Chapter 1

Introduction to Engineering Principles and Units

This chapter presents a series of problems that introduce the student to the use of units and methods for expressing different variables such as temperature and composition. Likewise, implementation of material balance and energy in fuel cells are illustrated in the following set of problem modules.

- 1.3-1 Determination of a Solution Density
- 1.4-1 Gas-Law Constant
- 1.4-2 Composition of a Gas Mixture
- 1.5-3 Combustion of Fuel Gas
- 1.6-1 Pre-heating of Methane and Steam
- 1.6-2 Heating of an Ethanol Solution
- 1.6-3 Calculation of Heat Transfer Rate using Steam Tables
- 1.6-4 Incomplete Combustion of Methane
- 1.6-5 Standard Enthalpy of Reaction
- 1.7-1 Cooling of a Fuel Cell
- 1.7-2 Simultaneous Material and Energy Balances
- 1.7-3 Oxidation of Woody Biomass

Example 1.3-1: Composition of a Methanol Solution

A Direct-Methanol Fuel Cell is being fed with a liquid mixture of 80 mol % methanol and 20 mol % water at a temperature of 20 °C. Calculate the mass fractions and the mass of each component of this mixture in g and lb_m.

Strategy

We will select a basis of 100 moles of mixture and use the molecular weights of methanol and water to determine the mass.

Solution

In the basis of 100 moles of mixture we selected, there will be 80 moles of methanol and 20 moles of water.

We need to use the molecular weight of each component to determine the mass of methanol and water in the mixture, as shown in the following equations:

$$\begin{split} \mathbf{m}_{\mathrm{H}_{2}\mathrm{O}} &= \mathbf{n}_{\mathrm{H}_{2}\mathrm{O}} \mathbf{M}_{\mathrm{H}_{2}\mathrm{O}} \\ \\ \mathbf{m}_{\mathrm{CH}_{3}\mathrm{OH}} &= \mathbf{n}_{\mathrm{CH}_{3}\mathrm{OH}} \mathbf{M}_{\mathrm{CH}_{3}\mathrm{OH}} \end{split}$$

Substituting the corresponding quantities into these equations yields:

$$m_{H_2O} = (20 \text{ moles } H_2O) \left(\frac{18 \text{ g } H_2O}{1 \text{ mol } H_2O}\right)$$

$$\boxed{m_{H_2O} = \underline{\qquad} \text{ g } H_2O}$$

$$m_{CH_3OH} = (\underline{\qquad} \text{ moles } CH_3OH) \left(\frac{32 \text{ g } CH_3OH}{1 \text{ mol } CH_3OH}\right)$$

$$\boxed{m_{CH_3OH} = \underline{\qquad} \text{ g } CH_3OH}$$

These values can be converted into lb_m by multiplying the results by the conversion factor between lb_m and g:



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$$m_{CH_{3}OH} = \underline{\qquad} g CH_{3}OH \left(\frac{1 \ lb_{m}}{453.59 \ g}\right)$$
$$\underline{m_{CH_{3}OH}} = \underline{\qquad} lb_{m}$$

To determine the mass fractions of methanol and water, first we need to calculate the mass of mixture by adding the individual weights of its components:

$$m_{mixture} = m_{H_2O} + m_{CH_3OH}$$

$$m_{mixture} = \underline{\qquad} lb_m + \underline{\qquad} lb_m$$

$$m_{mixture} = 6.438 \ lb_m$$

Now we can calculate the mass fractions by dividing the mass of each component by the mass of the mixture:



Example 1.4-1: Gas-Law Constant

Calculate the value of the gas-constant R if the pressure is in mm Hg, the moles are measured in g mol units, the volume is in liters and the temperature is in K. Convert this value to $\frac{\text{cal}}{\text{mol} \cdot \text{K}}$.

Strategy

We can calculate the constant R by solving it from the ideal-gas law at standard conditions.

Solution

The ideal-gas equation of state can be solved for R to yield:

$$R = \frac{pV}{nT}$$

At standard conditions, P = 760 mm Hg, V = 22.414 L, n = 1 mol and T = 273.15 K. Substituting these values into the ideal gas equation of state, we have:

$$R = \frac{(760 \text{ mm Hg})(22.414 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})}$$
$$R = \underline{\qquad} \frac{L \cdot \text{mm Hg}}{\text{mol} \cdot \text{K}}$$

To obtain the value of R in $\frac{\text{cal}}{\text{mol} \cdot \text{K}}$, we can start by converting it to SI units as shown below:

$$R = 62.364 \frac{L \cdot mm Hg}{mol \cdot K} \left(\frac{Pa}{760 mm Hg} \right) \left(\frac{1 m^3}{1000 L} \right)$$

$$R = \underline{\qquad} \frac{Pa \cdot m^3}{mol \cdot K}$$

A Pascal is defined as:

$$Pa = \frac{N}{m^2}$$

If we multiply the Pa by m³, we get:

$$Pa \cdot m^3 = \frac{N}{m^2}m^3 = N \cdot m = Joule(J)$$

Now we can use a conversion factor between Joules and calories to determine the value of R in the desired units:



Example 1.4-2: Composition of a Gas Mixture

Hydrogen can be produced by an ethanol reforming process. The gas produced by the reformer is exiting at a pressure of 2144 kPa and has the following composition.

Component	Molar Fraction
H ₂	0.392
H ₂ O	0.438
СО	0.081
CO ₂	0.080
CH ₄	0.009

Determine the partial pressure of each component.

Strategy

The definition of partial pressure will allow us to solve this problem.

Solution

To calculate the partial pressure of each gas in the stream exiting the reformer, we can use the following equation:

$$P_i = y_i P$$

where:

 y_i = molar fraction of the species *i* present in the gas mixture.

 P_i = Partial pressure of the species *i* present in the gas mixture.

P = absolute pressure of the system.

