Supplemental Material for Elementary Principles of Chemical Processes

Chapter 9
Balances on Reactive Processes

Name: ____________
Date: ____________

Chapter 9 includes problems that involve material and energy balances in processes where chemical reactions are occurring. In addition, this chapter will illustrate concepts related to reactive processes such as heat of formation, heat of combustion, exothermic and endothermic reactions, etc. The following sets of problem modules will apply the fundamentals on reactive processes to hydrogen technology and fuel cells.

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Student View

Example 9.1-1 Calculation of Heats of Reaction

a) A solid-oxide fuel cell is fed with carbon monoxide and reacts with air to produce CO_2. This reaction will produce 2 electrons which are used to power an electric circuit external to the fuel cell. The reaction equation is shown below:

$$2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)} \qquad \Delta H_r^o = -565.96\frac{\text{kJ}}{\text{mol}}$$

This reaction does not occur for other types of fuel cells which use a catalyst, such as polymer-electrolyte membrane or phosphoric-acid fuel cells. The presence of carbon monoxide on the anode side of these types of fuel cells will cause catalyst poisoning, reducing the efficiency and voltage of the fuel cell.

Determine the rate of enthalpy change for a carbon dioxide production rate of $208\frac{\text{mol}}{\text{hr}}$.

Strategy

This problem can be solved by using the heat of reaction value given in the stoichiometric equation and calculating the extent of reaction. ξ.

Solution

The extent of the reaction occurring in the fuel cell can be obtained by the following equation:

$$\dot{\xi} = \frac{(\dot{n}_{CO_2})_r}{|\nu_{CO_2}|}$$

where:

$(\dot{n}_{CO_2})_r$ = molar flow rate of CO_2 generated or consumed by the reaction.

ν_{CO_2} = stoichiometric coefficient of CO_2 in the chemical reaction equation.

Substituting the numeric values of $(\dot{n}_{CO_2})_r$ and ν_{CO_2} into the equation for the extent of reaction, we get:

$$\dot{\xi} = \frac{208\frac{\text{mol}}{\text{hr}}}{2}$$

$$\dot{\xi} = \underline{\qquad}\frac{\text{mol}}{\text{hr}}$$

Now the rate of change in the enthalpy for the oxidation of carbon monoxide can be calculated as follows:

$$\Delta\dot{H} = \dot{\xi}\ \Delta H_r^o$$

Entering the known quantities for the extent of reaction and the enthalpy of reaction into this equation yields:

$$\Delta\dot{H} = \left(\underline{\qquad}\ \frac{\text{mol}}{\text{hr}}\right)\left(-565.96\frac{\text{kJ}}{\text{mol}}\right)\cdot\left(\frac{1\ \text{hr}}{3600\ \text{s}}\right)$$

$$\boxed{\Delta\dot{H} = \underline{\qquad\quad}\ \text{kW}}$$

b) The synthesis gas obtained from a coal gasification process can be used for producing methanol, which is used as fuel in direct-methanol fuel cells. Determine the rate of production of methanol if the reaction shown below is releasing 21.6 kW of energy.

$$CO_{(g)} + 2H_{2(g)} \longrightarrow CH_3OH_{(l)} \qquad\qquad \Delta H_r^o = -128.08\frac{\text{kJ}}{\text{mol}}$$

Strategy

The enthalpy of reaction for methanol production will be used to calculate the production of methanol based on the extent of reaction.

Solution

The extent of reaction definition used in part a) of this problem can be used to solve for the production of methanol as follows:

$$\dot{\xi} = \frac{(\dot{n}_{CH_3OH})_r}{|\nu_{CH_3OH}|}$$

$$(\dot{n}_{CH_3OH})_r = \dot{\xi}\cdot|\nu_{CH_3OH}|$$

Now we have an equation to calculate the molar flow rate of methanol. However, the extent of reaction $\dot{\xi}$, must be calculated first. To do this, we will use the definition of the change in enthalpy for the chemical reaction:

$$\Delta\dot{H} = \dot{\xi}\ \Delta H_r^o$$

Solving for $\dot{\xi}$ and substituting the corresponding quantities into this equation yields:

$$\dot{\xi} = \frac{\Delta \dot{H}}{\Delta H_r^o} = \frac{\underline{\qquad}\,\frac{\text{kJ}}{\text{s}}}{-128.08\,\frac{\text{kJ}}{\text{mol}}} = \underline{\qquad}\,\frac{\text{mol}}{\text{s}}$$

The rate in enthalpy change was considered to be negative since the problem is stating that the reaction is releasing energy (exothermic reaction).

Now we can enter the calculated extent of reaction into the equation previously solved for the molar production rate of methanol, to get:

$$(\dot{n}_{CH_3OH})_r = \left(\underline{\qquad}\,\frac{\text{mol}}{\text{s}}\right)(1)\left(\frac{3600\text{ s}}{1\text{ hr}}\right)$$

$$\boxed{(\dot{n}_{CH_3OH})_r = \underline{\qquad}\,\frac{\text{mol}}{\text{hr}}}$$

Example 9.1-2 Evaluation of $\Delta\hat{U}_r$

a) The following reaction is occurring inside a solid-oxide fuel cell:

$$2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)} \qquad \Delta H_r^o = -565.96\frac{kJ}{mol}$$

Determine the standard internal energy of reaction, $\Delta\hat{U}_r^o$.

Strategy

The molar internal energy can be calculated by using its definition as a function of the stoichiometric coefficient of the gas species in the reaction.

Solution

The internal energy of reaction can be calculated by the following equation:

$$\Delta\hat{U}_r(T) = \Delta\hat{H}_r(T) - RT\left(\sum_{\substack{\text{gaseous}\\\text{products}}} |\nu_i| - \sum_{\substack{\text{gaseous}\\\text{reactants}}} |\nu_i|\right)$$

This equation can be applied to the conditions in this problem to yield:

$$\Delta\hat{U}_r^o = \Delta\hat{H}_r^o - RT\left(|\nu_{CO_2}| - |\nu_{CO}| - |\nu_{O_2}|\right)$$

Since we are asked to calculate the internal energy of reaction at standard conditions, the temperature will be 25 °C.

Substituting the known quantities into this equation, we get:

$$\Delta\hat{U}_r^o = -565.96\frac{kJ}{mol} - \left(\underline{\hspace{4cm}}\frac{kJ}{mol\cdot K}\right)(298\text{ K})\left(\underline{\hspace{1cm}} - 1 - 2\right)$$

$$\boxed{\Delta\hat{U}_r^o = \underline{\hspace{3cm}}\frac{kJ}{mol}}$$

b) Direct-methanol fuel cells have application in portable devices such as mobile phones and laptop computers. The following reaction between carbon monoxide and hydrogen is used to produce the fuel for this kind of fuel cells:

$$CO_{(g)} + 2H_{2(g)} \longrightarrow CH_3OH_{(l)} \qquad \Delta H_r^o = -128.08\frac{kJ}{mol}$$

Determine the standard internal energy of reaction, $\Delta\hat{U}_r^o$.

Strategy

To solve this problem, we will have to apply the internal energy of reaction definition to the chemical reaction equation.

Solution

This definition of the internal energy of reaction can be applied to the conditions in this problem to yield:

$$\Delta\hat{U}_r^o = \Delta\hat{H}_r^o - RT\left(-|\nu_{CO}| - |\nu_{O_2}|\right)$$

Since the reaction is occurring at room temperature, the produced methanol is in the liquid phase. This is why the stoichiometric coefficient of methanol is neglected in this equation.

Again, the temperature at standard conditions will be considered to be 25 °C.

By entering numeric values into the standard internal energy of reaction equation, we get:

$$\Delta\hat{U}_r^o = -128.08\frac{\text{kJ}}{\text{mol}} - \left(\_\_\_\_\_\_\_\_\_\_\frac{\text{kJ}}{\text{mol}\cdot\text{K}}\right)(298\text{ K})\left(\_\_\_ - 2 - 1\right)$$

$$\boxed{\Delta\hat{U}_r^o = \_\_\_\_\_\_\_\_\_\_\frac{\text{kJ}}{\text{mol}}}$$

Example 9.2-1 Hess's Law

Hydrogen is a gas used as a fuel in different types of fuel cells, such as phosphoric acid, solid oxide and proton-exchange membrane fuel cells. This fuel can be obtained from natural gas through the following reactions:

Steam-Methane Reforming: $CH_{4(g)} + H_2O_{(g)} \longrightarrow CO_{(g)} + 3H_{2(g)}$ $\Delta H_r^o = 206.16\frac{kJ}{mol}$

Water-Gas Shift Reaction: $CO_{(g)} + H_2O_{(g)} \longrightarrow CO_{2(g)} + H_{2(g)}$ $\Delta H_r^o = -41.15\frac{kJ}{mol}$

Determine the enthalpy of the following reaction by applying Hess's Law:

$$2CH_4 + 3H_2O \longrightarrow CO + CO_2 + 7H_2$$

Strategy

Hess's Law allows us to treat chemical reaction equations as algebraic equations. This way we can multiply the reactions by constants or add or subtract different chemical reactions.

Solution

The following reaction, does not occur directly, but it is a combination of the two reactions used to produce hydrogen from natural gas:

$$2CH_4 + 3H_2O \longrightarrow CO + CO_2 + 7H_2$$

We can see that there are two molecules of methane. The only reaction in the hydrogen production process where methane is present is the steam-methane reaction. In order to get two methane molecules, we can multiply the steam-methane reforming reaction by two to get:

$$2CH_4 + 2H_2O \longrightarrow 2CO + 6H_2 \qquad \Delta H_r^o = 412.32\frac{kJ}{mol}$$

It can be seen that as we multiply the equation by 2, the standard heat of reaction is also multiplied by 2.

Another observation we can make from the equation we need to calculate the heat of reaction for is that there are 3 molecules of water reacting. This means we need to add or substract another reaction to the steam-methane reforming reaction in a way that there are 3 water molecules in the reactants.

Thus, if we add the water-gas shift reaction to the steam-methane reforming reaction (multiplied by 2), we get:

$$(\_\_\_\_\_\_\_ + 2H_2O \longrightarrow 2CO + \_\_\_\_\_\_) + (CO + H_2O \longrightarrow CO_2 + H_2)$$

$$2CH_4 + 3H_2O + CO \longrightarrow CO_2 + 2CO + 7H_2$$

If we look at this equation as an algebraic expression, one of the carbon monoxide molecules in the products will cancel with the carbon monoxide molecule in the reactants, to yield:

$$2CH_4 + 3H_2O \longrightarrow CO_2 + CO + 7H_2$$

Now, this is the equation given in the problem statement. To determine its heat of reaction, we will need to do the same algebraic operation with the individual heats of reaction:

$$(2CH_4 + 2H_2O \longrightarrow 2CO + 6H_2) + (CO + H_2O \longrightarrow CO_2 + H_2)$$

$$\_\_\_\_\_\_\_\_ \frac{kJ}{mol} \qquad + \qquad \left(-41.15\frac{kJ}{mol}\right)$$

Thus, the heat of the final reaction is found to be:

$$\boxed{\Delta H_r^o = \_\_\_\_\_\_\_\_\_ \frac{kJ}{mol}}$$

Example 9.3-1 Determination of a Heat of Reaction from Heats of Formation

Determine the standard heat of the methanol reaction taking place in a direct-methanol fuel cell to generate electricity:

$$CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$$

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:

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

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

$$\Delta\hat{H}_r^o = |\nu_{CO_2}| \Delta\hat{H}_{f,CO_2}^o + \underline{\hspace{4cm}} - |\nu_{O_2}| \Delta\hat{H}_{f,O_2}^o - \underline{\hspace{4cm}}$$

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:

$$\Delta\hat{H}_r^o = |\nu_{CO_2}| \Delta\hat{H}_{f,CO_2}^o + |\nu_{H_2O}| \Delta\hat{H}_{f,H_2O}^o - |\nu_{CH_3OH}| \Delta\hat{H}_{f,CH_3OH}^o$$

The individual heats of formation for each one of these molecules can be found in Tables 2-220 (inorganic compounds) and 2-221 (organic compounds) of *Perry's Chemical Engineers' Handbook*, 7th Edition.

$$\Delta\hat{H}_{f,CO_2}^o = -393.51\frac{\text{kJ}}{\text{mol}}$$

$$\Delta\hat{H}_{f,H_2O}^o = \underline{\hspace{2.5cm}}\frac{\text{kJ}}{\text{mol}}$$

$$\Delta\hat{H}_{f,CH_3OH}^o = \underline{\hspace{2.5cm}}\frac{\text{kJ}}{\text{mol}}$$

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

$$\Delta\hat{H}_r^o = (\ \_\_\_\ )\left(-393.51\frac{\text{kJ}}{\text{mol}}\right) + (2)\left(\_\_\_\_\_\_\_\_\frac{\text{kJ}}{\text{mol}}\right) - (1)\left(\_\_\_\_\_\_\_\_\frac{\text{kJ}}{\text{mol}}\right)$$

$$\boxed{\Delta\hat{H}_r^o = -726.59\frac{\text{kJ}}{\text{mol}}}$$

Example 9.4-1 Calculation of a Heat of Reaction from Heats of Combustion

a) The following reaction is occurring in a steam-methane reforming plant to produce hydrogen fuel, which can be used in different types of proton-exchange membrane fuel cells.

$$CH_4 + H_2O_{(g)} \longrightarrow CO + 3H_2$$

Determine the standard heat of reaction $\Delta\hat{H}_r^o$ from the heats of combustion of pure substances involved in this reaction.

