

Reference temperature = 675°C

$$\Delta\dot{H} = \xi\,\Delta H_{\text{Rx}}\big|_{675^\circ\text{C}} + \sum_{\text{product}} n_i \int_{675^\circ\text{C}}^{T} C_{pi}\,\mathrm{d}T - \sum_{\text{reactant}} n_i \int_{675^\circ\text{C}}^{675^\circ\text{C}} C_{pi}\,\mathrm{d}T$$

The heat capacity of this problem is constant and the effect of temperature on the heat capacity is negligible:

$$\Delta H_{\text{Rx}}\big|_{675^\circ\text{C}} = \Delta H^{\circ}_{\text{Rx}} + \Delta C_{\text{p}}(675 - 25)$$

The standard heat of reaction at 25°C is

$$\Delta H^{\circ}_{\text{Rx}} = \Delta H^{\circ}_{\text{f, HCHO}} + \Delta H^{\circ}_{\text{f, H}_2} - \Delta H^{\circ}_{\text{f, CH}_3\text{OH}} = -27.7 + 0 - (-48.08)$$
$$= 20.38\ \text{kcal/mol}$$

The change in the heat capacity, ΔC_{p}, is given by

$$\Delta C_{\text{p}} = C_{\text{p H}_2} + C_{\text{p HCHO}} - C_{\text{p CH}_3\text{OH}}$$

Substituting known values to calculate the heat of reaction at 675°C,

$$\Delta H_{\text{Rx}}\big|_{675^\circ\text{C}} = 20.38\ \text{kcal/mol} + (7 + 12 - 17)\left[\frac{1\ \text{kcal}}{1000\ \text{cal}}\right](675 - 25)$$
$$= 21.68\ \text{kcal/mol}$$

The rate of change in enthalpy is

$$\Delta\dot{H} = \xi\,\Delta H_{\text{Rx}}\big|_{675^\circ\text{C}} + \left(n_{\text{HCHO}}C_{\text{PHCHO}} + n_{\text{CH}_3\text{OH}}C_{\text{PCH}_3\text{OH}} + n_{\text{H}_2}C_{\text{PH}_2}\right)(T_2 - 675) - 0$$

Substitute the extent of reaction, heat of reaction, and heat capacities to calculate the exit temperature:

$$0 = 25 \times 21.68\ \text{kcal/mol} + (25 \times 12 + 75 \times 17 + 25 \times 7)\left(\frac{1\ \text{kcal}}{1000\ \text{cal}}\right)(T_2 - 675)$$

Rearranging and simplifying,

$$0 = 542 + 1.75(T_2 - 675)$$

Solving for T,

$$T = 365.3^\circ\text{C}$$

2.5 Combustion Processes

Combustion or burning is an exothermic chemical reaction between a fuel and an oxidant accompanied by the production of heat and conversion of chemical species [4]. For example, the complete combustion of methane is given by the following reaction:

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

The result is carbon dioxide and water vapor, with a standard enthalpy of reaction at 25° C and 1 atm being −242 kJ/mol; complete combustion is almost impossible to achieve. As actual combustion reactions come to equilibrium, a wide variety of major and minor species will be present, such as carbon monoxide. Total inlet oxygen is the sum of the theoretical oxygen and excess oxygen. The equation for percent excess air is as follows:

$$\%\ \text{excess air} = \frac{(\text{moles of air})_{\text{fed}} - (\text{moles of air})_{\text{theoretical}}}{(\text{moles of air})_{\text{theoretical}}}$$

Theoretical oxygen is the calculated amount of oxygen required to oxidize a compound to its final oxidation products. In the methane oxidation reaction, 2 mol of oxygen is required to oxidize 1 mol of methane. For 100 mol of CH_4 the theoretical oxygen is calculated as follows:

$$\text{Theoretical oxygen demand} = 100\ \text{mol}\ CH_4 \times \frac{2\ \text{mol}\ O_2}{1\ \text{mol}\ CH_4} = 200\ \text{mol of}\ O_2$$