Substituting the corresponding molar fraction and the absolute pressure of the system into the definition of partial pressure, we have:

$$P_{H_2} = y_{H_2} P = 0.392(____ kPa)$$

$$P_{H_2} = 840.45 \text{ kPa}$$

$$P_{H_20} = y_{H_20} P = 0.438(____ kPa)$$

$$P_{H_20} = ____ kPa$$



Example 1.5-3: Combustion of Fuel Gas

In the steam-methane reforming process for producing hydrogen, part of the reformer exit gas is being burned with 25 % excess oxygen from air in order to supply heat for the reforming reaction to occur. The fuel being burned has the following composition:

Component	Mol %
H ₂	41.9
H ₂ O	5.1
СО	1.7
CO ₂	41.9
CH ₄	9.4

The combustion reactions occurring inside the firebox are shown below. The combustion of methane is only 87 % complete.

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

2)
$$\operatorname{CO} + \frac{1}{2}\operatorname{O}_2 \longrightarrow \operatorname{CO}_2$$

3) $\operatorname{H}_2 + \frac{1}{2}\operatorname{O}_2 \longrightarrow \operatorname{H}_2\operatorname{O}$

Determine the composition of the gas produced by the combustion reaction assuming an air composition of 21 mol % oxygen and 79 mol % nitrogen.

Strategy

We can perform molecular material balances around the combustion chamber to determine the amounts of each species in the exhaust gases. A basis of 100 moles of fuel will be selected for simplicity.

Solution

We can start by performing a methane balance around the combustion chamber:

CH4 balance

Input = Output + Consumption

Input = 9.4 moles CH_4

The amount of methane exiting in the flue gas can be determined using the definition of fractional conversion:

$$\mathbf{x}_{CH_4} = \frac{\mathbf{n}_{CH_4,in} - \mathbf{n}_{CH_4,out}}{\mathbf{n}_{CH_4,in}}$$

Solving for the $n_{CH_4,out}$ and substituting the corresponding quantities yields:

$$n_{CH_4,out} = n_{CH_4,in} - x_{CH_4} n_{CH_4,in}$$
$$n_{CH_4,out} = 9.4 \text{ moles} - (9.4 \text{ moles})$$
$$n_{CH_4,out} = - \text{moles}$$

Since no information is given about the fractional conversion for reactions 2) and 3), complete combustion will be assumed. Thus,

$$\boldsymbol{n}_{_{CO,out}}=\boldsymbol{n}_{_{\mathrm{H}_2,out}}=\boldsymbol{0}$$

We can proceed to perform a material balance on carbon dioxide as follows:

CO₂ balance

Input + Generation = Output

Input = _____ moles

By looking at the chemical reactions, it can be seen that both reactions 1) and 2) are generating carbon dioxide. From the stoichiometric coefficients of these reactions, we can see that one mole of fuel is producing one mole of CO_2 . Thus,

 $n_{_{CO_2,generated}} = n_{_{CH_4,reacted}} + n_{_{CO,reacted}}$

Substituting numeric values into this equation, we get:

 $n_{CO_{\gamma},generated} =$ _____(9.4 moles)+_____ moles

 $n_{CO_2,generated} = 9.88 \text{ moles } CO_2$

We can substitute this result into the material balance equation for CO₂ to yield:

 $n_{CO_2,out} =$ _____ moles + 9.88 moles

 $n_{CO_2,out} =$ _____ moles

In a similar way, we can perform material balances for water, considering the generation of water by reactions 1) and 3). In these reactions, it can be seen that 1 mole of fuel is producing 1 mole of water:

H₂O balance

Input + Generation = Output

Input = 5.1 moles

The amount of water generated by the chemical reactions will be given by:

 $\mathbf{n}_{_{\mathrm{H_2O},\mathrm{generated}}} = \mathbf{n}_{_{\mathrm{H_2},\mathrm{reacted}}} + 2\mathbf{n}_{_{\mathrm{CH_4},\mathrm{reacted}}}$

Substituting numeric values into this equation, we have:

 $n_{H_2O,generated} = _$ moles + 2(____)(9.4 moles)

 $n_{H_2O,generated} =$ _____ moles

We can substitute this result into the material balance equation for H₂O to get:

 $n_{H_{2}O,out} = 5.1 \text{ moles} + ____ \text{moles}$

n_{H2O,out} = _____ moles

To determine the oxygen exiting in the product stream, we will perform a material balance for molecular oxygen:

O_2 balance

Input = Output + Consumption

To determine the amount of oxygen that must be fed into the reactor, first we need to determine the theoretical amount of oxygen required by each reaction. This value can be calculated by multiplying the amount of fuel in the feed (carbon monoxide, methane or hydrogen) by the stoichiometric ratio of fuel to oxygen. Thus,

$$n_{O_2,r1} = 41.9 \text{ moles } CH_4 \left(\frac{2 \text{ moles } O_2}{\text{mol } CH_4}\right) = \underline{\qquad} \text{moles } O_2$$

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$$n_{O_2,r^2} = \underline{\qquad} \text{ moles } CO\left(\underline{\qquad} \frac{\text{ moles } O_2}{\text{ mol } CO}\right) = 0.85 \text{ moles } O_2$$
$$n_{O_2,r^3} = 41.9 \text{ moles } H_2\left(\underline{\qquad} \frac{\text{ moles } O_2}{\text{ mol } H_2}\right) = \underline{\qquad} \text{ moles } O_2$$

Knowing the values of oxygen consumed by each reaction, we can calculate the total amount of oxygen required by this process:

Consumption = $n_{O_2,r1} + n_{O_2,r2} + n_{O_2,r3}$

Consumption = _____ moles $O_2 + 0.85$ moles $O_2 +$ _____ moles O_2

Consumption = 105.6 moles O₂

Since there is 25 % excess oxygen, the number of moles of oxygen entering the reactor will be given by:

Input = _____ (Consumption) = _____ (105.6 moles O_2)

Input = _____ moles O_2

Solving for the amount of oxygen exiting the reactor in the balance equation for molecular oxygen and substituting the amount of oxygen fed and reacted, we get:

Output = Input – Consumption

 $n_{O_2,out} =$ _____ moles -105.6 moles

 $n_{O_2,out} = _$ ____ moles

Finally, since the oxygen is entering the process as air, we need to take into account that nitrogen is entering into the firebox in this process. However, all the nitrogen will exit in the product stream since it is not being consumed nor generated by the chemical reactions. Thus,

N₂ balance

$$n_{N_{2},in} = n_{N_{2},out}$$

The amount of nitrogen fed into the system can be determined by multiplying the molar fraction of nitrogen in the air by the amount of air fed:

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$$n_{N_2,in} = n_{N_2,out} = \left(\frac{\text{moles } N_2}{0.21 \text{ moles } O_2}\right) (\underline{\qquad} \text{moles } O_2)$$

 $n_{N_2,in} = n_{N_2,out} = 496.57 \text{ moles } N_2$

Now that we know the amount of moles of all the species, we can calculate the total number of moles exiting the combustion chamber.

$$n_{out} = n_{CH_4,out} + n_{CO_2,out} + n_{H_2O,out} + n_{N_2,out} + n_{O_2,out}$$

$$n_{out} = \underline{\qquad} moles + \underline{\qquad} moles + 63.36 moles + 496.57 moles + \underline{\qquad} moles$$

The molar fraction of each component of the exhaust gases can be obtained by dividing the number of moles of each component by the total number of moles. Thus,



Example 1.6-1: Pre-heating of Methane and Steam

a) The steam used for producing hydrogen by steam-methane reforming process is leaving the boiler at a temperature of 400 °C, a pressure of 1 atm, and a flow rate of $38.31 \frac{\text{kmol}}{\text{hr}}$. However, before entering the reformer, it must be heated to a temperature of 450 °C at constant pressure. Determine the power required in kW to heat the steam to this temperature.

Strategy

Since there is no phase change involved in this heating process, the definition of sensible heat can be used to determine the power required.

Solution

The following equation is used to determine the heat required for increasing the temperature of a substance:

$$\dot{\mathbf{Q}} = \dot{\mathbf{n}}\hat{\mathbf{C}}_{\mathrm{p,i}}(\mathbf{T}_2 - \mathbf{T}_1)$$

where:

 \dot{Q} = Power required for changing the temperature of a mass of substance from T₁ to T₂.

 \dot{n} = Molar flow rate of substance *i*.

 C_{p_i} = Heat capacity of substance *i*.

 T_1 = Initial temperature

 T_2 = Final temperature

The value of the heat capacity of steam at the final temperature of 450°C can be obtained using linear interpolation between 400°C and 500°C with the data found in Table 1.6-1 of Geankoplis as shown in the following steps:

$$\frac{T_{\text{mid}} - T_{\text{low}}}{T_{\text{high}} - T_{\text{low}}} = \frac{C_{\text{p,H}_2 \text{O} @ T_{\text{mid}}} - C_{\text{p,H}_2 \text{O} @ T_{\text{low}}}}{C_{\text{p,H}_2 \text{O} @ T_{\text{high}}} - C_{\text{p,H}_2 \text{O} @ T_{\text{low}}}}$$

Inserting the numbers from Table 1.6-1, we have:

$$\frac{450 \text{ °C} - 400 \text{ °C}}{500 \text{ °C} - 400 \text{ °C}} = \frac{C_{p,H_2O @ 450 \text{ °C}} - 35.21}{____ -35.21}$$

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Solving for the heat capacity at the process temperature of 450 °C, we get:

$$C_{p,H_2O} = \underline{\qquad} \frac{J}{mol \cdot K}$$

Substituting all known values into the equation for the power yields:

b) Determine the heat transfer rate required to bring methane from the gas lines at room temperature to the operating temperature of the steam-methane reforming process from part a). Methane is being consumed at a rate of $12.8 \frac{\text{kmol}}{\text{hr}}$

Strategy

In a similar way to part a) of this problem, we can use the definition of sensible heat to calculate the heat required.

Solution

We can substitute the corresponding values for the initial and final conditions of methane into the equation used to calculate sensible heat in part a).

$$\dot{\mathbf{Q}} = \left[12.8 \frac{\mathrm{kmol}}{\mathrm{hr}} \left(\frac{1 \, \mathrm{hr}}{3600 \, \mathrm{s}}\right) \left(\frac{1000 \, \mathrm{moles}}{1 \, \mathrm{kmol}}\right)\right] \left(\frac{1000 \, \mathrm{moles}}{1000 \, \mathrm{J}}\right) \left(\frac{1 \, \mathrm{kJ}}{1000 \, \mathrm{J}}\right) (450^{\circ}\mathrm{C} - 25^{\circ}\mathrm{C})$$

$$\boxed{\dot{\mathbf{Q}} = \underline{\qquad \qquad } \mathrm{kW}}$$

The heat capacity value for methane was obtained through linear interpolation using data from Table 1.6-1 of Geankoplis, at a temperature of 450°C.

Example 1.6-2: Heating of an Ethanol Solution

A gas mixture containing 87.5 mole % water and 12.5 mole % ethanol is being heated from 210.4 °C to 350 °C before entering a pre-reformer unit to produce hydrogen for use in Proton-Exchange Membrane Fuel Cells. This mixture will enter the pre-reformer at a flow rate of $61.4 \frac{\text{kmol}}{\text{hr}}$

Calculate the heat required to bring the ethanol/water mixture to the operating conditions of the ethanol-reforming process. The heat capacity of ethanol vapor at the average temperature of 280.2 °C is $98.9 \frac{J}{\text{mol} \cdot \text{K}}$. This value was calculated using the equation for heat capacity of ethanol vapor as a function of temperature, with parameters obtained from Table B.2 of Elementary Principles of Chemical Processes by Felder & Rousseau.

Strategy

This problem can be solved by calculating and adding the sensible heat of each component of the mixture.