Strategy

In order to calculate the heat of reaction, we will need to use the heat of combustion data, which is the heat produced by the reaction of a substance with oxygen to yield specific products.

Solution

The heat of combustion data for the gases involved in the steam-methane reforming reaction can be obtained from Table 2-221 of *Perry's Chemical Engineers' Handbook*, 7th Edition:

$$\Delta\hat{H}^o_{c,CH_4} = -802.6\frac{kJ}{mol}$$

$$\Delta\hat{H}^o_{c,H_2O} = \underline{\hspace{3cm}}$$

$$\Delta\hat{H}^o_{c,H_2} = -241.8\frac{kJ}{mol}$$

$$\Delta\hat{H}^o_{c,CO} = \underline{\hspace{3cm}}\frac{kJ}{mol}$$

The definition of the standard heat of reaction in terms of the individual standard heats of combustion is given by the following equation:

$$\Delta\hat{H}_r^o = \sum_{reactants} |\nu_i| (\Delta H_c^o)_i - \sum_{products} |\nu_i| (\Delta H_c^o)_i$$

where:

ν_i = stoichiometric coefficient of the species i

The definition of the standard heat of reaction can be applied for the particular reaction given for this problem, to get:

$$\Delta\hat{H}_r^o = |\nu_{CH_4}| (\Delta H_c^o)_{CH_4} + |\nu_{H_2O}| (\Delta H_c^o)_{H_2O} - |\nu_{H_2}| (\Delta H_c^o)_{H_2} - |\nu_{CO}| (\Delta H_c^o)_{CO}$$

Substituting the numeric values for the stoichiometric coefficients and the individual heats of combustion into this equation yields:

$$\Delta\hat{H}_r^o = (1)\left(-802.6\frac{\text{kJ}}{\text{mol}}\right) + (1)\left(\_\_\_\_\_\_\_\_\frac{\text{kJ}}{\text{mol}}\right) - (3)\left(-241.8\frac{\text{kJ}}{\text{mol}}\right) - (1)\left(\_\_\_\_\_\_\_\_\frac{\text{kJ}}{\text{mol}}\right)$$

$$\boxed{\Delta\hat{H}_r^o = \_\_\_\_\_\_\_\_\_\frac{\text{kJ}}{\text{mol}}}$$

b) Using Hess's Law, demonstrate that it is valid to use the heats of combustion to determine the standard heat of the steam-methane reforming reaction.

Strategy

Another application of Hess's Law allows us to calculate the standard heats of reactions that involve combustible substances and products obtained through combustion reactions.

Solution

The following combustion reactions will be combined using Hess's Law to get the reaction occurring in a steam-methane reforming process:

1) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O_{(g)}$ $\qquad \Delta\hat{H}_{r,1}^o = -802.31\frac{\text{kJ}}{\text{mol}}$

2) $CO + \frac{1}{2}O_2 \longrightarrow CO_2$ $\qquad \Delta\hat{H}_{r,2}^o = -282.98\frac{\text{kJ}}{\text{mol}}$

3) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O_{(g)}$ $\qquad \Delta\hat{H}_{r,3}^o = -241.83\frac{\text{kJ}}{\text{mol}}$

The standard heats of reaction for reactions 1, 2 and 3 were obtained using the standard heats of formation of the molecules involved in each of these reactions, which are tabulated in Table B.1 of Felder & Rousseau.

In the steam-methane reforming reaction, 3 molecules of hydrogen are being produced. From the three combustion reactions shown above, reaction 3 is the only reaction where hydrogen is involved. In addition, the only combustion reaction containing methane, which is one of the reactants in the steam-methane reforming reaction, is reaction 1. Thus, if we multiply reaction 3 by 3 and substract it from reaction 1, we get:

$(CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O_{(g)}) - (3H_2 + \_\_\_\_O_2 \longrightarrow 3H_2O_{(g)})$

4) $CH_4 + 2O_2 + \_\_\_\_\_\_\_ \longrightarrow \_\_\_\_\_ + 2H_2O_{(g)} + 3H_2 + \frac{3}{2}O_2$

The enthalpy for this hypothetical chemical reaction will be given by:

$$\Delta\hat{H}^{o}_{r,4} = \Delta\hat{H}^{o}_{r,1} - 3\Delta\hat{H}^{o}_{r,3} = \left(\underline{\hspace{3cm}} \frac{\text{kJ}}{\text{mol}} \right) - 3\left(-241.83 \frac{\text{kJ}}{\text{mol}} \right)$$

Looking at reaction 4 as an algebraic expression, similar terms can be reduced to get:

4) $CH_4 + H_2O_{(g)} + \frac{1}{2}O_2 \longrightarrow CO_2 + 3H_2$ $\quad \Delta\hat{H}^{o}_{r,4} = \underline{\hspace{3cm}} \frac{\text{kJ}}{\text{mol}}$

If we substract reaction 2 from reaction 4, we have:

$$(CH_4 + H_2O_{(g)} + \frac{1}{2}O_2 \longrightarrow CO_2 + 3H_2) - (CO + \frac{1}{2}O_2 \longrightarrow CO_2)$$

5) $CH_4 + H_2O_{(g)} + \frac{1}{2}O_2 + CO_2 \longrightarrow CO_2 + 3H_2 + CO + \frac{1}{2}O_2$

with a standard enthalpy of reaction given by:

$$\Delta\hat{H}^{o}_{r,5} = \Delta\hat{H}^{o}_{r,4} - \Delta\hat{H}^{o}_{r,2} = \left(\underline{\hspace{3cm}} \frac{\text{kJ}}{\text{mol}} \right) - \left(-282.98 \frac{\text{kJ}}{\text{mol}} \right)$$

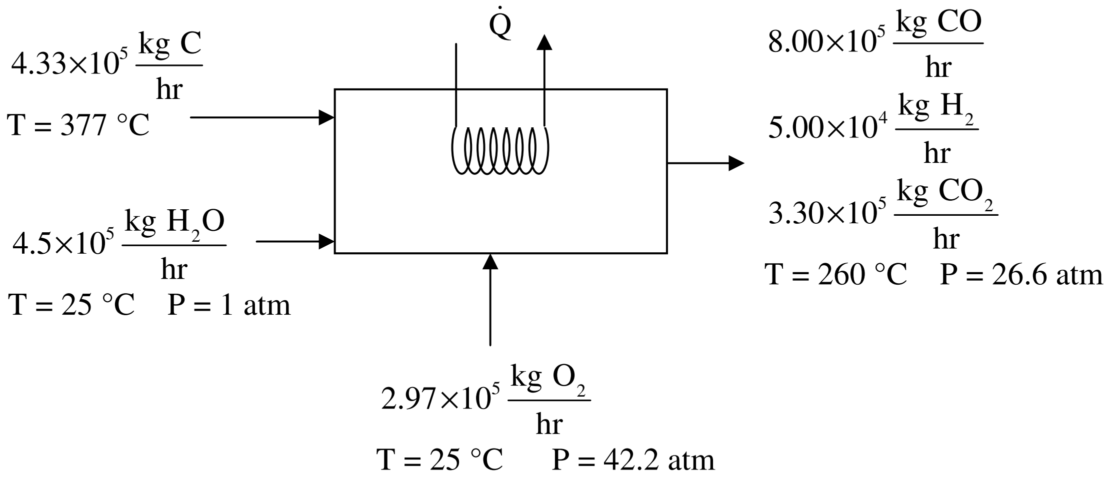
After reducing similar terms in reaction 5, we get the reaction occurring in the steam methane reforming process:

5) $CH_4 + H_2O_{(g)} \longrightarrow CO + 3H_2$ $\quad \Delta\hat{H}^{o}_{r,5} = \underline{\hspace{3cm}} \frac{\text{kJ}}{\text{mol}}$

It can be seen that the standard heat of reaction obtained using heats of formation is almost identical to the standard heat of reaction obtained by looking for tabulated heats of combustion. Hence, it is valid to use standard heats of combustion for the species involved in the steam-methane reforming process.

Example 9.5-1 Energy Balance on a Coal Gasification Process

A central coal gasification plant is producing hydrogen as shown in the diagram below:



The following reactions are occurring in the coal gasification process:

$$C_{(s)} + \frac{1}{2}O_2 \longrightarrow CO \qquad \dot{n}_{C,1} = 4.30\times10^4 \frac{\text{kg C}}{\text{hr}} \qquad \Delta\hat{H}^o_{r,1} = -110.52\frac{\text{kJ}}{\text{mol}}$$

$$C_{(s)} + O_2 \longrightarrow CO_2 \qquad \dot{n}_{C,2} = 9.00\times10^4 \frac{\text{kg C}}{\text{hr}} \qquad \Delta\hat{H}^o_{r,2} = -393.5\frac{\text{kJ}}{\text{mol}}$$

$$C_{(s)} + H_2O_{(l)} \longrightarrow CO + H_2 \qquad \dot{n}_{C,3} = 3.00\times10^5 \frac{\text{kg C}}{\text{hr}} \qquad \Delta\hat{H}^o_{r,3} = 175.32\frac{\text{kJ}}{\text{mol}}$$

The numbers at the right of each chemical reaction are showing the consumption rate of carbon and the enthalpy of each reaction. Determine the amount of heat released by the coal gasification process if the reference states for all substances are at a temperature of 25 °C and a pressure of 1 atm.

Strategy

This problem can be solved by performing energy balances around the reactor. Since there are three chemical reactions occurring in this process, they must be considered when evaluating the heat transfer rates.

Solution

The energy balance equation for this problem is given by:

$\dot{Q} = \Delta\dot{H}$ (negligible potential and kinetic energies and no shaft work since there are no mechanical parts moving)

The rate of change in enthalpy for this problem, considering the chemical reactions, can be calculated using the equation shown below:

$$\Delta\dot{H} = \sum \dot{\xi}_i \Delta\hat{H}^{o}_{r,i} + \sum \dot{n}_{out}\hat{H}_{out} - \sum \dot{n}_{in}\hat{H}_{in}$$

Applying this equation to the conditions in this problem, we get:

$$\Delta\dot{H} = \dot{\xi}_1 \Delta\hat{H}^{o}_{r,1} + \dot{\xi}_2 \Delta\hat{H}^{o}_{r,2} + \dot{\xi}_3 \Delta\hat{H}^{o}_{r,3} + \dot{n}_{CO}\hat{H}_{CO} + \dot{n}_{CO_2}\hat{H}_{CO_2} + \dot{n}_{H_2}\hat{H}_{H_2} - \dot{n}_{C}\hat{H}_{C} - \dot{n}_{H_2O}\hat{H}_{H_2O} - \dot{n}_{O_2}\hat{H}_{O_2}$$

The flow rates and enthalpies for each one of the compounds in this problem are summarized in the following table:

Substance	$\dot{n}_{in}\left(\frac{\text{mol}}{\text{hr}}\right)$	$\hat{H}_{in}\left(\frac{\text{kJ}}{\text{mol}}\right)$	$\dot{n}_{out}\left(\frac{\text{mol}}{\text{hr}}\right)$	$\hat{H}_{out}\left(\frac{\text{kJ}}{\text{mol}}\right)$
C	$\dot{n}_C$	$\hat{H}_C$	–	–
O_2	$\dot{n}_{O_2}$	0	–	–
H_2O	$\dot{n}_{H_2O}$	0	–	–
CO	–	–	$\dot{n}_{CO}$	$\hat{H}_{CO}$
CO_2	–	–	$\dot{n}_{CO_2}$	$\hat{H}_{CO_2}$
H_2	–	–	$\dot{n}_{H_2}$	$\hat{H}_{H_2}$

Since the water and oxygen are entering the reactor at the reference state conditions, there is no enthalpy change between the reference and process conditions. Thus, their enthalpies are equal to zero.