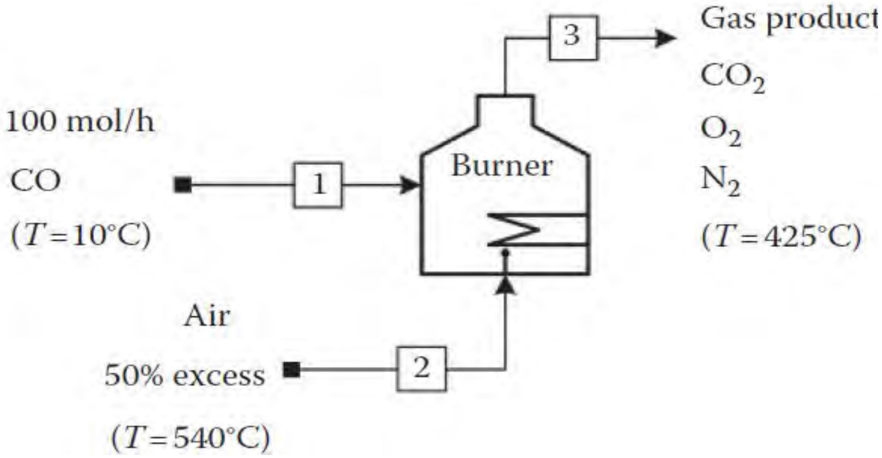
If the oxygen fed to the reactor is in excess amount than the theoretical oxygen, then the percent excess oxygen is

$$\%\ \text{excess}\ O_2 = \frac{(\text{moles of}\ O_2)_{\text{fed}} - (\text{moles of}\ O_2)_{\text{theoretical}}}{(\text{moles of}\ O_2)_{\text{theoretical}}}$$

Example 2.13 Combustion of Carbon Monoxide

Problem

Carbon monoxide (CO) at 10° C is completely burned at 1 atm pressure with 50% excess air that is fed to a burner at a temperature of 540° C. The combustion products leave the burner chamber at a temperature of 425° C. Given 100 mol/h of carbon monoxide, calculate the heat evolved from the burner.



EXAMPLE FIGURE 2.13.1: Schematic of the combustion of carbon monoxide.

Solution

Known quantities: CO and air inlet temperature and pressure, complete combustion, 50% excess air.

Find: Heat evolved from the burner.

Analysis: Perform material balance and then energy balance.

Material balance

Basis: 100 mol/h of inlet CO

The following reaction takes place in the burner:

$$CO\,(g) + \frac{1}{2}O_2\,(g) \rightarrow CO_2\,(g)$$

The schematic diagram of the burning process is shown in Example Figure 2.13.1.

$$\text{Theoretical } O_2\text{: } 100\text{ mol/h CO}\left(\frac{0.5\text{ mol } O_2}{1\text{ mol CO}}\right) = 50\text{ mol/h } O_2$$

Total inlet oxygen is the sum of the theoretical oxygen and excess oxygen. For 50% excess air, the total inlet oxygen is the theoretical plus excess oxygen:

$$\dot{n}^{o}_{O_2} = 1.0\left(50\text{ mol } O_2\right) + 0.5\left(500\text{ mol } O_2\right) = 75\text{ mol/h } O_2$$

Nitrogen is inert and the total inlet nitrogen is the number of moles of nitrogen in the air associated with the 75 mol of oxygen. That is,

$$\dot{n}^{o}_{N_2} = \frac{79}{21} \times \text{Total inlet oxygen} = \frac{79}{21} \times 75\text{ mol} = 282\text{ mol/h } N_2$$

Since the reaction goes to completion (i.e., complete composition), no carbon monoxide leaves the reactor, all is burned. Mole balance of carbon monoxide (CO) is calculated using the extent of reaction method:

$$n_{CO} = n_{CO}^{o} - \xi$$

$$0 = 100 - \xi \Rightarrow \xi = 100 \text{ mol}$$

Component mole balance

$$CO_2\text{:}\ n_{CO_2} = 0 + \xi$$

$$O_2\text{ :}\ n_{O_2} = n_{O_2}^{o} - 0.5\xi$$

$$\dot{n}_{O_2} = 75 - 0.5 \times 100 = 25 \text{ mol/h}$$

The exit number of moles of carbon dioxide is 100 mol; *n*CO2 = 100 mol. Nitrogen is an inert gas and is not involved in the reaction. Accordingly, the inlet number of moles equals the exit number of moles:

$$\dot{n}_{N_2} = 282 \text{ mol/h}$$

Energy balance

Reference temperature, $T\text{ref} = 25^{\circ}$ C

The standard heat of reaction is calculated as

$$\Delta H_{Rx}^{o} = \Delta H_{f,CO_2}^{o} - \Delta H_{f,CO}^{o} - \frac{1}{2}\Delta H_{f,O_2}^{o}$$

$$\Delta H_{Rx}^{o} = -393.5 \text{ kJ/mol} - (-110.52 \text{ kJ/mol}) - 0 = -282.98 \text{ kJ/mol}$$

Heat capacities $C\,\mathrm{p}i$ (J/mol.C) as a function of temperature of components involved in the process are

$$C_{PO_2} = 29.1 + 0.01158T - 0.6076 \times 10^{-5} T^2$$

$$C_{PN_2} = 29 + 0.002199T + 0.5723 \times 10^{-5} T^2$$

$$C_{PCO} = 28.95 + 0.00411T + 0.3548 \times 10^{-5} T^2$$

$$C_{PCO_2} = 36.11 + 0.04233T - 2.887 \times 10^{-5} T^2$$

Enthalpies of inlet components:

The enthalpies of inlet components are defined from the following expressions. The integration is from the reference temperature to the inlet temperature.