Solution

The sensible heat of a mixture can be obtained from the following equation:

$$\dot{\mathbf{Q}}_{\text{mixture}} = \left(\sum \dot{\mathbf{n}}_{i} \hat{\mathbf{C}}_{p,i}\right) (\mathbf{T}_{2} - \mathbf{T}_{1})$$

Applying this equation to the number of components of the mixture in this problem, we get:

$$\dot{Q}_{mixture} = \left(\dot{n}_{H_2O} \hat{C}_{p,H_2O} + \dot{n}_{C_2H_5OH} \hat{C}_{p,C_2H_5OH} \right) (T_2 - T_1)$$

The flow rate of water and ethanol can be calculated by multiplying their corresponding molar fractions by the overall flow rate of the mixture:

$$\begin{split} \dot{n}_{H_{2}O} &= y_{H_{2}O} \dot{n} & \dot{n}_{C_{2}H_{5}OH} = y_{C_{2}H_{5}OH} \dot{n} \\ \dot{n}_{H_{2}O} &= 0.875 \bigg(61.4 \frac{\text{kmol}}{\text{hr}} \bigg) & \dot{n}_{C_{2}H_{5}OH} = \underline{\qquad} \bigg(61.4 \frac{\text{kmol}}{\text{hr}} \bigg) \\ \dot{n}_{H_{2}O} &= \underline{\qquad} \frac{\text{kmol}}{\text{hr}} & \dot{n}_{C_{2}H_{5}OH} = \underline{\qquad} \frac{\text{kmol}}{\text{hr}} \end{split}$$

The specific heat of water can be obtained using linear interpolation between the temperatures of 300 °C and 400 °C with data from Table 1.6-1 of Geankoplis. Thus,

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$$C_{p,H_2^{O} @ 350^{\circ}C} = \underline{\qquad} \frac{J}{mol \cdot K}$$

Now we can substitute all the values we found into the equation for the sensible heat of the mixture to yield:



\dot{Q}_{mixture}	=102.0 kW
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Example 1.6-3: Calculation of Heat Transfer Rate using Steam Tables

Liquid water at 30 °C is fed into a steam-methane reforming plant for producing syngas which can be used as fuel for solid oxide fuel cells. Before entering the reformer, the water must be boiled and heated to a temperature of 450 °C and at a pressure of 2180 kPa. Use steam tables to determine the following:

a) The amount of heat required for heating 1 mol of water from 30 °C to the boiling point at 2180 kPa.

b) The amount of heat required to vaporize 1 mol of water.

c) The amount of heat needed for heating 1 mol of saturated steam to a temperature of 450 °C.

Strategy

To determine the amount of heat required for parts a) to c) in this problem we will make use of thermodynamic properties of water and steam.

Solution

To solve parts a), b) and c) of this problem, we need to look for 4 different enthalpy values of water and steam, which are described below:

 $H_{a,1}$ = Enthalpy of liquid water at 30 °C

 $H_{b,l}$ = Enthalpy of saturated liquid water at the boiling temperature at a pressure of 2180 kPa

 $H_{b,v}$ = Enthalpy of saturated steam at the boiling temperature at a pressure of 2180 kPa

 $H_{c,v}$ = Enthalpy of superheated steam at the process temperature of 450 °C

After finding these 4 enthalpies in the steam tables, the enthalpies we need to calculate to solve this problem will be given by the following equations:

$H_a = H_{b,l} - H_{a,l}$ $H_b = H_{b,v} - H_{b,l}$ $H_c = H_{c,v} - H_{b,v}$

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The enthalpies of liquid water can be found in Table 2-305 of *Perry's Chemical Engineers' Handbook* 8th Edition. However, we will have to use linear interpolation for determining the enthalpies at the temperature and pressure given in the problem statement. The data given in this table is shown below:

		Pressure (kPa)		
		1000	2180	5000
(K)	300	$2.0444 \frac{\text{kJ}}{\text{mol}}$	Ĥ _{@ 2180 kPa,300K}	<u>kJ</u> mol
rature	303.15	$\hat{H}_{@\ 1000\ kPa,303.15K}$	Ĥ _{@ 2180 kPa,303.15K}	Ĥ _{@ 5000 kPa,303.15K}
Temper	400	$9.6106 \frac{\text{kJ}}{\text{mol}}$	Ĥ _{@ 2180 kPa,400K}	$9.6601 \frac{\text{kJ}}{\text{mol}}$

Where the caret (^) indicates the enthalpy is per mole.

From the table shown above, we need to calculate first the values of the enthalpy at a constant temperature of 303.5 K at a pressure of 1000 kPa. We setup the linear interpolation as:

$$\frac{T_{\text{mid}} - T_{\text{low}}}{T_{\text{high}} - T_{\text{low}}} = \frac{\hat{H}_{@T_{\text{mid}}} - \hat{H}_{@T_{\text{low}}}}{\hat{H}_{@T_{\text{high}}} - \hat{H}_{@T_{\text{low}}}}$$

Inserting the numbers from the table, we have:

$$\frac{-300 \text{ K}}{400 \text{ K} - 300 \text{ K}} = \frac{\hat{H}_{@ 1000 \text{ kPa},303.15\text{ K}} - 2.0444}{-2.0444}$$

Solving for H @ 1000 kPa, 303.15, K:

$$\hat{H}_{@\ 1000\ kPa,303.15K} = \left[\frac{K-300\ K}{400\ K-300\ K}\left(\underline{\qquad}-2.0444\right)\right] + 2.0444 = 2.2827\frac{kJ}{mol}$$

Repeating this procedure for the enthalpies at a pressure of 5000 kPa we have:

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		Pressure (kPa)		
		1000	2180	5000
re	300	$2.0444 \frac{\text{kJ}}{\text{mol}}$	Ĥ _{@ 2180 kPa,300K}	<u>kJ</u>
peratu	303.15	$2.2827 \frac{\text{kJ}}{\text{mol}}$	Ĥ _{@ 2180 kPa,303.15K}	<u>kJ</u>
Teml (K)	400	$9.6106 \frac{\text{kJ}}{\text{mol}}$	Ĥ _{@ 2180 kPa,400K}	$9.6601 \frac{\text{kJ}}{\text{mol}}$

After substituting the calculated values for the enthalpies at T = 303.15 K in the table, we get:

At this point, we can solve for the enthalpy at the operation conditions in the process described in this problem.

Interpolating across at a constant temperature and solving for $\hat{H}_{_{@\ 2180\ kPa,303.15K}}$ yields:

Thus, the enthalpy of liquid water at 30°C is estimated to be:

$$\hat{H}_{a,l} = \hat{H}_{@\ 2180 \text{ kPa},303.15 \text{ K}} \approx \underline{\qquad } \frac{\text{kJ}}{\text{mol}}$$

Now we can proceed to look in Table A.2-9 of Geankoplis for the enthalpy values of saturated water and saturated steam. Again, we will have to use linear interpolation to calculate the enthalpies of saturated water and steam at a pressure of 2180 kPa using the values from the following table.