The process diagram is showing the mass flow rates for all the compounds. In order to calculate the molar flow rates, the mass flow rates must be divided by the corresponding molecular weight, as shown in the following calculations:

$$\dot{n}_C = \frac{\dot{m}_C}{M_C} = \frac{\underline{\qquad\qquad}\ \frac{\text{kg C}}{\text{hr}}}{\left(\underline{\quad}\ \frac{\text{kg C}}{\text{1 kmol C}}\right)\left(\frac{\text{1 kmol}}{\text{1000 moles}}\right)} = 3.608\times10^{7}\ \frac{\text{mol C}}{\text{hr}}$$

$$\dot{n}_{O_2} = \frac{\dot{m}_{O_2}}{M_{O_2}} = \frac{\underline{\qquad\qquad}\ \frac{\text{kg } O_2}{\text{hr}}}{\left(\underline{\quad}\ \frac{\text{kg } O_2}{\text{1 kmol } O_2}\right)\left(\frac{\text{1 kmol}}{\text{1000 moles}}\right)} = \underline{\qquad\qquad}\ \frac{\text{mol } O_2}{\text{hr}}$$

$$\dot{n}_{H_2O} = \frac{\dot{m}_{H_2O}}{M_{H_2O}} = \frac{\underline{\hspace{2.5cm}}\ \frac{\text{kg } H_2O}{\text{hr}}}{\left(\frac{18 \text{ kg } H_2O}{1 \text{ kmol } H_2O}\right)\left(\frac{1 \text{ kmol}}{1000 \text{ moles}}\right)} = \underline{\hspace{2.5cm}}\ \frac{\text{mol } H_2O}{\text{hr}}$$

$$\dot{n}_{CO} = \frac{\dot{m}_{CO}}{M_{CO}} = \frac{\underline{\hspace{2.5cm}}\ \frac{\text{kg CO}}{\text{hr}}}{\left(\frac{\underline{\hspace{1cm}} \text{ kg CO}}{1 \text{ kmol CO}}\right)\left(\frac{1 \text{ kmol}}{1000 \text{ moles}}\right)} = \underline{\hspace{2.5cm}}\ \frac{\text{mol CO}}{\text{hr}}$$

$$\dot{n}_{CO_2} = \frac{\dot{m}_{CO_2}}{M_{CO_2}} = \frac{\underline{\hspace{2.5cm}}\ \frac{\text{kg } CO_2}{\text{hr}}}{\left(\frac{44 \text{ kg } CO_2}{1 \text{ kmol } CO_2}\right)\left(\frac{1 \text{ kmol}}{1000 \text{ moles}}\right)} = \underline{\hspace{2.5cm}}\ \frac{\text{mol } CO_2}{\text{hr}}$$

$$\dot{n}_{H_2} = \frac{\dot{m}_{H_2}}{M_{H_2}} = \frac{\underline{\hspace{2.5cm}}\ \frac{\text{kg } H_2}{\text{hr}}}{\left(\frac{2 \text{ kg } H_2}{1 \text{ kmol } H_2}\right)\left(\frac{1 \text{ kmol}}{1000 \text{ moles}}\right)} = \underline{\hspace{2.5cm}}\ \frac{\text{mol } H_2}{\text{hr}}$$

The enthalpies of the gas species in this process, can be obtained from Table B.8 of Felder & Rousseau by linear interpolation at the corresponding temperature.

The linear interpolation is set as:

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

Solving this equation for the unknown enthalpy $\hat{H}_i$ gives:

$$\hat{H}_i = \left(\frac{T_{mid} - T_{low}}{T_{high} - T_{low}}\right)\left(\hat{H}_{T_{high}} - \hat{H}_{T_{low}}\right) + \hat{H}_{T_{low}}$$

The following tables are showing the data from Table B.8 of Felder & Rousseau used to obtain the enthalpy at the actual process conditions:

Carbon dioxide

T (°C)	$\hat{H}\left(\frac{\text{kJ}}{\text{mol}}\right)$
200	5.16
260	______
300	8.17

Carbon monoxide

T (°C)	$\hat{H}\left(\frac{\text{kJ}}{\text{mol}}\right)$
200	7.08
260	**9.78**
300	11.58

Hydrogen

T (°C)	$\hat{H}\left(\frac{\text{kJ}}{\text{mol}}\right)$
200	5.06
260	______
300	7.96

Substituting these tabulated values into the interpolation equation solved for the unknown enthalpy $\hat{H}_i$, we have:

$$\hat{H}_{CO} = \left(\frac{260°\text{C} - 200°\text{C}}{300°\text{C} - 200°\text{C}}\right)\left(8.17\frac{\text{kJ}}{\text{mol}} - 5.16\frac{\text{kJ}}{\text{mol}}\right) + 5.16\frac{\text{kJ}}{\text{mol}} = \underline{\qquad}\frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}_{CO_2} = \left(\frac{260°\text{C} - 200°\text{C}}{300°\text{C} - 200°\text{C}}\right)\left(\underline{\qquad}\frac{\text{kJ}}{\text{mol}} - \underline{\qquad}\frac{\text{kJ}}{\text{mol}}\right) + \underline{\qquad}\frac{\text{kJ}}{\text{mol}} = 9.78\frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}_{H_2} = \left(\frac{260°\text{C} - 200°\text{C}}{300°\text{C} - 200°\text{C}}\right)\left(7.96\frac{\text{kJ}}{\text{mol}} - \underline{\qquad}\frac{\text{kJ}}{\text{mol}}\right) + \underline{\qquad}\frac{\text{kJ}}{\text{mol}} = \underline{\qquad}\frac{\text{kJ}}{\text{mol}}$$

So far, we have calculated the enthalpy of oxygen, carbon monoxide, carbon dioxide and hydrogen due to the temperature difference with respect to the reference temperature. It can be seen in the process diagram that there is a difference in the pressure of these species with respect to the reference pressure. However, if we assume ideal gas behavior, the change in enthalpy with respect to pressure at constant temperature is equal to zero.

Since we do not have tabulated values for the enthalpies of carbon, we will use the definition of enthalpy as a function of the heat capacity.

$$\hat{H}_C\left(\frac{\text{kJ}}{\text{mol}}\right) = \int_{T_{ref}}^{T} C_{p,C}(T)dT$$

The heat capacity equation as a function of temperature for carbon was obtained from Table 2-151 of *Perry's Chemical Engineers' Handbook*, 8th Edition:

$$C_{p,C}\left(\frac{\text{kJ}}{\text{mol}\cdot°\text{C}}\right) = \left(1.118\times10^{-2}\right) + (\underline{\qquad\qquad})T - \frac{(\underline{\qquad\quad})}{T^2}$$

After substituting this expression into the enthalpy of carbon and integrating, we get:

$$\hat{H}_C\left(\frac{\text{kJ}}{\text{mol}}\right)=\left(1.118\times10^{-2}\right)\left[(\underline{\qquad}\,{}^\circ\text{C})-(25^\circ\text{C})\right]+(\underline{\qquad\qquad\quad})\left[(\underline{\qquad}\,{}^\circ\text{C})^2-(25^\circ\text{C})^2\right]$$
$$+\frac{(\underline{\qquad\quad})}{\left[(\underline{\qquad}\,{}^\circ\text{C})-(25^\circ\text{C})\right]}$$

$$\hat{H}_C=\underline{\qquad\quad}\ \frac{\text{kJ}}{\text{mol}}$$

Now all the calculated enthalpies and molar flow rates can be entered into the table to get:

Substance	$\dot{n}_{in}\left(\frac{\text{mol}}{\text{hr}}\right)$	$\hat{H}_{in}\left(\frac{\text{kJ}}{\text{mol}}\right)$	$\dot{n}_{out}\left(\frac{\text{mol}}{\text{hr}}\right)$	$\hat{H}_{out}\left(\frac{\text{kJ}}{\text{mol}}\right)$
C	$3.608\times10^{7}\ \frac{\text{mol C}}{\text{hr}}$	$\underline{\qquad\quad}$	–	–
O_2	$\underline{\qquad\qquad}\ \frac{\text{mol } O_2}{\text{hr}}$	0	–	–
H_2O	$\underline{\qquad\qquad}\ \frac{\text{mol } H_2}{\text{hr}}$	0	–	–
CO	–	–	$\underline{\qquad\qquad}\ \frac{\text{mol CO}}{\text{hr}}$	$\underline{\qquad\quad}$
CO_2	–	–	$\underline{\qquad\qquad}\ \frac{\text{mol } CO_2}{\text{hr}}$	9.78
H_2	–	–	$\underline{\qquad\qquad}\ \frac{\text{mol } H_2}{\text{hr}}$	$\underline{\qquad\quad}$

To calculate the heat released by the coal gasification process, we now need to determine the heat transfer rates due to the chemical reactions. In order to do this, first we need to calculate the extent of each one of the reactions occurring in this process. The extent of each one of the reactions can be calculated as follows:

$$\dot{\xi}_1=\frac{(\dot{n}_{C,1})}{|\nu_{C,1}|}=\frac{4.30\times10^{4}\ \frac{\text{kg C}}{\text{hr}}\left(\frac{1\text{ kmol C}}{12\text{ kg C}}\right)\left(\frac{1000\text{ moles}}{1\text{ kmol}}\right)}{1}=\underline{\qquad\qquad}\ \frac{\text{moles C}}{\text{hr}}$$

$$\dot{\xi}_2=\frac{(\dot{n}_{C,2})}{|\nu_{C,2}|}=\frac{\underline{\qquad\qquad}\ \frac{\text{kg C}}{\text{hr}}\left(\frac{1\text{ kmol C}}{12\text{ kg C}}\right)\left(\frac{1000\text{ moles}}{1\text{ kmol}}\right)}{1}=\underline{\qquad\qquad}\ \frac{\text{moles C}}{\text{hr}}$$

$$\dot{\xi}_3 = \frac{(\dot{n}_{C,3})}{|\nu_{C,3}|} = \frac{\underline{\hspace{3cm}}\ \frac{\text{kg C}}{\text{hr}}\left(\frac{1\text{ kmol C}}{12\text{ kg C}}\right)\left(\frac{1000\text{ moles}}{1\text{ kmol}}\right)}{1} = \underline{\hspace{3cm}}\ \frac{\text{moles C}}{\text{hr}}$$

The final step to solve this problem, is to substitute all the corresponding quantities into the energy balance equation, to get:

$$\begin{aligned}\Delta\dot{H} = &\left(\underline{\hspace{3cm}}\ \frac{\text{moles}}{\text{hr}}\right)\left(-110.52\frac{\text{kJ}}{\text{mol}}\right)+\left(\underline{\hspace{3cm}}\ \frac{\text{moles}}{\text{hr}}\right)\left(-393.5\frac{\text{kJ}}{\text{mol}}\right)\\ &+\left(\underline{\hspace{3cm}}\ \frac{\text{moles}}{\text{hr}}\right)\left(175.32\frac{\text{kJ}}{\text{mol}}\right)+\left(2.857\times10^{7}\ \frac{\text{mol CO}}{\text{hr}}\right)\left(6.97\frac{\text{kJ}}{\text{mol}}\right)\\ &+\left(\underline{\hspace{3cm}}\ \frac{\text{mol CO}_2}{\text{hr}}\right)\left(9.78\frac{\text{kJ}}{\text{mol}}\right)+\left(\underline{\hspace{3cm}}\ \frac{\text{mol H}_2}{\text{hr}}\right)\left(6.80\frac{\text{kJ}}{\text{mol}}\right)\\ &-\left(3.608\times10^{7}\ \frac{\text{mol}}{\text{hr}}\right)\left(\underline{\hspace{2cm}}\ \frac{\text{kJ}}{\text{mol}}\right)-\left(2.5\times10^{7}\ \frac{\text{mol}}{\text{hr}}\right)(0)-\left(9.281\times10^{6}\ \frac{\text{mol O}_2}{\text{hr}}\right)(0)\end{aligned}$$

$$\dot{Q} = \Delta\dot{H} = \underline{\hspace{3cm}}\ \frac{\text{kJ}}{\text{hr}}\left(\frac{1\text{ hr}}{3600\text{ s}}\right)$$

$$\boxed{\dot{Q} = \underline{\hspace{3cm}}\text{ kW}}$$

As the value of $\dot{Q}$ is positive, this amount of energy needs to be input to this endothermic process.

9.5-2 Calculation of Heat of Formation of Woody Biomass

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

Element	Mol %
C	33.3
H	46.7
O	20.0

The following equation represents the combustion reaction of woody biomass.

$$C_{0.333}H_{0.467}O_{0.200} + O_2 \longrightarrow CO_2 + H_2O_{(v)}$$

Note that this is the unbalanced equation for the combustion of biomass.