Specific molar enthalpy of oxygen is obtained as follows

$$\bar{h}_{\text{in}}(\text{O}_2) = \frac{1\ \text{kJ}}{1000\ \text{J}} \int_{25^\circ\text{C}}^{540^\circ\text{C}} C_{p\,\text{O}_2}\ dT = 16.38\ \text{kJ/mol}$$

Specific inlet enthalpy of nitrogen is calculated as follows:

$$\bar{h}_{\text{in}}(\text{N}_2) = \frac{1\ \text{kJ}}{1000\ \text{J}} \int_{25^\circ\text{C}}^{540^\circ\text{C}} C_{p\,\text{N}_2}\ dT = 15.49\ \text{kJ/mol}$$

Specific inlet enthalpy of carbon monoxide is obtained as follows:

$$\bar{h}_{\text{in}}(\text{CO}) = \frac{1\ \text{kJ}}{1000\ \text{J}} \int_{25^\circ\text{C}}^{10^\circ\text{C}} C_{p\,\text{CO}}\ dT = -0.4353\ \text{kJ/mol}$$

Enthalpies of exit components:

The enthalpies of exit components are defined from the following expressions. The integration is from the reference temperature to the exit temperature:

$$\text{Oxygen:}\ \bar{h}_{\text{out}}(\text{O}_2) = \frac{1\ \text{kJ}}{1000\ \text{J}} \int_{25^\circ\text{C}}^{425^\circ\text{C}} C_{p\,\text{O}_2} dT = 12.54\ \text{kJ/mol}$$

$$\text{Nitrogen:}\ \bar{h}_{\text{out}}(\text{N}_2) = \frac{1\ \text{kJ}}{1000\ \text{J}} \int_{25^\circ\text{C}}^{425^\circ\text{C}} C_{p\,\text{N}_2} dT = 11.92\ \text{kJ/mol}$$

$$\text{Carbon dioxide:}\ \bar{h}_{\text{out}}(\text{CO}_2) = \frac{1\ \text{kJ}}{1000\ \text{J}} \int_{25^\circ\text{C}}^{425^\circ\text{C}} C_{p\,\text{CO}_2} dT = 17.58\ \text{kJ/mol}$$

Summary of the calculated enthalpies is shown in the following table:

Compound i	$\dot{n}_{i,\text{in}}$ **(mol/h)**	$\bar{h}_{i,\text{in}}$ **(kJ/mol)**	$\dot{n}_{i,\text{out}}$ **(mol/h)**	$\bar{h}_{i,\text{out}}$ **(kJ/mol)**
O_2	75	16.38	25	12.54
N_2	282	15.49	282	11.92
CO	100	−0.44	0	—
CO_2	0	—	100	17.58

The heat removed from the burner, Q, is given by

$$Q = \Delta H = \xi \Delta H_r^\circ + \sum_{\text{out}} n_i \bar{h}_i - \sum_{\text{in}} n_i \bar{h}_i$$

Substituting inlet and exit moles multiplied by specific enthalpies of inlet and exit streams, respectively, from the table in the earlier equation yields the heat released from the burner, Q:

$$Q = \xi \times \Delta H^{o}_{Rx} + \left\{\dot{n}_{O_2}\bar{h}_{O_2} + \dot{n}_{N_2}\bar{h}_{N_2} + \dot{n}_{CO_2}\bar{h}_{CO_2}\right\}_{out} - \left\{\dot{n}_{O_2}\bar{h}_{O_2} + \dot{n}_{N_2}\bar{h}_{N_2} + \dot{n}_{CO}\bar{h}_{CO}\right\}_{in}$$

Substitute component specific enthalpies:

$$Q = 100 \times (-282.98\ \text{kJ/mol}) + \{25(12.54) + 282(11.92) + 100(17.58)\}$$
$$-\{75(16.38) + 282(15.49) + 100(-0.44)\}$$

The heat lost from the reactor is

$$Q = -284{,}177\ \text{kJ/h}\left(-78.94\ \text{kW}\right)$$

The negative sign indicates that heat is released from the process.