		$H_1\left(\frac{kJ}{kg}\right)$	$H_v\left(\frac{kJ}{kg}\right)$
	1553.8		2793.2
ure	2180	$\tilde{H}_{b,l} = 924.46$	Ĥ _{b,v} =
Press (kPa)	2548	966.78	

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The unknown enthalpies were calculated by interpolation as shown in the following equations:

$$\tilde{H}_{b,l} = \left[\frac{2180 \text{ kPa} - 1553.8 \text{ kPa}}{2548 \text{ kPa} - 1553.8 \text{ kPa}} (966.78 - \underline{\qquad})\right] + \underline{\qquad} = 924.46 \frac{\text{kJ}}{\text{kg}}$$
$$\tilde{H}_{b,v} = \left[\frac{2180 \text{ kPa} - 1553.8 \text{ kPa}}{2548 \text{ kPa} - 1553.8 \text{ kPa}} (\underline{\qquad} - 2793.2)\right] + 2793.2 = \underline{\qquad} \frac{\text{kJ}}{\text{kg}}$$

To calculate the remaining unknown enthalpy, we need to look for data for superheated steam as we did for calculating H_{a,l}. With the values obtained from Table A.2-10 of Geankoplis, the table for the process conditions will be given by:

		Pressure (kPa)		
		2000	2180	2500
e	420	$3291.6 \frac{\text{kJ}}{\text{kg}}$		$3284.0 \frac{\text{kJ}}{\text{kg}}$
oeratu	450	$3357.6 \frac{\text{kJ}}{\text{kg}}$	$\tilde{H}_{c,v} = \underline{\qquad} \frac{kJ}{kg}$	<u>kJ</u> kg
Tem] (°C)	500	$3467.6 \frac{\text{kJ}}{\text{kg}}$		$3462.1\frac{\text{kJ}}{\text{kg}}$

where the values in bold were calculated by interpolation as shown in the steps below:

$$\tilde{H}_{@\ 2000\ kPa,450^{\circ}C} = \left[\frac{450^{\circ}C - 420^{\circ}C}{500^{\circ}C - 420^{\circ}C} (3467.6 - 3291.6)\right] + 3291.6 = 3357.6 \frac{kJ}{kg}$$

Finally, we can apply the equations shown above for the enthalpies H_a, H_b and H_c to yield:

$$\hat{H}_{a} = \hat{H}_{b,l} - \hat{H}_{a,l} = 1 \text{ mol} \left[924.46 \frac{\text{kJ}}{\text{kg}} \left(\frac{18 \text{ kg}}{1 \text{ kmol}} \right) \left(\frac{1 \text{ kmol}}{1000 \text{ mol}} \right) - \underline{\qquad} \frac{\text{kJ}}{\text{mol}} \right]$$

$$\frac{\hat{H}_{a} = 14.34 \text{ kJ}}{\text{long Gaviola}} \qquad 20 \qquad \text{Student View}$$

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Example 1.6-4: Incomplete Combustion of Methane

A mixture of air and methane is being fed to the firebox in a steam-methane reforming process. The methane in this mixture is being burned in order to provide heat for the steam-methane reforming reaction to occur.

The fuel mixture is entering at a rate of $213.5 \frac{\text{kmol}}{\text{hr}}$ and has a molar fraction of 0.0111 of methane.

90 % of the methane is burning to produce CO_2 , and the rest is undergoing incomplete combustion to produce CO. These combustion reactions are shown below:

1) CH₄ + 2O₂
$$\leftarrow$$
 CO₂ + 2H₂O_(g)
2) CH₄ + $\frac{3}{2}$ O₂ \leftarrow CO + 2H₂O_(g)
 $\Delta \hat{H}^{o}_{r,2} = -519670 \frac{kJ}{kmol}$

Calculate the amount of heat transferred by these two reactions in $\frac{\text{kcal}}{\text{hr}}$.

Note: The standard heats of reaction may be obtained from Table A.3-2 of Geankoplis or using standard heats of formation of the molecules involved in the chemical reaction, shown in Table A.3-1.

Strategy

This problem can be solved by using tabulated data for standard heats of reaction. We need to take into account the selectivity of CO_2 to CO.

Solution

The amount of heat transferred by the two reactions will be given by the following equation:

$$\dot{\mathbf{Q}} = \Delta \dot{\mathbf{H}} = \dot{\mathbf{n}}_{\mathrm{CO}_{2}} \left(\Delta \hat{\mathbf{H}}_{\mathrm{r},\mathrm{l}}^{\mathrm{o}} \right) + \dot{\mathbf{n}}_{\mathrm{CO}} \left(\Delta \hat{\mathbf{H}}_{\mathrm{r},2}^{\mathrm{o}} \right)$$

where:

 \dot{n}_{co_2} = Molar flow rate of carbon monoxide being produced by reaction 2 $\left(\Delta \hat{H}_{r,1}^{o}\right)$ = Standard enthalpy of reaction 1 \dot{n}_{co} = Molar flow rate of carbon monoxide being produced by reaction 2 $\left(\Delta \hat{H}_{r,2}^{o}\right)$ = Standard enthalpy of reaction 2

The flow rates of carbon dioxide and carbon monoxide can be calculated by multiplying the overall flow rate of fuel/air mixture by the molar fraction of methane. Then, we multiply this amount by the amount of methane being converted to carbon dioxide and carbon monoxide respectively.

If we look at the stoichiometric coefficient of both chemical reactions, it can be seen that the ratio of carbon dioxide to methane in reaction 1 and the ratio carbon monoxide to methane in reaction 2 are both equal to one. Thus, the amount of methane consumed by reaction 1 will be equal to the amount of carbon dioxide produced. Similarly, the amount of carbon monoxide produced by reaction 2 will be equal to the amount of methane consumed by reaction 2.

$$\dot{n}_{CO_2} = \dot{n}_{CH_4, r1} = \underline{\qquad} \left(\underline{\qquad} \frac{\text{kmol CH}_4}{\text{kmol}} \right) \left(213.5 \frac{\text{kmol}}{\text{hr}} \right)$$
$$\dot{n}_{CO_2} = 2.13 \frac{\text{kmol CO}_2}{\text{hr}}$$

For carbon monoxide:

$$\dot{n}_{CO} = \dot{n}_{CH_4, r2} = \underline{\qquad} \left(\underbrace{-------\frac{kmol CH_4}{kmol}} \right) \left(213.5 \frac{kmol}{hr} \right)$$
$$\dot{n}_{CO} = \underline{--------\frac{kmol CO}{hr}}$$

Now we can substitute the molar flow rates and the enthalpies of reaction into the equation for the heat transfer rate \dot{Q} to get:



Example 1.6-5: Standard Enthalpy of Reaction

The water-gas shift reaction produces hydrogen from steam and carbon monoxide and is described by the following equation:

$$CO + H_2O_{(g)} \leftarrow CO_2 + H_2$$

Determine the standard heat of this reaction.