Determine the molar and mass heats of formation of the biomass assuming that the products of the combustion reaction are leaving at 25°C. The heat of combustion of this type of biomass is $-116.62\frac{\text{kJ}}{\text{mol}}$.

Strategy

The heat of formation of biomass can be determined by using the definition of standard heat of reaction.

Solution

First of all, we need to balance the chemical reaction equation. After writing the corresponding stoichiometric coefficients, the balanced equation will be given by:

$$C_{0.333}H_{0.467}O_{0.200} + \_\_\_\_\_\_\_\_ O_2 \longrightarrow 0.333CO_2 + 0.2335H_2O$$

The heat transfer rate from this reaction can be obtained using the equation for the standard heat of reaction:

$$\hat{Q} = \Delta\hat{H}_r^o = \sum_{\text{products}} |\nu_i| \Delta\hat{H}_{f,i}^o - \sum_{\text{reactants}} |\nu_i| \Delta\hat{H}_{f,i}^o$$

Applying this equation for the chemical reaction taking place in this process, we have:

$$\hat{Q} = \left|\nu_{H_2O}\right| \Delta\hat{H}_{f,H_2O}^o + \left|\nu_{CO_2}\right| \Delta\hat{H}_{f,CO_2}^o - \left|\nu_{\text{biomass}}\right| \Delta\hat{H}_{f,\text{biomass}}^o$$

The heats of formation of CO_2 and $H_2O_{(v)}$ can be obtained from Table B.1 of Felder & Rousseau to be:

$$\Delta\hat{H}^{o}_{f,H_2O} = \underline{\hspace{3cm}} \frac{\text{kJ}}{\text{mol}}$$

$$\Delta\hat{H}^{o}_{f,CO_2} = \underline{\hspace{3cm}} \frac{\text{kJ}}{\text{mol}}$$

The higher heating value of a fuel is defined as the amount of heat released by combustion of a specified amount of fuel after the products of the combustion reaction have returned to a temperature of 25°C. Since the products of this reaction are exiting the reactor at 25°C, the amount of heat transferred to the system will be equal to the higher heating value of the biomass, which can be calculated as follows:

$$\text{HHV}_{\text{biomass}} = \text{LHV}_{\text{biomass}} + n_{H_2O}\Delta\hat{H}_{v,H_2O}$$

where:

$\text{LHV}_{\text{biomass}}$ = Lower heating value of biomass

$\Delta\hat{H}_{v,H_2O}$ = Heat of vaporization of water (found in Table B.1 of Felder & Rousseau)

n_{H_2O} = number of moles of water produced by the combustion reaction per mol of fuel

The lower heating value of a fuel is equal to the negative of its heat of combustion. Thus, substituting all the corresponding quantities into this equation yields:

$$\text{HHV}_{\text{biomass}} = 116.62\frac{\text{kJ}}{\text{mol biomass}} + \left(\underline{\hspace{3cm}}\frac{\text{mol } H_2O}{\text{mol biomass}}\right)\left(\underline{\hspace{3cm}}\frac{\text{kJ}}{\text{mol } H_2O}\right)$$

$$\text{HHV}_{\text{biomass}} = \underline{\hspace{2cm}}\frac{\text{kJ}}{\text{mol biomass}}$$

Since the process of combustion of biomass and the cooling of the products to a temperature of 25° C is an exothermic process, the amount of heat transferred will be negative:

$$\hat{Q} = -\text{HHV}_{\text{biomass}} = -126.9\frac{\text{kJ}}{\text{mol biomass}}$$

Now we know all the unknown values have been calculated, the equation for the standard enthalpy of reaction can be solved for the heat of formation of biomass to yield:

$$\Delta\hat{H}^{o}_{f,\text{biomass}} = \frac{HHV_{\text{biomass}} - \left|\nu_{H_2O}\right|\Delta\hat{H}^{o}_{f,H_2O} - \left|\nu_{CO_2}\right|\Delta\hat{H}^{o}_{f,CO_2}}{-\left|\nu_{\text{biomass}}\right|}$$

Substituting the stoichiometric coefficient and enthalpies of formation of the products, as well as the higher heating value of biomass, we get:

$$\Delta\hat{H}^{o}_{f,\text{biomass}} = \frac{\underline{\qquad\quad}\,\frac{\text{kJ}}{\text{mol biomass}} - 0.2335\left(\underline{\qquad\quad}\,\frac{\text{kJ}}{\text{mol}}\right) - 0.333\left(\underline{\qquad\quad}\,\frac{\text{kJ}}{\text{mol}}\right)}{-1}$$

$$\boxed{\Delta\hat{H}^{o}_{f,\text{biomass}} = \underline{\qquad\quad}\,\frac{\text{kJ}}{\text{mol biomass}}}$$

We can estimate the energy available in 1 kg of biomass by dividing this result by the molecular weight of the biomass, which is calculated using the molar fraction of each component, as shown in the following steps:

$$M_{\text{biomass}} = x_C M_C + x_H M_H + x_O M_O$$

Substituting the corresponding values in this equation yields:

$$M_{\text{biomass}} = 0.333\left(\frac{\underline{\quad}\text{ g C}}{1\text{ mol C}}\right)\left(\frac{1\text{ kg}}{1000\text{ g}}\right) + \underline{\qquad}\left(\frac{\underline{\quad}\text{ g H}}{1\text{ mol H}}\right)\left(\frac{1\text{ kg}}{1000\text{ g}}\right) + \underline{\qquad}\left(\frac{16\text{ g O}}{1\text{ mol O}}\right)\left(\frac{1\text{ kg}}{1000\text{ g}}\right)$$

$$M_{\text{biomass}} = \underline{\qquad\quad}\,\frac{\text{kg}}{\text{mol}}$$

Finally, the amount of energy available per kg of biomass is given by:

$$\Delta\tilde{H}^{o}_{f,\text{biomass}} = \frac{\underline{\qquad\quad}\,\frac{\text{kJ}}{\text{mol}}\left(\frac{1\text{ MJ}}{1000\text{ kJ}}\right)}{\underline{\qquad\quad}\,\frac{\text{kg}}{\text{mol}}}$$

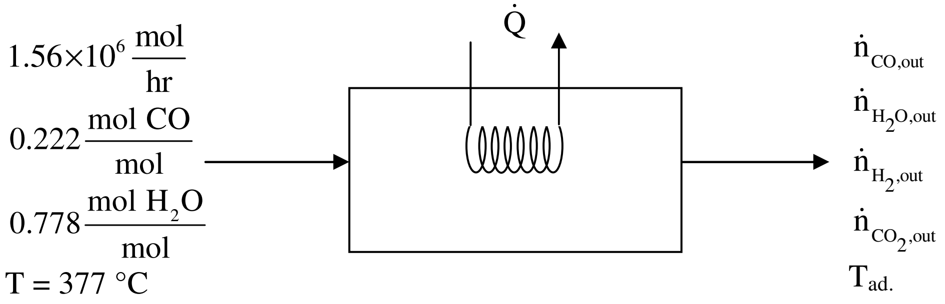
$$\boxed{\Delta\tilde{H}^{o}_{f,\text{biomass}} = \underline{\qquad}\,\frac{\text{MJ}}{\text{kg}}}$$

9.5-3 Energy Balance on an Adiabatic Reactor

The following water-gas shift reaction is occurring in a mid-scale adiabatic reactor:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

The following flowchart is showing the process conditions for the water-gas shift reaction process:



Determine the temperature of the product stream if 36 % of the carbon monoxide is converted into products.

Strategy

We will have to perform an energy balance on the reactor. The molar flow rates of each gas in the product stream will be calculated using the information regarding the conversion of carbon monoxide.

Solution

The energy balance equation applied for the process occurring in this problem is given by:

$$\dot{Q} = \Delta\dot{H} = \xi\Delta\hat{H}_r^o + \sum \dot{n}_{out}\hat{H}_{out} - \sum \dot{n}_{in}\hat{H}_{in} = 0$$

Notice that the energy balance equation was set equal to zero. This is due to the fact that the reactor is operating adiabatically.

The extent of reaction is defined by the following equation:

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

The extent of reaction will be calculated for the carbon monoxide, since it is the limiting reactant. It can be seen that the flow rate of carbon monoxide leaving the reactor is not given directly in the process diagram. However, it can be calculated using the value given for the fractional conversion of this gas.

The following equation defines the fractional conversion x for carbon monoxide:

$$x_{CO} = \frac{\left(\dot{n}_{CO,in}\right) - \left(\dot{n}_{CO,out}\right)}{\left(\dot{n}_{CO,in}\right)}$$

Substituting the known flow rate and the fractional conversion x_{CO}, and solving for the flow rate of carbon monoxide leaving the reactor, we get:

$$\left(\dot{n}_{CO,out}\right) = \left(\dot{n}_{CO,in}\right)\left(1 - x_{CO}\right) = \left[\left(\text{\_\_\_\_\_\_\_\_\_\_}\frac{\text{mol}}{\text{hr}}\right)\left(0.222\frac{\text{mol CO}}{\text{mol}}\right)(1 - \text{\_\_\_\_\_\_})\right]$$

$$\left(\dot{n}_{CO,out}\right) = \text{\_\_\_\_\_\_\_\_\_\_}\frac{\text{mol CO}}{\text{hr}}$$

This value and the flow rate of carbon monoxide entering the reactor can be substituted into the definition of the extent of reaction ξ to give:

$$\xi = \frac{|(\dot{n}_{CO})_{out} - (\dot{n}_{CO})_{in}|}{|\nu_{CO}|} = \frac{\left|\text{\_\_\_\_\_\_\_\_\_\_}\frac{\text{mol}}{\text{hr}} - \left(\text{\_\_\_\_\_\_\_\_\_\_}\frac{\text{mol}}{\text{hr}}\right)\left(0.222\frac{\text{mol CO}}{\text{mol}}\right)\right|}{|-1|}$$

$$\xi = \text{\_\_\_\_\_\_\_\_\_\_}\frac{\text{mol}}{\text{hr}}$$

The next unknown term in the energy balance equation is the standard enthalpy of reaction $\Delta\hat{H}_r^o$, which can be calculated from the heats of formation of the species involved in the water-gas shift reaction. These heats of formation can be obtained from Table 2-220 of *Perry's Chemical Engineers' Handbook*, 7th Edition.

$$\Delta\hat{H}_r^o = \nu_{CO_2}\Delta\hat{H}_{f,CO_2}^o + \nu_{H_2}\Delta\hat{H}_{f,H_2}^o + \nu_{H_2O}\Delta\hat{H}_{f,H_2O}^o + \nu_{CO}\Delta\hat{H}_{f,CO}^o$$

$$\Delta\hat{H}_r^o = (1)\left(\text{\_\_\_\_\_\_\_\_\_\_}\frac{\text{kJ}}{\text{mol}}\right) + (1)\left(\text{\_\_\_\_\_\_\_\_\_\_}\frac{\text{kJ}}{\text{mol}}\right) + (-1)\left(-241.83\frac{\text{kJ}}{\text{mol}}\right) + (-1)\left(\text{\_\_\_\_\_\_\_\_\_\_}\frac{\text{kJ}}{\text{mol}}\right)$$

$$\Delta\hat{H}_r^o = \text{\_\_\_\_\_\_\_\_\_\_}\frac{\text{kJ}}{\text{mol}}$$

The following table is summarizing the flow rates and enthalpies that need to be calculated in order to determine the temperature of the products. The reference states selected for the gases involved in the water-gas shift reaction process are shown above the table.

References: $CO_{(g)}$, $H_2O_{(g)}$, $H_{2\,(g)}$, $CO_{2\,(g)}$ @ T = 25ºC, P = 1 atm

Substance	$\dot{n}_{in}\left(\frac{mol}{hr}\right)$	$\hat{H}_{in}\left(\frac{kJ}{mol}\right)$	$\dot{n}_{out}\left(\frac{mol}{hr}\right)$	$\hat{H}_{out}\left(\frac{kJ}{mol}\right)$
CO	$\dot{n}_{CO,in}$	$\hat{H}_{CO,in}$	__________	$\hat{H}_{CO,out}$
H_2O	$\dot{n}_{H_2O,in}$	$\hat{H}_{H_2O,in}$	$\dot{n}_{H_2O,out}$	$\hat{H}_{H_2O,out}$
H_2	–	–	$\dot{n}_{H_2,out}$	$\hat{H}_{H_2,out}$
CO_2	–	–	$\dot{n}_{CO_2,out}$	$\hat{H}_{CO_2,out}$

The enthalpies of the species entering the reactor can be obtained by multiplying the overall inlet flow rate by the corresponding molar fraction:

$$\dot{n}_{CO,in} = y_{CO,in}\dot{n}_{in} = \left(1.56\times10^6\,\frac{mol}{hr}\right)\left(\_\_\_\_\_\_\_\_\_\_\,\frac{mol\ CO}{mol}\right) = \_\_\_\_\_\_\_\_\_\_\,\frac{mol\ CO}{hr}$$

$$\dot{n}_{H_2O,in} = y_{H_2O,in}\dot{n}_{in} = \left(1.56\times10^6\,\frac{mol}{hr}\right)\left(\_\_\_\_\_\_\_\_\_\_\,\frac{mol\ H_2O}{mol}\right) = \_\_\_\_\_\_\_\_\_\_\,\frac{mol\ H_2O}{hr}$$

To calculate the flow rates of the species leaving the reactor, we will use the fractional conversion of carbon monoxide.