2.6 Energy Balance in Bioprocesses

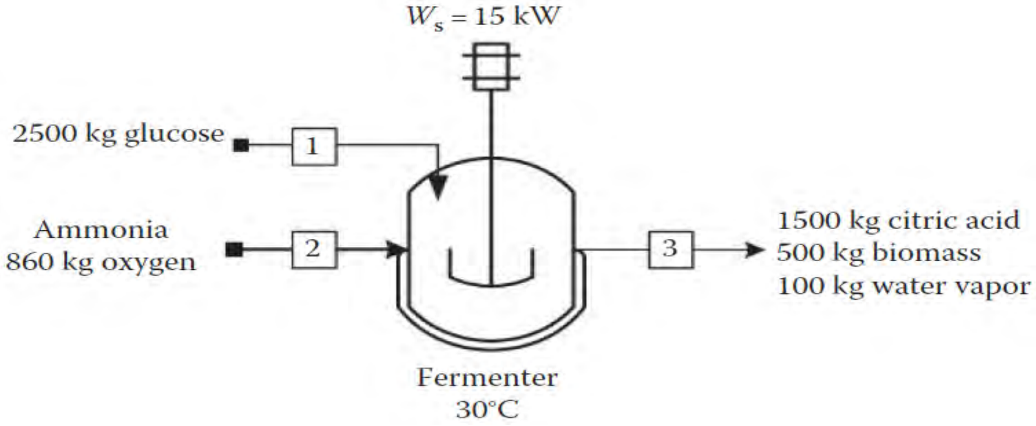
Energy contributions of bioprocesses contributions to sensible heat are insignificant compared with the total magnitude of $\Delta H\text{R}^{o}\text{x}$ and can, therefore, be ignored without much loss of accuracy. This situation is typical of most reactions in bioprocessing where the actual temperature of reaction is not significantly different from 25° C [5-7].

Example 2.14 Fermentation and Citric Acid Production

Problem

An amount of 2500 kg of glucose and 860 kg of oxygen are consumed to produce 1500 kg citric acid, 500 kg biomass, and other products. Ammonia is used as a nitrogen source. Power input to the system by mechanical agitation of the broth is about 15 kW; approximately 100 kg water is evaporated during the culture period. Estimate the cooling requirements during 2 days of operation. The latent heat of evaporation of water at 30° C is 2430.7 kJ/kg. The heat of reaction at 30° C is −460 kJ/mol O2 consumed. The batch reactor operates at 30° C. The reaction taking place in the fermenter is given by

$$\text{Glucose} + \text{O2} + NH_3 \longrightarrow \text{Biomass} + CO_2 + H_2O + \text{citric acid}$$



EXAMPLE FIGURE 2.14.1: Production of a citric acid fermenter.

Solution

Known quantities: Inlet flow and exit mass flow rate, shaft work, fermenter initial temperature.

Find: Heat transfer from the reactor.

Analysis: The reaction that takes place in the current fermentation process (Example Figure 2.14.1) follows the reaction shown above

The general energy balance equation is

$$Q - W_s = \xi \Delta H_{\text{reaction}} + m_v \Delta H_v$$

Heat released due to the reaction is

$$\xi \Delta H_{\text{reaction}} = 860\ \text{kgO}_2\ \text{consumed} \left| \frac{1000\ \text{g}}{1\ \text{kg}} \right| \frac{1\ \text{mol}}{32\ \text{g}} \left(\frac{-460\ \text{kJ}}{\text{mol}} \right) = -1.24 \times 10^7\ \text{kJ}$$

Heat needed for evaporation is

$$m_v \Delta H_v = (100\ \text{kg})(2430.7\ \text{kJ/kg}) = 2.43 \times 10^5\ \text{kJ}$$

The system shaft work is expressed as

$$W_s = \left(-15\ \frac{\text{kJ}}{\text{s}} \right) (2\ \text{days}) \frac{3600\ \text{s}}{1\ \text{h}} \left| \frac{24\ \text{h}}{1\ \text{day}} \right. = -2.59 \times 10^6\ \text{kJ}$$

The general energy balance equation is

$$Q - W_s = \xi \Delta H_{\text{rxn}} + m_v \Delta H_v$$

Substitute known quantities to yield

$$Q - (-2.59 \times 10^6 \text{ kJ}) = -1.24 \times 10^7 \text{ kJ} + 2.43 \times 10^5 \text{ kJ}$$

$$Q = -1.475 \times 10^7 \text{ kJ}$$

The negative sign indicates that heat is removed from the system.

2.7 Energy Balance in Membrane Reactors

A membrane reactor is actually just a plug-flow reactor that contains an additional cylinder of some porous material within it. Its configuration is similar to that of a shell-and-tube heat exchanger, with a tube within the shell of the exchanger. This porous inner cylinder is the membrane that gives the membrane reactor its name.