Strategy

The heat of a given reaction can be obtained based on the stoichiometric coefficient of the species involved in the chemical reaction and their individual heats of formation.

Solution

The heat of reaction can be calculated using the following equation:

$$\Delta \hat{H}_{r}^{o} = \sum_{\text{products}} | \mathbf{v}_{i} | \Delta \hat{H}_{f,i}^{o} - \sum_{\text{reactants}} | \mathbf{v}_{i} | \Delta \hat{H}_{f,i}^{o}$$

Applying this equation to the number of products and reactants for the reaction of methanol in the fuel cell yields:

$$\Delta \hat{H}_{r}^{o} = |\nu_{CO_{2}}| \Delta \hat{H}_{f,CO_{2}}^{o} + |\nu_{H_{2}}| \Delta \hat{H}_{f,H_{2}}^{o} - |\nu_{H_{2}O}| \Delta \hat{H}_{f,H_{2}O}^{o} - |\nu_{CO}| \Delta \hat{H}_{f,CO}^{o} - |\nu_{H_{2}O}| \Delta \hat{H}_{f,CO}^{o} - |\nu_{H_{2}O}| \Delta \hat{H}_{f,H_{2}O}^{o} - |\mu_{H_{2}O}| \Delta \hat{H}_{f,H_{2}O}^{o} - |\mu_{H_$$

Since an element is a pure chemical substance, there is no energy transfer involved in its formation. Thus, the heat of reaction equation will be reduced to:

$$\Delta \hat{H}_{r}^{\circ} = \nu_{CO_{2}} \mid \Delta \hat{H}_{f,CO_{2}}^{\circ} - \mid \nu_{H_{2}O} \mid \Delta \hat{H}_{f,H_{2}O}^{\circ} - \mid \nu_{CO} \mid \Delta \hat{H}_{f,CO}^{\circ}$$

The individual heats of formation for each one of these molecules can be found in Table A.3-1 of Geankoplis:

$$\Delta \hat{H}^{o}_{f,CO_{2}} = -393.51 \frac{kJ}{mol}$$
$$\Delta \hat{H}^{o}_{f,H_{2}O} = \underline{\qquad} \frac{kJ}{mol}$$

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$$\Delta \hat{H}^{\circ}_{f,CO} = \underline{\qquad} \frac{kJ}{mol}$$

Substituting these values and the stoichiometric coefficients into the heat of reaction equation, we have:

$$\Delta \hat{H}_{r}^{o} = (1) \left(-393.51 \frac{kJ}{mol}\right) - (1) \left(-\underline{\qquad \qquad } \frac{kJ}{mol}\right) - (\underline{\qquad \qquad } \frac{kJ}{mol}\right) - (\underline{\qquad \qquad } \frac{kJ}{mol}\right)$$

$$\Delta \hat{H}_{r}^{o} = -41.16 \frac{kJ}{mol}$$

Example 1.7-1: Cooling of a Fuel Cell

The bipolar plates are the component of a fuel cell responsible of transferring the heat out of the fuel cell. A modified design of the bipolar plate is shown in the following figure. This design has additional channels which allow cooling of the fuel cell by circulating a fluid such as air or water.



A fuel cell stack in a vehicle initially at a temperature of 80 °C is being cooled by water at room temperature. The fuel cell is being cooled down to a temperature of 45 °C. Determine the water flow rate required in $\frac{L}{\min}$ if the fuel cell reaches the temperature of 45 °C in 10 seconds.

The following data is available for the bipolar plate.

V = 168.75 cm³

$$\rho = 1.3413 \frac{g}{cm^3}$$

$$\tilde{C}_p = 1.62 \frac{kJ}{kg \cdot {}^{\circ}C}$$

The cooling water is exiting the cooling channels at a temperature of 33 °C.

Strategy

We can set the energy balance by equaling the amount of heat lost by the fuel cell to the amount of heat gained by the water. Since only liquid and solid phases are present in this problem, the heat capacities of water and the bipolar plates may be assumed constant.

Solution

The energy balance for this problem may be written as follows:

Heat gained by water = Heat lost by fuel cell

$$\Delta H_{H_2O} = \Delta H_{\text{fuel cell}}$$

Both amounts of heat in the energy balance can be obtained using the equation for sensible heat.

$$\Delta H_{H_{2}O} = \left(\dot{m}_{H_{2}O}\tilde{C}_{p,H_{2}O}\Delta T_{H_{2}O}\right)t$$
$$\Delta H_{fuel cell} = \underline{\qquad} (\underline{\qquad})\Delta T_{fuel cell}$$

where:

 $\dot{m}_{H_2O} = mass$ flow rate of water $\tilde{C}_{p,H_2O} = mass$ specific heat of liquid water t = time required for cooling the bipolar plate to the final temperature of 45 °C $m_{bp} = mass$ of bipolar plate $\tilde{C}_{p,H_2O} = mass$ specific heat of bipolar plates

Note that the equation for the change in enthalpy of water is multiplied by a time period t. This is done so we can obtain the total amount of energy transferred as heat to the water instead of the heat transfer rate.