In the chemical reaction equation, it can be seen that the ratio of the number of moles of steam to the number of moles of carbon monoxide is equal to one. Thus, the number of moles of water and carbon monoxide reacted will be the same. This can be written as:

$$\dot{n}_{CO,r} = \dot{n}_{H_2O,r} = \dot{n}_{CO,in}x_{CO} = \left(\_\_\_\_\_\_\_\_\_\_\,\frac{mol\ CO}{hr}\right)(\_\_\_\_\_\_)$$

$$\dot{n}_{H_2O,r} = \_\_\_\_\_\_\_\_\_\_\,\frac{mol\ H_2O}{hr}$$

Hence, the flow rate of water in the product stream will be given by:

$$\dot{n}_{H_2O,out} = \dot{n}_{H_2O,in} - \dot{n}_{H_2O,r} = \_\_\_\_\_\_\_\_\_\_\,\frac{mol\ H_2O}{hr} - \_\_\_\_\_\_\_\_\_\_\,\frac{mol\ H_2O}{hr}$$

$$\dot{n}_{H_2O,out} = \_\_\_\_\_\_\_\_\_\_ \frac{\text{mol } H_2O}{\text{hr}}$$

By analyzing at the stoichiometry of the chemical reaction, it can be seen that 1 mol of carbon monoxide produces 1 mol of hydrogen and 1 mol of carbon dioxide. Hence, the number of moles of hydrogen and carbon dioxide produced will be equal to the amount of carbon monoxide reacted.

$$\dot{n}_{CO,r} = \dot{n}_{H_2,out} = \dot{n}_{CO_2,out} = 1.25\times10^5 \frac{\text{mol}}{\text{hr}}$$

The enthalpies of the gases in the inlet stream can be obtained from Table B.8 of Felder & Rousseau by linear interpolation for the temperature of 472ºC:

Carbon monoxide

T (°C)	$\hat{H}\left(\frac{\text{kJ}}{\text{mol}}\right)$
400	11.25
472	**13.50**
500	14.38

Steam

T (°C)	$\hat{H}\left(\frac{\text{kJ}}{\text{mol}}\right)$
400	13.23
472	______
500	17.01

The linear interpolation is set as:

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

Solving this equation for the unknown enthalpy $\hat{H}_i$ gives:

$$\hat{H}_i = \left(\frac{T_{mid} - T_{low}}{T_{high} - T_{low}}\right)\left(\hat{H}_{T_{high}} - \hat{H}_{T_{low}}\right) + \hat{H}_{T_{low}}$$

Substituting the tabulated values into this equation, we have:

$$\hat{H}_{CO,in} = \left(\frac{\_\_\_\_\_ {}^\circ C - 400^\circ C}{\_\_\_\_\_ {}^\circ C - 400^\circ C}\right)\left(14.38\frac{\text{kJ}}{\text{mol}} - \_\_\_\_\_\_\_ \frac{\text{kJ}}{\text{mol}}\right) + \_\_\_\_\_\_\_ \frac{\text{kJ}}{\text{mol}} = 13.50\frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}_{H_2O}=\left(\frac{\underline{\qquad}\,°C-400°C}{\underline{\qquad}\,°C-400°C}\right)\left(17.01\frac{kJ}{mol}-\underline{\qquad\quad}\frac{kJ}{mol}\right)+\underline{\qquad\quad}\frac{kJ}{mol}=\underline{\qquad\quad}\frac{kJ}{mol}$$

To calculate the remaining enthalpies, we will use the definition of enthalpy:

$$\dot{H}_i=\int_{T_{ref}}^{T_{ad}}C_{p,\,i}(T)dT$$

where:

i represents each one of the species leaving the reactor.

The equations for the heat capacity at constant pressure for the species in this problem can be obtained from Table B.2 of Felder & Rousseau to be:

$$C_{p,CO(g)}\left(\frac{kJ}{mol\cdot °C}\right)=\left(2.895\times10^{-2}\right)+(\underline{\qquad\qquad\quad})T+\left(3.548\times10^{-9}\right)T^2-\left(2.220\times10^{-12}\right)T^3$$

$$C_{p,H_2O(g)}\left(\frac{kJ}{mol\cdot °C}\right)=(\underline{\qquad\qquad\quad})+\left(6.88\times10^{-6}\right)T+\left(7.604\times10^{-9}\right)T^2-(\underline{\qquad\qquad\quad})T^3$$

$$C_{p,CO_2}\left(\frac{kJ}{mol\cdot °C}\right)=(\underline{\qquad\qquad\quad})+\left(4.233\times10^{-5}\right)T-(\underline{\qquad\qquad\quad})T^2+(\underline{\qquad\qquad\quad})T^3$$

$$C_{p,H_2}\left(\frac{kJ}{mol\cdot °C}\right)=(\underline{\qquad\qquad\quad})+(\underline{\qquad\qquad\quad})T+(\underline{\qquad\qquad\quad})T^2$$
$$-(\underline{\qquad\qquad\quad})T^3$$

Substituting and integrating the corresponding heat capacity equations into the definition of enthalpy, we get:

$$\hat{H}_{CO,out}\left(\frac{kJ}{mol}\right)=\left(2.895\times10^{-2}\right)T+(\underline{\qquad\qquad\quad})T^2+\left(1.183\times10^{-9}\right)T^3-\left(5.550\times10^{-13}\right)T^4\Big|_{T_{ref}}^{T_{ad}}$$

$$\hat{H}_{H_2O,out}\left(\frac{kJ}{mol}\right)=(\underline{\qquad\qquad\quad})T+\left(3.440\times10^{-6}\right)T^2+\left(2.535\times10^{-9}\right)T^3-(\underline{\qquad\qquad\quad})T^4\Big|_{T_{ref}}^{T_{ad}}$$

$$\hat{H}_{H_2,out}\left(\frac{kJ}{mol}\right)=\Big[(\underline{\qquad\qquad\quad})T+\left(3.825\times10^{-8}\right)T^2+(\underline{\qquad\qquad\quad})T^3$$
$$-(\underline{\qquad\qquad\quad})T^4\Big]\Big|_{T_{ref}}^{T_{ad}}$$

$$\hat{H}_{CO_2,out}\left(\frac{kJ}{mol}\right)=\Big[\left(\underline{\hspace{3cm}}\right)T+\left(\underline{\hspace{3cm}}\right)T^2-\left(\underline{\hspace{3cm}}\right)T^3$$
$$+\left(\underline{\hspace{3cm}}\right)T^4\Big]\Big|_{T_{ref}}^{T_{ad}}$$

Entering the temperature values into these equations yields:

$$\hat{H}_{CO,out}\left(\frac{kJ}{mol}\right)=\left(2.895\times10^{-2}\right)\left[T_{ad}-25^\circ C\right]+\left(\underline{\hspace{3cm}}\right)\left[\left(T_{ad}\right)^2-\left(25^\circ C\right)^2\right]$$
$$+\left(1.183\times10^{-9}\right)\left[\left(T_{ad}\right)^3-\left(25^\circ C\right)^3\right]-\left(5.550\times10^{-13}\right)\left[\left(T_{ad}\right)^4-\left(25^\circ C\right)^4\right]$$

$$\hat{H}_{CO,out}=\left(2.895\times10^{-2}\right)T_{ad}+\left(\underline{\hspace{3cm}}\right)T_{ad}{}^2+\left(1.183\times10^{-9}\right)T_{ad}{}^3-\left(5.550\times10^{-13}\right)T_{ad}{}^4-\underline{\hspace{1.5cm}}$$

$$\hat{H}_{H_2O,out}\left(\frac{kJ}{mol}\right)=\left(\underline{\hspace{3cm}}\right)\left[T_{ad}-25^\circ C\right]+\left(3.440\times10^{-6}\right)\left[\left(T_{ad}\right)^2-\left(25^\circ C\right)^2\right]$$
$$+\left(2.535\times10^{-9}\right)\left[\left(T_{ad}\right)^3-\left(25^\circ C\right)^3\right]-\left(\underline{\hspace{3cm}}\right)\left[\left(T_{ad}\right)^4-\left(25^\circ C\right)^4\right]$$

$$\hat{H}_{H_2O,out}=\left(\underline{\hspace{3cm}}\right)T_{ad}+\left(3.440\times10^{-6}\right)T_{ad}{}^2+\left(2.535\times10^{-9}\right)T_{ad}{}^3-\left(\underline{\hspace{3cm}}\right)T_{ad}{}^4$$
$$-\underline{\hspace{1.5cm}}$$

$$\hat{H}_{H_2,out}\left(\frac{kJ}{mol}\right)=\left(\underline{\hspace{3cm}}\right)\left[T_{ad}-25^\circ C\right]+\left(3.825\times10^{-8}\right)\left[\left(T_{ad}\right)^2-\left(25^\circ C\right)^2\right]$$
$$+\left(\underline{\hspace{3cm}}\right)\left[\left(T_{ad}\right)^3-\left(25^\circ C\right)^3\right]-\left(\underline{\hspace{3cm}}\right)\left[\left(T_{ad}\right)^4-\left(25^\circ C\right)^4\right]$$

$$\hat{H}_{H_2,out}=\left(\underline{\hspace{3cm}}\right)T_{ad}+\left(3.825\times10^{-8}\right)T_{ad}{}^2+\left(\underline{\hspace{3cm}}\right)T_{ad}{}^3-\left(\underline{\hspace{3cm}}\right)T_{ad}{}^4$$
$$-0.721$$

$$\hat{H}_{CO_2,out}\left(\frac{kJ}{mol}\right)=\left(\underline{\hspace{3cm}}\right)\left[T_{ad}-25^\circ C\right]+\left(\underline{\hspace{3cm}}\right)\left[\left(T_{ad}\right)^2-\left(25^\circ C\right)^2\right]$$
$$-\left(\underline{\hspace{3cm}}\right)\left[\left(T_{ad}\right)^3-\left(25^\circ C\right)^3\right]+\left(\underline{\hspace{3cm}}\right)\left[\left(T_{ad}\right)^4-\left(25^\circ C\right)^4\right]$$

$$\hat{H}_{CO_2,out} = (\underline{\qquad\qquad})T_{ad} + (\underline{\qquad\qquad})T_{ad}^{2} - (\underline{\qquad\qquad})T_{ad}^{3} + (\underline{\qquad\qquad})T_{ad}^{4} - 0.916$$

The energy balance equation applied for the number of chemical substances in this problem will be given by:

$$\xi\Delta\hat{H}_r^o + \dot{n}_{CO,out}\hat{H}_{CO,out} + \dot{n}_{H_2O,out}\hat{H}_{H_2O,out} + \dot{n}_{CO_2,out}\hat{H}_{CO_2,out} + \dot{n}_{H_2,out}\hat{H}_{H_2,out} - \dot{n}_{CO,in}\hat{H}_{CO,in} - \dot{n}_{H_2O,in}\hat{H}_{H_2O,in} = 0$$