Example 2.15 Membrane Reactor

Problem

A membrane reactor is used to produce formaldehyde by dehydrogenation of methanol. The conversion of methanol to formaldehyde takes place on the tube side of the membrane, which is an endothermic reaction:

$$CH_3OH \rightarrow HCHO + H_2 \quad \Delta H^{o}_{Rx} = 85.3 \text{ kJ/mol}$$

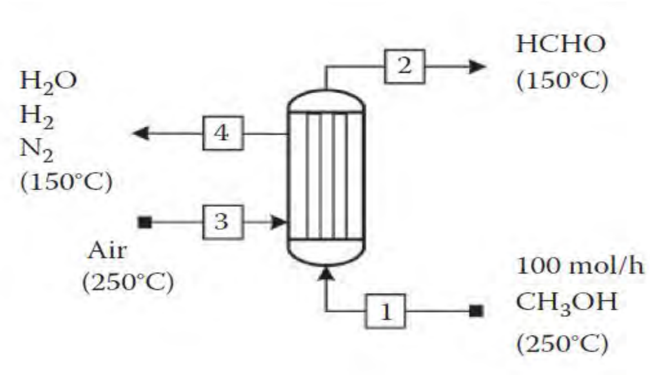
The following side reaction takes place as well on the shell side of the membrane. The reaction is exothermic and its heat is utilized to preserve the temperature of the gas stream at 150° C:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H^{o}_{Rx} = -241.83 \text{ kJ/mol}$$

Methanol vapor stream at a flow rate of 100 mol/min and 250° C enters the tube side of the membrane. Assume that the entire methanol reacts to form formaldehyde and the whole produced hydrogen penetrates through the membrane tube walls to the shell side where sufficient amount of it is burned on the shell side. Sufficient amount of oxygen from air is supplied and reacts completely with the hydrogen. How much hydrogen must be burned to keep the reactor effluent temperature at 150° C? What is the molar flow rate of the stream leaving the reactor?

Data:

The average molar heat capacities of the various materials in this temperature range are: CH_3OH = 0.0568 kJ/(mol ° C), HCHO = 0.0380 kJ/(mol ° C), H_2 = 0.0289 kJ/(mol ° C), O_2 = 0.0309 kJ/(mol ° C), N_2 = 0.0296 kJ/(mol ° C), and H_2O = 0.0341 kJ/(mol ° C).



of 150° C. The schematic diagram of the membrane reactor is shown in Example Figure 9.15.1. The hydrogen reaction takes place on the shell side with sufficient amount of oxygen associated with inlet air. All inlet oxygen is consumed.

Solution

Known quantities: Inlet flow of methanol, complete conversion of methanol, and inlet oxygen.

Find: Amount of hydrogen burned to keep the membrane effluent streams at 150° C.

Analysis: First we need to determine how much heat is required for the methanol to formaldehyde reaction to be kept at the temperature of 150° C. The schematic diagram of the membrane reactor is shown in Example Figure 2.15.1. The hydrogen reaction takes place on the shell side with sufficient amount of oxygen associated with inlet air. All inlet oxygen is consumed.

***Material balance* (tube side):**

The exit stream from the tube side contains formaldehyde, and hydrogen penetrates membrane walls to the shell side; since complete reaction is achieved, 100 mol/min of formaldehyde leave the tube side, and 100 mol/min of hydrogen penetrate the membrane walls to the shell side. of 150° C. The schematic diagram of the membrane reactor is shown in Example Figure 2.15.1. The hydrogen reaction takes place on the shell side with sufficient amount of oxygen associated with inlet air. All inlet oxygen is consumed.

Material balance (tube side):

The exit stream from the tube side contains formaldehyde, and hydrogen penetrates membrane walls to the shell side; since complete reaction is achieved, 100 mol/min of formaldehyde leave the tube side, and 100 mol/min of hydrogen penetrate the membrane walls to the shell side.