We can start by calculating the change in enthalpy of water as shown in the following steps:

$$\Delta H_{H_2O} = \left(\dot{m}_{H_2O}\tilde{C}_{p,H_2O}\Delta T\right)t$$

The specific heat of water can be obtained from Table A.2-5 of Geankoplis to be:

$$\tilde{C}_{p,H_2O} = \underline{\qquad} \frac{kJ}{kg \cdot C}$$

Substituting this value, the time period *t* and the corresponding temperatures into the equation for the change in enthalpy of water yields:

$$\Delta H_{H_2O} = \dot{m}_{H_2O} \left(\underbrace{- kJ}_{kg \cdot °C} \right) (33°C - 25°C) (\underbrace{- s}_{kg \cdot °C} \right)$$

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Now we proceed to calculate the change in the enthalpy of the fuel cell:

$$\Delta H_{_{fuel cell}} = m_{_{bp}} \tilde{C}_{_{p,bp}} \Delta T$$

The mass of the bipolar plate can be calculated using the volume and density data given in the problem statement:

$$m_{bp} = \rho_{bp} V_{bp} = \left(1.3413 \ \frac{g}{cm^3}\right) \left(\underline{\qquad} cm^3\right) \left(\underline{\} cm^3\right) \left(\underline{\}$$

Substituting this result, the heat capacity value of the bipolar plates and the initial and final temperatures of the fuel cell into the equation for $\Delta H_{fuel cell}$ we get:

$$\Delta H_{\text{fuel cell}} = (\underline{\qquad} kg) \left(1.62 \ \frac{kJ}{kg \cdot C} \right) (\underline{\qquad} C - \underline{\qquad} C)$$
$$\Delta H_{\text{fuel cell}} = \underline{\qquad} kJ$$

Now we can substitute the equations for $\Delta H_{fuel cell}$ and ΔH_{H_2O} into the energy balance equation:

$$\dot{m}_{H_2O}\left(\underline{\qquad}\frac{kJ}{kg\cdot C}\right)(33^{\circ}C-25^{\circ}C)(10 \text{ s}) = \underline{\qquad} kJ$$

Solving for the mass flow rate of water we have:

$$\dot{m}_{H_2O} = \frac{kJ}{\left(\frac{kJ}{kg \cdot {}^{\circ}C}\right)(33^{\circ}C - 25^{\circ}C)(10 \text{ s})}$$
$$\dot{m}_{H_2O} = 0.038 \frac{kg}{s}$$

We need to convert the mass flow rate to volumetric flow rate as follows:



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Example 1.7-2: Simultaneous Material and Energy Balances

The steam-methane reforming process is carried out in a plant operating on the scale of a large central station, which is capable of producing $1 \times 10^6 \frac{\text{kg H}_2}{\text{day}}$ (equivalent to 1 million gallons of gasoline). Since the reaction for producing hydrogen from methane and steam is endothermic, heat is being added to the reactor. The following diagram is describing this process.



Determine the heat added to the reactor if all of the methane is converted into products.

Strategy

We can determine the heat transfer rate \dot{Q} by performing material and energy balances around the reaction chamber.

Solution

The flow rates of hydrogen and carbon monoxide out of the reactor can be determined by the ratio of their stoichiometric coefficients to the stoichiometric coefficient of methane (limiting reactant). Thus,

$$\frac{\dot{\mathbf{n}}_{\rm CO}}{\dot{\mathbf{n}}_{\rm CH_4}} = 1 \qquad \qquad \frac{\dot{\mathbf{n}}_{\rm H_2}}{\dot{\mathbf{n}}_{\rm CH_4}} = \underline{\qquad}$$

Solving these equations for the unknown molar flow rates n_{H_2} , n_{CO} , we get:

$$\dot{n}_{CO} = \dot{n}_{CH_4}$$
 $\dot{n}_{H_2} = _ \dot{n}_{CH_4}$

The molar flow rate of methane entering the reactor can be obtained by multiplying the overall flow rate by the molar fraction of methane to yield:

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$$\dot{n}_{CH_4} = y_{CH_4} \dot{n} = 0.237 \frac{\text{mol CH}_4}{\text{mol}} \left(\underbrace{-----\frac{\text{mol}}{\text{min}}}_{\text{min}} \right)$$
$$\dot{n}_{CH_4} = \underbrace{------\frac{\text{mol CH}_4}{\text{min}}}_{\text{min}}$$

Substituting this result into the equations for the molar flow rates n_{H_2} , n_{CO} we can obtain the individual flow rates of each gas in the product stream:

Now we can proceed to perform energy balances to determine the heat transfer rate. For this we will select a reference state of 25 °C (298 K).

The general balance equation is given by:

$$\sum H_{R} + \left(-\Delta H_{298}^{o}\right) + q = \sum H_{P}$$

Input items

The heat entering the reactor is equal to the sum of the changes in the enthalpies of the reactants between the reference state and the process conditions. Thus,

The heat capacities were obtained using linear interpolation with the data from Table 1.6-1 of Geankoplis at the temperature of $431^{\circ}C$ (704 K).

The standard enthalpy of reaction must be included in the input items as shown in the general energy balance equation.

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Output items

In a similar way we can obtain the enthalpies of the gases leaving in the product stream as shown in the following steps. The heat capacities of carbon monoxide and hydrogen were obtained by linear interpolation of the data in Table 1.6-1 of Geankoplis at a temperature of 810 $^{\circ}$ C (1083 K).

$$\dot{H}_{co} = \dot{n}\hat{C}_{p,co}\Delta T = \left(\underbrace{----\frac{mol\ CO}{min}}_{min}\right)\left(\underbrace{-----\frac{kJ}{mol\cdot^{\circ}C}}_{mol\cdot^{\circ}C}\right)(810^{\circ}C - 25^{\circ}C)\left(\frac{1\ min}{60\ s}\right)$$
$$\dot{H}_{co} = 42.50\ kW$$
$$\dot{H}_{H_2} = \dot{n}\hat{C}_{p,H_2}\Delta T = \left(\underbrace{----\frac{mol\ H_2}{min}}_{min}\right)\left(\underbrace{-----\frac{kJ}{mol\cdot^{\circ}C}}_{mol\cdot^{\circ}C}\right)(810^{\circ}C - 25^{\circ}C)\left(\frac{1\ min}{60\ s}\right)$$
$$\dot{H}_{H_2} = \underbrace{-----}_{H_2}\ kW$$

Now we can substitute the enthalpies we calculated into the general balance equation and solve it for the heat added to the system q to get:

$$\sum H_{R} + (-\Delta H_{298}^{o}) + q = \sum H_{P}$$

$$\dot{q} = \sum H_{P} - \sum H_{R} - (-\Delta H_{298}^{o})$$

$$\dot{q} = \dot{H}_{C0} + \dot{H}_{H_{2}} - \dot{H}_{CH_{4}} - \dot{H}_{H_{2}0} - (-\Delta H_{298}^{o})$$

$$\dot{q} = 42.50 \text{ kW} + \underline{\qquad} \text{ kW} - 32.99 \text{ kW} - \underline{\qquad} \text{ kW} + \underline{\qquad} \text{ kW}$$

The positive sign of \dot{q} indicates that heat is being added to the system.