The enthalpy equations for the gases in the product stream as a function of the adiabatic temperature T_{ad} are being multiplied by their corresponding molar flow rates in the energy balance equation. After entering the flow rate quantities, we have:

$$\dot{n}_{CO,out}\hat{H}_{CO,out} = \left(\underline{\qquad\qquad}\frac{mol}{hr}\right)\left[(2.895\times10^{-2})T_{ad} + (\underline{\qquad\qquad})T_{ad}^{2} + (1.183\times10^{-9})T_{ad}^{3} - (5.550\times10^{-13})T_{ad}^{4} - \underline{\qquad}\right]\frac{kJ}{mol}$$

$$\dot{n}_{CO,out}\hat{H}_{CO,out}\left(\frac{kJ}{hr}\right) = (6426.9)T_{ad} + (\underline{\quad})T_{ad}^{2} + (2.626\times10^{-4})T_{ad}^{3} - (1.232\times10^{-7})T_{ad}^{4} - (\underline{\qquad\quad})$$

$$\dot{n}_{H_2O,out}\hat{H}_{H_2O,out} = \underline{\qquad\qquad}\frac{mol}{hr}\left[(\underline{\qquad\qquad})T_{ad} + (3.440\times10^{-6})T_{ad}^{2} + (2.535\times10^{-9})T_{ad}^{3} - (\underline{\qquad\qquad})T_{ad}^{4} - \underline{\qquad}\right]\frac{kJ}{mol}$$

$$\dot{n}_{H_2O,out}\hat{H}_{H_2O,out}\left(\frac{kJ}{hr}\right) = (\underline{\qquad\quad})T_{ad} + (3.732)T_{ad}^{2} + (2.750\times10^{-3})T_{ad}^{3} - (\underline{\qquad\qquad})T_{ad}^{4} - (9.103\times10^{5})$$

$$\dot{n}_{H_2,out}\hat{H}_{H_2,out} = 1.25\times10^{5}\frac{mol}{hr}\left[(\underline{\qquad\qquad})T_{ad} + (3.825\times10^{-8})T_{ad}^{2} + (\underline{\qquad\qquad})T_{ad}^{3} - (\underline{\qquad\qquad})T_{ad}^{4} - 0.721\right]\frac{kJ}{mol}$$

$$\dot{n}_{H_2,out}\hat{H}_{H_2,out}\left(\frac{kJ}{hr}\right) = (\underline{\quad\;})T_{ad} + (4.781\times10^{-3})T_{ad}^{2} + (\underline{\qquad\qquad})T_{ad}^{3} - (\underline{\qquad\qquad})T_{ad}^{4} - (90125)$$

$$\dot{n}_{CO_2,out}\hat{H}_{CO_2,out} = 1.25\times10^5\,\frac{mol}{hr}\Big[(\underline{\qquad\qquad\quad})T_{ad} + (\underline{\qquad\qquad\quad})T_{ad}^{\;2} - (\underline{\qquad\qquad\quad})T_{ad}^{\;3}$$
$$+(\underline{\qquad\qquad\quad})T_{ad}^{\;4} - 0.916\Big]\frac{kJ}{mol}$$

$$\dot{n}_{CO_2,out}\hat{H}_{CO_2,out}\left(\frac{kJ}{hr}\right) = (\underline{\qquad\quad})T_{ad} + (\underline{\qquad\quad})T_{ad}^{\;2} - (\underline{\qquad\qquad\quad})T_{ad}^{\;3}$$
$$+(\underline{\qquad\qquad\quad})T_{ad}^{\;4} - 1.145\times10^5$$

Substituting the known quantities and the enthalpy equations into the energy balance gives:

$$\Delta\dot{H} = \left(1.24\times10^5\,\frac{mol}{hr}\right)\left(-41.16\frac{kJ}{mol}\right) + \Big[(6426.9)T_{ad} + (\underline{\qquad})T_{ad}^{\;2} + (2.626\times10^{-4})T_{ad}^{\;3}$$
$$-(1.232\times10^{-7})T_{ad}^{\;4} - (\underline{\qquad\quad\;})\Big]\frac{kJ}{hr} + \Big[(\underline{\qquad\quad})T_{ad} + (3.732)T_{ad}^{\;2} + (2.750\times10^{-3})T_{ad}^{\;3}$$
$$-(\underline{\qquad\qquad\quad})T_{ad}^{\;4} - (\underline{\qquad\qquad\quad})\Big]\frac{kJ}{hr} + \Big[(\underline{\qquad\quad})T_{ad} + (2.646)T_{ad}^{\;2}$$
$$-(\underline{\qquad\qquad\quad})T_{ad}^{\;3} + (\underline{\qquad\qquad\quad})T_{ad}^{\;4} - (1.145\times10^5)\Big]\frac{kJ}{hr} + \Big[(\underline{\qquad})T_{ad}$$
$$+(\underline{\qquad\qquad\quad})T_{ad}^{\;2} + (\underline{\qquad\qquad\quad})T_{ad}^{\;3} - (\underline{\qquad\qquad})T_{ad}^{\;4} - (9.013\times10^4)\Big]\frac{kJ}{hr}$$
$$-\left(3.46\times10^5\,\frac{mol\ CO}{hr}\right)\left(\underline{\qquad\quad}\frac{kJ}{mol}\right) - \left(\underline{\qquad\qquad}\frac{mol}{hr}\right)\left(15.95\frac{kJ}{mol}\right) = 0$$

Similar terms can be reduced in this equation to get:

$$\Delta\dot{H} = -(\underline{\qquad\qquad\quad})T_{ad}^{\;4} + (\underline{\qquad\qquad\quad})T_{ad}^{\;3} + (6.839)T_{ad}^{\;2} + (50849.8)T_{ad} - (\underline{\qquad\qquad\quad}) = 0$$

The adiabatic temperature T_{ad} can be obtained by solving this equation using numerical methods or computer software. The temperature was found to be:

$$\boxed{T_{ad} = \underline{\qquad\quad}\ ^{\circ}C}$$

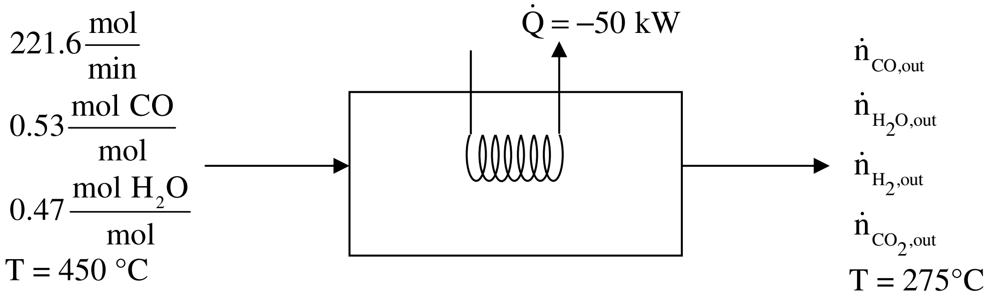
This temperature can be substituted into the enthalpy equations for each substance. After doing this, the table with the molar flow rates and enthalpies would be:

Substance	$\dot{n}_{in}\left(\frac{mol}{hr}\right)$	$\hat{H}_{in}\left(\frac{kJ}{mol}\right)$	$\dot{n}_{out}\left(\frac{mol}{hr}\right)$	$\hat{H}_{out}\left(\frac{kJ}{mol}\right)$
CO	3.46×10^5	13.50	2.22×10^5	16.01
H_2O	1.21×10^6	_______	1.085×10^6	_______
H_2	–	–	1.25×10^5	_______
CO_2	–	–	1.25×10^5	_______

9.5-4 Simultaneous Material and Energy Balances

The water-gas shift reaction process described in example 9.5-3 is now carried out in a plant operating on small (distributed) scale. The feed contains 53 mol % of carbon monoxide and the rest is steam. In order to keep the temperature from increasing, thus decreasing the forward reaction rate, heat is being removed from the reactor at a rate of 50 kW.

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$



Determine the fractional conversion of carbon monoxide into products.

Strategy

We can perform an energy balance on the reactor to help determining the fractional conversion of carbon monoxide. However, since there are 4 unknown flow rates in this process, we will need additional equations to solve this problem. Therefore, we will use material balances for the elements present in this process.

Solution

The fractional conversion of carbon monoxide is given by:

$$x_{CO} = \frac{\dot{n}_{CO,in} - \dot{n}_{CO,out}}{\dot{n}_{CO,in}}$$

We can calculate the flow rate of carbon monoxide and steam in the inlet stream by multiplying the overall flow rate by the molar fraction:

$$\dot{n}_{CO,in} = y_{CO,in}\dot{n}_{in}$$

$$\dot{n}_{H_2O,in} = y_{H_2O,in}\dot{n}_{in} ,$$

where $\dot{n}_{in}$ is the total molar flow rate entering the reactor.

Substituting numeric values into these equations, we have:

$$\dot{n}_{CO,in} = \left(0.53\frac{\text{mol CO}}{\text{mol}}\right)\left(\underline{\qquad}\frac{\text{mol}}{\text{min}}\right) = 117.45\frac{\text{mol CO}}{\text{min}}$$

$$\dot{n}_{H_2O,in} = \left(\underline{\qquad}\frac{\text{mol H}_2\text{O}}{\text{mol}}\right)\left(\underline{\qquad}\frac{\text{mol}}{\text{min}}\right) = \underline{\qquad}\frac{\text{mol H}_2\text{O}}{\text{min}}$$

To determine the molar flow rate of carbon monoxide in the product stream, we will have to perform material balances around the reactor for the three different atomic species forming the gases involved in the water-gas shift reaction:

Balance on C

Input = Output

$$\left(\underline{\qquad}\frac{\text{mol CO}}{\text{min}}\right)\left(\frac{1\text{ mol C}}{1\text{ mol CO}}\right) = \dot{n}_{CO,out}\left(\frac{\text{mol CO}}{\text{min}}\right)\left(\frac{1\text{ mol C}}{1\text{ mol CO}}\right) + \underline{\qquad}\left(\frac{\text{mol CO}}{\text{min}}\right)\left(\frac{1\text{ mol C}}{1\text{ mol CO}}\right)$$

Solving this equation for $\dot{n}_{CO,out}$, we get:

$$\dot{n}_{CO,out} = \left(\underline{\qquad}\frac{\text{mol CO}}{\text{min}}\right) - \underline{\qquad}\left(\frac{\text{mol CO}}{\text{min}}\right)$$

Balance on O

Input = Output

$$\begin{aligned}\left(\underline{\qquad}\frac{\text{mol CO}}{\text{min}}\right)\left(\frac{\underline{\quad}\text{ mol O}}{1\text{ mol CO}}\right) + \left(\underline{\qquad}\frac{\text{mol H}_2\text{O}}{\text{min}}\right)\left(\frac{1\text{ mol O}}{1\text{ mol H}_2\text{O}}\right) &= \dot{n}_{CO,out}\left(\frac{\text{mol CO}}{\text{min}}\right)\left(\frac{1\text{ mol O}}{1\text{ mol CO}}\right)\\ &+ \dot{n}_{CO_2,out}\left(\frac{\text{mol CO}_2}{\text{min}}\right)\left(\frac{2\text{ mol O}}{1\text{ mol CO}_2}\right)\\ &+ \dot{n}_{H_2O,out}\left(\frac{\text{mol H}_2\text{O}}{\text{min}}\right)\left(\frac{1\text{ mol O}}{1\text{ mol H}_2\text{O}}\right)\end{aligned}$$

Grouping the terms multiplied by the same factor and solving for $\dot{n}_{CO,out}$, yields:

$$\dot{n}_{CO,out} = \underline{\qquad}\frac{\text{mol CO}}{\text{min}} + \left(\underline{\qquad} - \dot{n}_{H_2O,out}\right)\frac{\text{mol CO}}{\text{min}} - 2\dot{n}_{CO_2,out}\frac{\text{mol CO}}{\text{min}}$$

Balance on H

Input = Output

$$\left(\underline{\hspace{3em}}\ \frac{\text{mol H}_2\text{O}}{\text{min}}\right)\left(\frac{2\text{ mol H}}{1\text{ mol H}_2\text{O}}\right)=\dot{n}_{\text{H}_2,\text{out}}\left(\frac{\text{mol H}_2}{\text{min}}\right)\left(\frac{\underline{\hspace{1em}}\ \text{mol H}}{1\text{ mol H}_2}\right)+\dot{n}_{\text{H}_2\text{O,out}}\left(\frac{\text{mol H}_2\text{O}}{\text{min}}\right)\left(\frac{2\text{ mol H}}{1\text{ mol H}_2\text{O}}\right)$$

The terms in this equation that are multiplied by the common factor $\left(\frac{2\text{ mol H}}{1\text{ mol H}_2\text{O}}\right)$ can be grouped. After grouping, we have:

$$\left(\frac{2\text{ mol H}}{1\text{ mol H}_2\text{O}}\right)\left[\underline{\hspace{4em}}\ \frac{\text{mol H}_2\text{O}}{\text{min}}-\underline{\hspace{4em}}\left(\frac{\text{mol H}_2\text{O}}{\text{min}}\right)\right]=\dot{n}_{\text{H}_2,\text{out}}\left(\frac{\text{mol H}_2}{\text{min}}\right)\left(\frac{2\text{ mol H}}{1\text{ mol H}_2}\right)$$

Solving for $\dot{n}_{\text{H}_2,\text{out}}$ yields:

$$\dot{n}_{\text{H}_2,\text{out}}\left(\frac{\text{mol H}_2}{\text{min}}\right)=\underline{\hspace{10em}}$$