Energy balance (tube side):

Tube side energy balance

$$Q_{tub} = \xi_1 \Delta H^{o}_{Rx,1} + \sum_{out} n_i \bar{h}_i - \sum_{in} n_i \bar{h}_i$$

The inlet stream to the tube side contains only methanol, where it reacts completely:

$$\sum_{in} n_i \bar{h}_i = n^{o}_{CH3OH} C_{pCH3OH} \left(T_1 - T_{ref}\right)$$

$$\sum_{in} n_i \bar{h}_i = 100 \frac{\text{mol}}{\text{min}} 0.0568 \frac{\text{kJ}}{\text{mol}\,^{\circ}\text{C}} (250 - 25)^{\circ}\text{C} = 12.78\ \text{kJ/min}$$

The heat of reaction term for methanol dehydrogenation can be computed from heats of formation of the two compounds. Thus,

$$\Delta H^{o}_{Rx} = -115.90 - (-201.2) = 85.3\ \text{kJ/mol}$$

$$\sum_{out} n_i \bar{h}_i = \left(\dot{n}_{HCHO} C_{p,HCHO} + \dot{n}_{H_2} C_{p,H_2}\right)\left(T_2 - T_{ref}\right)$$

Moles of formaldehyde and hydrogen produced are equal (100 mol/min):

$$\sum_{out} n_i \bar{h}_i = 100 \frac{\text{mol}}{\text{min}} (0.038 + 0.0289) \frac{\text{kJ}}{\text{mol}\,^{\circ}\text{C}} (150^{\circ}\text{C} - 25^{\circ}\text{C}) = 836.25\ \text{kJ/min}$$

Thus, the heat required to maintain the desired reactor temperature is

$$Q_{tub} = \dot{\xi} \Delta H^{o}_{Rx} + \sum_{out} \dot{n}_i \bar{h}_i - \sum_{in} \dot{n}_i \bar{h}_i = (100 \times 85.3) \frac{\text{kJ}}{\text{min}}$$
$$+ 836.25\ \text{kJ/min} - 12.78\ \text{kJ/min} = 8088.25\ \text{kJ/min}$$

That is, 8088 kJ/min of heat must be supplied by the hydrogen combustion reaction taking place on the shell side in order for the temperature at the completion of the reaction to be 150° C. Since the hydrogen combustion is also occurring at 150° C we need its heat of reaction at 150° C. This would correspond to the following enthalpy calculation pathway.

Material balance (shell side)

The following reaction takes place:

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \quad \xi_2$$

The specific molar flow rates of components leaving the shell side are

Unreacted hydrogen: $n_{H_2} = 100 - \xi_2$
Water vapor generated: $n_{H_2O} = \xi_2$
Nitrogen (inert): $n_{N_2} = n_{N_2}^o = \frac{0.79}{0.21} 0.5\xi_2$
Oxygen (complete conversion): $n_{O_2} = 0$

Energy balance (shell side)

On the shell side, hydrogen is burned with sufficient amount of oxygen from the air fed to the shell side. The exit stream of the shell side is water vapor, unreacted hydrogen, and nitrogen; accordingly, the following overall energy balance for the shell side can be written:

$$Q_{\text{shell}} = \xi_2 \Delta H_{\text{Rx},2}^o + \sum_{\text{out}} n_i \bar{h}_i - \sum_{\text{in}} n_i \bar{h}_i$$

Inlet stream to the shell

$$\sum_{\text{in}} n_i \bar{h}_i = \left\{ n_{H_2}^o C_{P,H_2} + n_{O_2}^o C_{P,O_2} + n_{N_2}^o C_{P,N_2} \right\} (T_3 - T_{\text{ref}})$$

$$n_{H_2}^o = 100 \text{ mol/min}$$

$$n_{N_2}^o = \frac{0.79}{0.21} n_{O_2}^o$$

$$\sum_{\text{in}} n_i \bar{h}_i = \left\{ 100(0.0289) + 0.5 n_{H_2}^o (0.0309) + \frac{0.79}{0.21} 0.5 n_{H_2}^o (0.0296) \right\} \times (250°\text{C} - 25°\text{C})$$

Simplifying yields

$$\sum_{\text{in}} n_i \bar{h}_i = 650.25 + 15.98 n_{H_2}^o$$

The shell side outlet stream enthalpy:

$$\sum_{\text{out}} n_i \bar{h}_i = \left\{ n_{H_2} C_{P,H_2} + n_{H_2O} C_{P,H_2O} + n_{N_2} C_{P,N_2} \right\} (T_4 - T_{\text{ref}})$$

Substituting heat capacity values and molar flow rates of the shell side exit stream gives

$$\sum_{\text{out}} n_i \bar{h}_i = \left\{(100-\xi_2)(0.0289)+\xi_2(0.0341)+\frac{0.79}{0.21}0.5\xi_2(0.0296)\right\}(150-25)°\text{C}$$