Example 1.7-3: Oxidation of Woody Biomass

Biomass gasification is a process used for producing hydrogen in large scale for use in fuel cells. The elemental analysis of dry woody biomass used in the gasification process yielded the following results:

Element	Mol %
С	33.3
Н	46.7
0	20.0

The following equation represents the combustion reaction of woody biomass.

$$C_{0.333}H_{0.467}O_{0.200} + 0.3498O_2 \longrightarrow 0.333CO_2 + 0.2335H_2O_{(g)} \qquad \Delta H^{\circ}_{r,25^{\circ}C} = -116.62 \frac{kJ}{mol}$$

Calculate the molar heat of combustion at the temperature of 600 °C.

The following equation may be used for estimating the heat capacity of dry wood.

$$\tilde{\mathbf{C}}_{p}\left(\frac{\mathbf{J}}{\mathbf{g}\cdot^{\circ}\mathbf{C}}\right) = 0.1031 + \left(3.867 \times 10^{-3}\right)\mathbf{T}$$

where:

T = Temperature in degrees Kelvin.

This equation was obtained from the book *Wood as an Engineering Material* published by the U.S. Department of Agriculture.

A diagram of the biomass oxidation process is shown in the figure below:



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Strategy

This problem can be solved by using energy balances around the combustion chamber. The reference temperature will be selected to be 25 °C and a basis of 1 mol of biomass will be selected.

Solution

First we need to determine the amount of steam and carbon dioxide in the exhaust gases as well as the amount of oxygen required by this process. These amounts can be calculated based on the stoichiometric coefficients of each molecule involved in the chemical reaction. Thus,

$$\frac{n_2}{n_1} = 0.3498$$
 $\frac{n_3}{n_1} =$ $\frac{n_4}{n_1} =$

Since we selected a basis of $n_1 = 1$ mol, the amount of moles of oxygen n_2 , carbon dioxide n_3 and steam n_4 are given by:

 $n_2 = 0.3498$ moles O_2 $n_3 =$ ____ moles CO_2 $n_4 =$ ____ moles H_2O

Now we can proceed to calculate the amount of heat entering through the reactants. Since there are no phase changes occurring for any of the species, the amount of heat can be calculated using the definition of sensible heat.

We can start from the general energy balance equation for a reactive process shown below:

$$\sum H_{R} + \left(-\Delta H_{r,25^{\circ}C}^{\circ}\right) + q = \sum H_{P}$$

Input items

H (biomass) =
$$m_{biomass} \tilde{C}_{p,biomass} \Delta T$$

The mass heat capacity of biomass can be obtained by substituting the temperature value of 40 $^{\circ}$ C (313.15 K) into the expression given in the problem statement:

$$\tilde{C}_{p}\left(\frac{J}{g \cdot {}^{\circ}C}\right) = \underline{\qquad} + (\underline{\qquad})(313.15 \text{ K})$$
$$\tilde{C}_{p} = \underline{\qquad} \frac{J}{g \cdot {}^{\circ}C}$$

Substituting this value into the equation for the enthalpy of biomass entering in the reactants stream we get:

$$H(\text{biomass}) = 1 \text{ mol biomass} \left(\frac{g}{1 \text{ mol biomass}} \right) \left(\frac{J}{g \cdot {}^{\circ}C} \right) \left(\frac{g}{g \cdot {}^{\circ}C} \right) \left(\frac{g}{g \cdot {}^{\circ}C} \right)$$

$$H(\text{biomass}) = \underline{J}$$

Similarly, we can calculate the heat entering through the oxygen as shown in the following steps:



Note: The heat capacity of oxygen was obtained from the data in Table 1.6-1 of Geankoplis.

The standard enthalpy of reaction at the temperature of 25 $^{\circ}$ C is given in the problem statement to be:

$$\Delta H^{o}_{r,25^{\circ}C} = -116.62 \frac{kJ}{mol} (\underline{\qquad} mol)$$
$$\Delta H^{o}_{r,25^{\circ}C} = \underline{\qquad} kJ$$

Output items

The enthalpies of steam and carbon dioxide can be obtained in a similar way to how we calculated the enthalpy of oxygen entering the reactor. For carbon dioxide and steam, the specific heat values were obtained through linear interpolation of the data from Table 1.6-1 of Geankoplis.



Substituting the calculated enthalpies and the heat of reaction at 25 °C into the general energy balance equation, we get:

$$\sum H_{R} + \left(-\Delta H_{r,25^{\circ}C}^{\circ}\right) + q = \sum H_{P}$$

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_____ J+____ J+(_____ J)+q=8861.5 J+____ J

The diagram of the combustion of biomass process is showing that the amount of heat released by the reaction is equal to the enthalpy of reaction at 600 $^{\circ}$ C. Thus, solving for q yields:

$$q = \Delta H_{r,600 \ ^{\circ}C}^{\circ} = \left[8861.5 \ J + \underline{\qquad} J - \underline{\qquad} J - \underline{\qquad} J - (\underline{\qquad} J) \right] \left(\frac{1 \ kJ}{1000 \ J} \right)$$

 $\Delta H^{o}_{r,600 \ ^{o}C} = \underline{\qquad} kJ$

To obtain the molar heat of combustion at 600 $^{\circ}$ C, we need to divide this value by the number of moles of biomass. Since we selected a basis of 1 mole of biomass reacting, the molar enthalpy will be given by:

$$\Delta \hat{H}^{\circ}_{r,600 \circ C} = \frac{\Delta H^{\circ}_{r,600 \circ C}}{n_{biomass}} = \underline{\qquad \qquad } kJ$$

$$\Delta \hat{H}^{\circ}_{r,600 \circ C} = \underline{\qquad \qquad } \frac{kJ}{mol}$$