So far, we have the following 3 equations with 4 unknown variables. Therefore, we need to obtain another equation from the energy balance in the reactor.

$$\dot{n}_{\text{CO,out}}\left(\frac{\text{mol CO}}{\text{min}}\right)=\underline{\hspace{5em}}-\dot{n}_{\text{CO}_2,\text{out}}$$

$$\dot{n}_{\text{CO,out}}\left(\frac{\text{mol CO}}{\text{min}}\right)=117.45+\left(104.15-\dot{n}_{\text{H}_2\text{O,out}}\right)-2\dot{n}_{\text{CO}_2,\text{out}}$$

$$\dot{n}_{\text{H}_2,\text{out}}\left(\frac{\text{mol H}_2}{\text{min}}\right)=\underline{\hspace{9em}}$$

Energy Balance

Input = Output

$\dot{Q}=\Delta\dot{H}=-50\text{ kW}$ (negligible potential and kinetic energies and no shaft work)

In this problem, the change in enthalpy $\Delta\dot{H}$ is given by:

$$\Delta\dot{H} = \sum \dot{n}_{out}\hat{H}_{out} - \sum \dot{n}_{in}\hat{H}_{in}$$

Applying this equation to the number of compounds involved in this reaction yields:

$$\Delta\dot{H} = \dot{n}_{CO,out}\hat{H}_{CO,out} + \dot{n}_{H_2O,out}\hat{H}_{H_2O,out} + \dot{n}_{CO_2,out}\hat{H}_{CO_2,out} + \dot{n}_{H_2,out}\hat{H}_{H_2,out} - \dot{n}_{CO,in}\hat{H}_{CO,in} - \dot{n}_{H_2O,in}\hat{H}_{H_2O,in} = -50\text{ kW}$$

The enthalpy of each substance will be obtained by the equation below:

$$\hat{H}_i = \Delta\hat{H}^o_{f,i} + \int_{T_{ref}}^{T} C_{p,i}(T)dT$$

The following table shows the reference states selected for this problem, as well as the flow rates and enthalpies that must be calculated. The reference states were selected for the chemical elements forming the substances involved in the reaction:

References: $C_{(s)}$, $H_{2(g)}$, $O_{2(g)}$ @ T = 25ºC, P = 1 atm

Substance	$\dot{n}_{in}\left(\frac{mol}{hr}\right)$	$\hat{H}_{in}\left(\frac{kJ}{mol}\right)$	$\dot{n}_{out}\left(\frac{mol}{hr}\right)$	$\hat{H}_{out}\left(\frac{kJ}{mol}\right)$
CO	$\dot{n}_{CO,in}$	$\hat{H}_{CO,in}$	$\dot{n}_{CO,out}$	$\hat{H}_{CO,out}$
H_2O	$\dot{n}_{H_2O,in}$	$\hat{H}_{H_2O,in}$	$\dot{n}_{H_2O,out}$	$\hat{H}_{H_2O,out}$
H_2	–	–	$\dot{n}_{H_2,out}$	$\hat{H}_{H_2,out}$
CO_2	–	–	$\dot{n}_{CO_2,out}$	$\hat{H}_{CO_2,out}$

The enthalpies of formation were obtained from Table 2-220 of Perry's Chemical Engineers' Handbook, 7th Edition.

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

$$\Delta\hat{H}^o_{f,CO_2} = \_\_\_\_\_\_\_\_\_\_ \frac{kJ}{mol}$$

$$\Delta\hat{H}^o_{f,H_2O} = \_\_\_\_\_\_\_\_\_\_ \frac{kJ}{mol}$$

The equations for the heat capacity at constant pressure for the species in this problem can be obtained from Table B.2 of Felder & Rousseau to be:

$$C_{p,CO(g)}\left(\frac{kJ}{mol\cdot °C}\right)=(\underline{\qquad\qquad})+\left(4.110\times10^{-6}\right)T+\left(3.548\times10^{-9}\right)T^2-\left(2.220\times10^{-12}\right)T^3$$

$$C_{p,H_2O(g)}\left(\frac{kJ}{mol\cdot °C}\right)=(\underline{\qquad\qquad})+(\underline{\qquad\qquad})T+\left(7.604\times10^{-9}\right)T^2-\left(3.593\times10^{-12}\right)T^3$$

$$C_{p,CO_2}\left(\frac{kJ}{mol\cdot °C}\right)=(\underline{\qquad\qquad})+\left(4.233\times10^{-5}\right)T-(\underline{\qquad\qquad})T^2+(\underline{\qquad\qquad})T^3$$

$$C_{p,H_2}\left(\frac{kJ}{mol\cdot °C}\right)=(\underline{\qquad\qquad})+(\underline{\qquad\qquad})T+\left(3.288\times10^{-9}\right)T^2-(\underline{\qquad\qquad})T^3$$

After substituting these equations into the definition of enthalpy, integrating and including the heats of formation, we get:

$$\hat{H}_{CO,in}\left(\frac{kJ}{mol}\right)=\Big[(\underline{\qquad\qquad})T+\left(2.055\times10^{-6}\right)T^2+\left(1.183\times10^{-9}\right)T^3$$
$$-\left(5.550\times10^{-13}\right)T^4\Big]\Big|_{T_{ref}}^{T_{in}}-110.52$$

$$\hat{H}_{H_2O,in}\left(\frac{kJ}{mol}\right)=\Big[(\underline{\qquad\qquad})T+(\underline{\qquad\qquad})T^2+\left(2.535\times10^{-9}\right)T^3$$
$$-\left(8.983\times10^{-13}\right)T^4\Big]\Big|_{T_{ref}}^{T_{in}}-241.83$$

$$\hat{H}_{CO,out}\left(\frac{kJ}{mol}\right)=\Big[(\underline{\qquad\qquad})T+\left(2.055\times10^{-6}\right)T^2+\left(1.183\times10^{-9}\right)T^3$$
$$-\left(5.550\times10^{-13}\right)T^4\Big]\Big|_{T_{ref}}^{T_{out}}-110.52$$

$$\hat{H}_{H_2O,out}\left(\frac{kJ}{mol}\right)=\Big[(\underline{\qquad\qquad\quad})T+(\underline{\qquad\qquad\quad})T^2+\left(2.535\times10^{-9}\right)T^3$$
$$-\left(8.983\times10^{-13}\right)T^4\Big]\Big|_{T_{ref}}^{T_{out}}-241.83$$

$$\hat{H}_{H_2,out}\left(\frac{kJ}{mol}\right)=\Big[(\underline{\qquad\qquad\quad})T+(\underline{\qquad\qquad\quad})T^2+\left(1.096\times10^{-9}\right)T^3$$
$$-(\underline{\qquad\qquad\quad})T\Big]^4\Big|_{T_{ref}}^{T_{out}}$$

$$\hat{H}_{CO_2,out}\left(\frac{kJ}{mol}\right)=\Big[(\underline{\qquad\qquad\qquad})T+\left(2.117\times10^{-5}\right)T^2-(\underline{\qquad\qquad\qquad})T^3$$

$$+(\underline{\qquad\qquad\qquad})T^4\Big]\Big|_{T_{ref}}^{T_{out}}-393.51$$

Where the inlet and outlet temperatures can be obtained from the process flow chart:

T_{in} = 450 °C
T_{out} = 275 °C

Entering the temperature values into these equations yields:

$$\hat{H}_{CO,in}\left(\frac{kJ}{mol}\right)=-110.52+(\underline{\qquad\qquad})[\underline{\qquad}{}^\circ C-25^\circ C]+\left(2.055\times10^{-6}\right)\left[(\underline{\qquad}{}^\circ C)^2-(25^\circ C)^2\right]$$

$$+\left(1.183\times10^{-9}\right)\left[(\underline{\qquad}{}^\circ C)^3-(25^\circ C)^3\right]-\left(5.550\times10^{-13}\right)\left[(\underline{\qquad}{}^\circ C)^4-(25^\circ C)^4\right]$$

$$\hat{H}_{CO,in}=\underline{\qquad\qquad}\frac{kJ}{mol}$$

$$\hat{H}_{H_2O,in}\left(\frac{kJ}{mol}\right)=-241.83+(\underline{\qquad\qquad})[\underline{\qquad}{}^\circ C-25^\circ C]+(\underline{\qquad\qquad})\left[(\underline{\qquad}{}^\circ C)^2-(25^\circ C)^2\right]$$

$$+\left(2.535\times10^{-9}\right)\left[(\underline{\qquad}{}^\circ C)^3-(25^\circ C)^3\right]-\left(8.983\times10^{-13}\right)\left[(\underline{\qquad}{}^\circ C)^4-(25^\circ C)^4\right]$$

$$\hat{H}_{H_2O,in}=\underline{\qquad\qquad}\frac{kJ}{mol}$$

$$\hat{H}_{CO,out}\left(\frac{kJ}{mol}\right)=-110.52+(\underline{\qquad\qquad})[\underline{\qquad}{}^\circ C-25^\circ C]+\left(2.055\times10^{-6}\right)\left[(\underline{\qquad}{}^\circ C)^2-(25^\circ C)^2\right]$$

$$+\left(1.183\times10^{-9}\right)\left[(\underline{\qquad}{}^\circ C)^3-(25^\circ C)^3\right]-\left(5.550\times10^{-13}\right)\left[(\underline{\qquad}{}^\circ C)^4-(25^\circ C)^4\right]$$

$$\hat{H}_{CO,out}=\underline{\qquad\qquad}\frac{kJ}{mol}$$

$$\hat{H}_{H_2O,out}\left(\frac{kJ}{mol}\right)=-241.83+(\underline{\hspace{3cm}})[\underline{\hspace{1cm}}{}^{\circ}C-25^{\circ}C]+(\underline{\hspace{3cm}})\left[(\underline{\hspace{1cm}}{}^{\circ}C)^2-(25^{\circ}C)^2\right]$$
$$+\left(2.535\times10^{-9}\right)\left[(\underline{\hspace{1cm}}{}^{\circ}C)^3-(25^{\circ}C)^3\right]-\left(8.983\times10^{-13}\right)\left[(\underline{\hspace{1cm}}{}^{\circ}C)^4-(25^{\circ}C)^4\right]$$

$$\hat{H}_{H_2O,out}=\underline{\hspace{2.5cm}}\frac{kJ}{mol}$$

$$\hat{H}_{H_2,out}\left(\frac{kJ}{mol}\right)=(\underline{\hspace{3cm}})[\underline{\hspace{1cm}}{}^{\circ}C-25^{\circ}C]+(\underline{\hspace{3cm}})\left[(\underline{\hspace{1cm}}{}^{\circ}C)^2-(25^{\circ}C)^2\right]$$
$$+\left(1.096\times10^{-9}\right)\left[(\underline{\hspace{1cm}}{}^{\circ}C)^3-(25^{\circ}C)^3\right]-(\underline{\hspace{3cm}})\left[(\underline{\hspace{1cm}}{}^{\circ}C)^4-(25^{\circ}C)^4\right]$$

$$\hat{H}_{H_2,out}=\underline{\hspace{1.5cm}}\frac{kJ}{mol}$$

$$\hat{H}_{CO_2,out}\left(\frac{kJ}{mol}\right)=-393.51+(\underline{\hspace{3cm}})[\underline{\hspace{1cm}}{}^{\circ}C-25^{\circ}C]+\left(2.117\times10^{-5}\right)\left[(\underline{\hspace{1cm}}{}^{\circ}C)^2-(25^{\circ}C)^2\right]$$
$$-(\underline{\hspace{3cm}})\left[(\underline{\hspace{1cm}}{}^{\circ}C)^3-(25^{\circ}C)^3\right]+(\underline{\hspace{3cm}})\left[(\underline{\hspace{1cm}}{}^{\circ}C)^4-(25^{\circ}C)^4\right]$$

$$\hat{H}_{CO_2,out}=\underline{\hspace{2.5cm}}\frac{kJ}{mol}$$

By substituting the enthalpy values we just calculated into the energy balance equation, we can obtain the fourth equation that will be used to determine the unknown molar flow rates. Since the flow rates are given in $\frac{mol}{min}$, the amount of energy transferred must be converted from kW to $\frac{kJ}{min}$:

$$-50\ \frac{kJ}{s}\left(\frac{60\ s}{1\ min}\right)=\dot{n}_{CO,out}\frac{mol\ CO}{min}\left(\underline{\hspace{3cm}}\frac{kJ}{mol\ CO}\right)+\dot{n}_{H_2O,out}\frac{mol\ H_2O}{min}\left(\underline{\hspace{3cm}}\frac{kJ}{mol\ H_2O}\right)$$
$$+\dot{n}_{CO_2,out}\frac{mol\ CO_2}{min}\left(-383.08\frac{kJ}{mol\ CO_2}\right)+\dot{n}_{H_2,out}\frac{mol\ H_2}{min}\left(\underline{\hspace{3cm}}\frac{kJ}{mol\ H_2}\right)$$
$$-\dot{n}_{CO,in}\frac{mol\ CO}{min}(\underline{\hspace{3cm}})-\dot{n}_{H_2O,in}\frac{mol\ H_2O}{min}\left(-226.72\frac{kJ}{mol\ H_2O}\right)$$