Thus we would get

$$\sum_{\text{out}} n_i \bar{h}_i = \{2.89-0.06\xi_2\}(150-25)°\text{C}$$

Simplifying further,

$$\sum_{\text{out}} n_i \bar{h}_i = 361.25-7.5\xi_2$$

The heat of reaction term is just the heat of formation of water as a vapor; this is - 241.83 kJ/mol. So for the hydrogen combustion reaction we get

$$Q_{\text{shell}} = \xi_2 \Delta H^{\circ}_{\text{Rx},2} + \sum_{\text{out}} n_i \bar{h}_i - \sum_{\text{in}} n_i \bar{h}_i$$

$$Q_{\text{shell}} = \xi_2(-241.83)+361.25-7.5\xi_2-650.25+15.98\xi_2$$

Simplifying,

$$Q_{\text{shell}} = -233.35\xi_2-289$$

Since heat lost from the shell side is gained by components on the tube side to maintain 150°C in the reactor,

$$Q_{\text{shell}} = -Q_{\text{tube}}$$

Substituting heat lost from the shell side and heat gained by the tube side yields

$$-233.35\xi_2-289 = -8088.25\ \text{kJ/min}$$

Solving for ξ_2,

$$\xi_2 = 33.42\ \text{mol/min}$$

Thus the combustion rate of hydrogen must be 33.4 mol/min.

2.8 Summary

The main difference between using a component balance and an element balance is that we must calculate the heat of reaction when using a component balance, but we simply use the heats of formation when writing down a balance based on the elements as the reference.

General procedure for energy balance with reaction

1. Draw the process flow diagram.
2. Complete the material balance calculations for the reactor (using either extent of reaction or atomic species balances).
3. Prepare the inlet and outlet enthalpy table, inserting known molar amounts (or flow rates) for each stream component (and phase).
4. Choose your reference state for specific enthalpy calculations.
5. Calculate each unknown stream component enthalpy, hi.
6. Calculate $\Delta H \cdot$ for the reactor.
7. Using the general energy balance equation, solve for the unknown quantity.

Steps 4-6 depend on the energy balance method used (i.e., heat of reaction or heat of formation).

Homework Problems

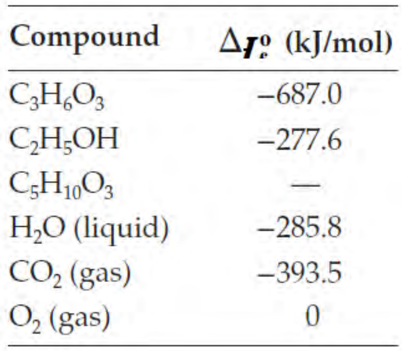
2-1 Determine the heat of reaction for the liquid phase of lactic acid ($C_3H_6O_3$) with ethanol (C_2H_5OH) to form ethyl lactate ($C_5H_{10}O_3$) and liquid water at 25° C. The heat of combustion of ethyl acetate is −2685 (kJ/mol). (−32.7 kJ/mol) The liquid-phase reaction of lactic acid with ethanol is

$C_3H_6O_3 + C_2H_5OH\_C_5H_{10}O_3 + H_2O$

The combustion reaction of ethyl lactate is

$C_5H_{10}O_3 + 6O_2 \_5CO_2 + 5H_2O$ (l)

The following table shows the standard heats of formation data:



Compound	Δ_f^o (kJ/mol)
$C_3H_6O_3$	−687.0
C_2H_5OH	−277.6
$C_5H_{10}O_3$	—
H_2O (liquid)	−285.8
CO_2 (gas)	−393.5
O_2 (gas)	0

2-2 Superheated steam at 40 bar and 350° C is produced from liquid water at 40 bar and 50° C in a methane-fired boiler. To ensure complete combustion of the methane, 10% excess air is provided. Both methane and combustion air enter the boiler at 25° C. Determine the outlet temperature of the flue gas from the boiler, if 19.85 kg/min of superheated steam is produced from the combustion of 1.4 kg/min of methane. Assume the boiler is perfectly insulated. (458° C)

2-3 Ammonia is synthesized through the reaction of nitrogen with hydrogen. The reactor feed temperature is 400° C. The fresh feed consists of 1 mol% argon and stoichiometric amount of nitrogen and hydrogen. The fractional conversion of N2 to NH_3 in the reactor is 0.15. The converter is operated adiabatically and the heat of reaction at 400° C is −53 kJ/mol. Given 100 mol of feed stream, estimate the temperature of the effluent gases from the converter. The average heat capacities at the pressure of the reactor for ammonia, hydrogen, nitrogen, and argon are 49.4, 29.5, 31.0, and 20.8 (J/mol ° C), respectively. (467.8° C)

2-4 Toluene reacts to form benzene and *o*-xylene according to the following reaction:

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

Toluene may also react with hydrogen in the reactor to form benzene and methane:

$$C_7H_8 + H_2 \longrightarrow C_6H_6 + CH_4$$

In this process, toluene reacts with a fractional conversion of 0.80, resulting in benzene and xylene yields of 0.505 and 0.495, respectively.

Here yields are defined as moles of component produced/moles of toluene reacted. If the fresh toluene stream, fresh hydrogen stream, and product stream are all at 400° C and 15 bar absolute, determine the heat requirements for the reactor to maintain reaction temperature at 400° C and a pressure of 15 bar absolute in the vapor phase. The fresh feed stream contains 225 mol/h of toluene. Average heat capacities:
benzene = 82.44 J/(mol K), toluene = 103.7 J/(mol K), *o*-xylene = 353.6 J/ (mol K), methane = 35.69 J/(mol K), and hydrogen = 28.82 J/(mol K).
(7725.4 kJ/h)

2.5 Methane at 25° C is burned in a boiler furnace with 10.0% excess air. The air enters the burner at a temperature of 100° C. Ninety percent of the methane fed is consumed; the product gas is analyzed and found to contain 10.0 mol CO_2 per 1 mol of CO. The exhaust gases exit the furnace at 400° C. Calculate the rate of heat transferred from the furnace, given that a molar flow rate of 100 mol/s CH_4 is fed to the furnace. (−58,626 kJ/s)

2.6 A certain bacterium is grown in a continuous culture at 30° C. Glucose is used as carbon source and ammonia is the nitrogen source. A mixture of glycerol and ethanol is produced. The reactant contains 36 kg/h glucose and 0.4 kg/h ammonia. The product stream contains 2.81 kg/h cells, 7.94 kg/h glycerol, 11.9 kg/h ethanol, and 0.15 kg/h water. Estimate the cooling requirement. (1.392 × 104 kJ) Heat of combustion:

Glucose = −1.558 × 104 kJ/kg
NH_3 = −2.251 × 104 kJ/kg
Glycerol = −1.799 × 104 kJ/kg
Ethanol = −2.971 × 104 kJ/kg
Cell = −2.120 × 104 kJ/kg

The reaction:
Glucose + NH_3 → Biomass + glycerol + ethanol + CO_2 + H_2

2.7 One mole of C_8H_{14} and 14.0 mol of oxygen are placed into a lab scale batch reactor. The reactor then is placed into a water bath at 25° C; the water bath contains 20.0 kg of water. The contents of the reactor are burned. The C_8H_{14} combusts completely to give H_2O and CO_2. At the end of the combustion, the water bath and the reactor and its contents are at 90° C. Under these conditions, the water produced during the combustion can be assumed to be completely in its liquid form. The top surface of the batch reactor is insulated such that all heat lost from the reactor goes to the water bath. What is the standard state heat of combustion of the C_8H_{14}? (−5500 kJ/mol) The following reaction took place:

$$C_8H_{14} + \frac{23}{2}O_2 \rightarrow 8CO_2 + 7H_2O$$

2.8 Natural gas stream contains 90 mol% methane and the balance H_2S. The stream flowing at a molar flow rate of 100 mol/min and 25° C enters a combustor chamber. Water in the shell side of the combustor is supplied to maintain the combustor exit stream temperature at 25° C. If 50% excess air is used for the combustion, what is the molar flow rate of the gases leaving the combustion process and what is the heat released from the combustor? (−77,395 kJ/min) The stream is burned completely where the following two reactions take place:

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

$$H_2S + 1.5O_2 \rightarrow H_2O + SO_2$$

9.9 Propane (C_3H_8) enters a combustion chamber at 200° C at a rate of 100 mol/h. The gas is mixed and burned with 50% excess air that enters the combustion chamber at 200oC. An analysis of the combustion gases reveals that 90% of the propane carbon burns to CO2, with the remaining 10% forming CO, if the exit temperature of the combustion gases is 200° C. The average specific heats of propane, oxygen, carbon dioxide, carbon monoxide, and water vapor are 73.5, 29.4, 37.4, 28.6, and 34.7 J/mol K, respectively. The standard heats of formation of propane, carbon dioxide, carbon monoxide, and water vapor are −103.85, −393.51, −110.52, and −241.86 kJ/mol, respectively. Determine the rate of heat transfer from the combustion chamber. (−54 kW)

2.10 Liquid octane (C_8H_{18}) enters the combustion chamber of a gas turbine steadily at 1 atm and 25° C, and it is burned with air that enters the combustion chamber at the same state. Determine the adiabatic flame temperature for a complete combustion at 400% theoretical air given 1 kmol octane. Assume constant heat capacities 45, 35, 30, and 30 kJ/kmol K, for CO_2, H_2O, O_2, and N_2, respectively. (977 K)

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