This equation can be solved for the molar flow rate of carbon monoxide exiting the reactor $\dot{n}_{CO,out}$, to yield:

$$\dot{n}_{\mathrm{CO,out}} = \frac{\left(-3000 + \underline{\hspace{1.5cm}}\,\dot{n}_{\mathrm{H_2O,out}} + 383.08\dot{n}_{\mathrm{CO_2,out}} - \underline{\hspace{1.5cm}}\,\dot{n}_{\mathrm{H_2,out}} - \underline{\hspace{1.5cm}}\,\dot{n}_{\mathrm{CO,in}} - 226.72\dot{n}_{\mathrm{H_2O,in}}\right)\frac{\mathrm{kJ}}{\mathrm{min}}}{\left(\underline{\hspace{1.5cm}}\,\frac{\mathrm{kJ}}{\mathrm{mol}}\right)}$$

$$\dot{n}_{\mathrm{CO,out}}\left(\frac{\mathrm{mol}}{\mathrm{min}}\right) = 29.095 - \underline{\hspace{1.5cm}}\,\dot{n}_{\mathrm{H_2O,out}} - 3.715\dot{n}_{\mathrm{CO_2,out}} + \underline{\hspace{1.5cm}}\,\dot{n}_{\mathrm{H_2,out}} + \underline{\hspace{1.5cm}}\,\dot{n}_{\mathrm{CO,in}} + 2.199\dot{n}_{\mathrm{H_2O,in}}$$

The four equations that will be used for determining the fractional conversion of carbon monoxide are summarized below:

$$\dot{n}_{\mathrm{CO,out}}\left(\frac{\mathrm{mol\ CO}}{\mathrm{min}}\right) = \underline{\hspace{1.5cm}} - \underline{\hspace{2cm}} \tag{1}$$

$$\dot{n}_{\mathrm{CO,out}}\left(\frac{\mathrm{mol\ CO}}{\mathrm{min}}\right) = 117.45 + \left(104.15 - \dot{n}_{\mathrm{H_2O,out}}\right) - 2\dot{n}_{\mathrm{CO_2,out}} \tag{2}$$

$$\dot{n}_{\mathrm{H_2,out}}\left(\frac{\mathrm{mol\ H_2}}{\mathrm{min}}\right) = \underline{\hspace{3cm}} \tag{3}$$

$$\dot{n}_{\mathrm{CO,out}}\left(\frac{\mathrm{mol}}{\mathrm{min}}\right) = 29.095 - \underline{\hspace{1.5cm}}\,\dot{n}_{\mathrm{H_2O,out}} - 3.715\dot{n}_{\mathrm{CO_2,out}} + \underline{\hspace{1.5cm}}\,\dot{n}_{\mathrm{H_2,out}} + \underline{\hspace{1.5cm}}\,\dot{n}_{\mathrm{CO,in}} + 2.199\dot{n}_{\mathrm{H_2O,in}} \tag{4}$$

Equations (1) and (3) can be substituted into equation (2) to give:

$$\underline{\hspace{1.5cm}} - \underline{\hspace{1.5cm}} = 117.45 + \dot{n}_{\mathrm{H_2,out}} - 2\dot{n}_{\mathrm{CO_2,out}} \tag{5}$$

This equation can be reduced as follows:

$$117.45 - 117.45 - \dot{n}_{\mathrm{CO_2,out}} + 2\dot{n}_{\mathrm{CO_2,out}} = \dot{n}_{\mathrm{H_2,out}}$$

$$\dot{n}_{\mathrm{CO_2,out}} = \dot{n}_{\mathrm{H_2,out}} \tag{6}$$

After substituting Equations (1) and (6) into Equation (4), we have:

$$117.45 - \dot{n}_{\mathrm{H_2}} = 29.095 - \underline{\hspace{1.5cm}}\,\dot{n}_{\mathrm{H_2O,out}} - 3.715\dot{n}_{\mathrm{CO_2,out}} + \underline{\hspace{1.5cm}}\,\dot{n}_{\mathrm{H_2,out}} + \underline{\hspace{1.5cm}}\,\dot{n}_{\mathrm{CO,in}} + 2.199\dot{n}_{\mathrm{H_2O,in}} \tag{7}$$

Recalling that $\dot{n}_{H_2,out} = 104.15 - \dot{n}_{H_2O,out}$, Equation (7) can be rewritten as:

$$117.45 - \left(104.15 - \dot{n}_{H_2O,out}\right) = 29.095 - \_\_\_\_\_\_\ \dot{n}_{H_2O,out} - 3.715\dot{n}_{CO_2,out} + \_\_\_\_\_\_\left(104.15 - \dot{n}_{H_2O,out}\right) + \_\_\_\_\_\_\ \dot{n}_{CO,in} + 2.199\dot{n}_{H_2O,in} \tag{8}$$

Substituting the molar flow rates of each reactant in the feed stream yields:

$$117.45 - \left(104.15 - \dot{n}_{H_2O,out}\right) = 29.095 - \_\_\_\_\_\_\ \dot{n}_{H_2O,out} - 3.715\dot{n}_{CO_2,out} + \_\_\_\_\_\_\left(104.15 - \dot{n}_{H_2O,out}\right) + \_\_\_\_\_\_\left(117.45\right) + 2.199\left(104.15\right)$$

Solving this equation for the molar flow rate of steam leaving the reactor, we have:

$$\dot{n}_{H_2O,out} - 2.261\dot{n}_{H_2O,out} + 3.715\dot{n}_{H_2O,out} - 0.07\dot{n}_{H_2O,out} = 117.45 - 104.15 - 29.095 + \_\_\_\_\_\_\_ - 7.29 - \_\_\_\_\_\left(117.45\right) - 2.199\left(104.15\right)$$

$$\dot{n}_{H_2O,out}\left(\frac{\text{mol } H_2O}{\text{min}}\right) = \frac{23.47}{\_\_\_\_\_\_}$$

$$\dot{n}_{H_2O,out} = 9.84\frac{\text{mol } H_2O}{\text{min}}$$

This result can be substituted into Equation (3) to calculate the production rate of hydrogen:

$$\dot{n}_{H_2,out}\left(\frac{\text{mol } H_2}{\text{min}}\right) = \_\_\_\_\_\_\_\_ - 9.84$$

$$\dot{n}_{H_2,out} = \_\_\_\_\_\_\_\_\_\_\frac{\text{mol } H_2}{\text{min}}$$

From Equation (6) and by the stoichiometry of the chemical reaction it is known that the production rate of carbon dioxide is equal to the production rate of hydrogen. Thus,

$$\dot{n}_{CO_2,out} = \_\_\_\_\_\_\_\_\_\_\frac{\text{mol } CO_2}{\text{min}}$$

Substituting this quantity into Equation (1) allows us to obtain the amount of carbon monoxide unreacted to be:

$$\dot{n}_{CO,out}\left(\frac{\text{mol CO}}{\text{min}}\right) = 117.45 - \_\_\_\_\_\_\_\_\_\_$$

$$\dot{n}_{CO,out} = \underline{\hspace{2cm}} \frac{\text{mol CO}}{\text{min}}$$

Now we know all the values required to calculate the fractional conversion of carbon monoxide. After entering these values into the definition of fractional conversion, we get:

$$x_{CO} = \frac{\dot{n}_{CO,in} - \dot{n}_{CO,out}}{\dot{n}_{CO,in}} = \frac{\left(117.45 - \underline{\hspace{2cm}}\right)\frac{\text{mol CO}}{\text{min}}}{117.45\frac{\text{mol CO}}{\text{min}}}$$

$$\boxed{x_{CO} = \underline{\hspace{1cm}}}$$

9.6-1 Calculation of a Heating Value

Solid-oxide fuel cells are a type of fuel cell which operates at high temperatures for large-scale power applications. Due to its high operation temperatures, the presence of a catalyst is not required to produce electrons from the fuel. Since catalyst poisoning is not a problem for this type of fuel cell, hydrocarbons may be used as fuel instead of hydrogen.

A mixture of 16 mol % butane and 84 mol % propane is fed into a solid-oxide fuel cell. Determine the higher heating value of the fuel in $\frac{\text{kJ}}{\text{g}}$. The reactions taking place in the fuel cell are shown below:

$$C_3H_{8(g)} + 5O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(v)} \qquad \Delta\hat{H}_c^o = -2043\frac{\text{kJ}}{\text{mol}}$$

$$C_4H_{10(g)} + \frac{13}{2}O_{2(g)} \longrightarrow 4CO_{2(g)} + 5H_2O_{(v)} \qquad \Delta\hat{H}_c^o = -2657\frac{\text{kJ}}{\text{mol}}$$

Strategy

To calculate the higher heating value, we can use the standard heats of combustion for each one of the reactions. In addition, the amount of water produced by each reaction will affect the higher heating value. A basis of 1 mol of fuel will be selected to simplify the calculations.

Solution

The higher heating value of a fuel can be obtained with the following equation:

$$\text{HHV} = \text{LHV} + n\Delta\hat{H}_v(H_2O,\ 25°C)$$

where:

LHV = Lower Heating Value ($\text{LHV} = -\Delta\hat{H}_c^o$)
n = Number of moles of water produced by the combustion reaction)
$\Delta\hat{H}_v$ = Heat of Vaporization of water at 25ºC

For a mixture, the heating value is given by:

$$\text{HHV}_m = \sum x_i\left(\text{HHV}\right)_i$$

For the fuel used in the solid-oxide fuel cell described in the problem statement, the higher heating value will be calculated with the following equation:

$$\text{HHV}_m = x_{C_3H_8}\left(\text{HHV}\right)_{C_3H_8} + x_{C_4H_{10}}\left(\text{HHV}\right)_{C_4H_{10}}$$

It can be seen that the higher heating value equation is including number of moles of water. Since the problem is asking for the higher heating value in $\frac{\text{kJ}}{\text{g}}$, we will have to convert the molar amounts into mass.

We can start by converting the selected molar basis into mass:

$$\begin{array}{lll} \text{1 mol fuel} \Longrightarrow & 0.84 \text{ mol } C_3H_8 \Longrightarrow & \underline{\hspace{1.5cm}} \text{ g } C_3H_8 \\ & 0.16 \text{ mol } C_4H_{10} \Longrightarrow & \underline{\ \ 9.28 \ \ \ \text{ g } C_4H_{10}} \\ & & \underline{\hspace{1.5cm}} \text{ g fuel} \end{array}$$

From the mass of each hydrocarbon entering the fuel cell, we are able to calculate their mass fractions as shown below:

$$x_{C_3H_8} = \frac{m_{C_3H_8}}{m_{fuel}} = \frac{\underline{\hspace{1.5cm}} \text{ g } C_3H_8}{\underline{\hspace{1.5cm}} \text{ g fuel}} \qquad x_{C_4H_{10}} = \frac{m_{C_4H_{10}}}{m_{fuel}} = \frac{9.28 \text{ g } C_4H_{10}}{\underline{\hspace{1.5cm}} \text{ g fuel}}$$

$$x_{C_3H_8} = 0.80 \frac{\text{g } C_3H_8}{\text{g fuel}} \qquad x_{C_4H_{10}} = \underline{\hspace{1.5cm}} \frac{\text{g } C_4H_{10}}{\text{g fuel}}$$

Now we can proceed to calculate the higher heating value of each one of the constituents of the fuel:

$$HHV_{C_3H_8} = LHV_{C_3H_8} + n\Delta\hat{H}_v$$

Substituting the known quantities into this equation yields:

$$HHV_{C_3H_8} = \left[\underline{\hspace{2cm}} \frac{\text{kJ}}{\text{mol } C_3H_8} + \frac{\underline{\hspace{0.8cm}} \text{ mol } H_2O}{\text{1 mol } C_3H_8} \left(44.013 \frac{\text{kJ}}{\text{mol } H_2O} \right) \right] \left(\frac{\text{1 mol } C_3H_8}{\underline{\hspace{1cm}} \text{ g } C_3H_8} \right)$$

$$HHV_{C_3H_8} = \underline{\hspace{2cm}} \frac{\text{kJ}}{\text{g } C_3H_8}$$

The heat of vaporization of water was obtained from Table B.1 of Felder & Rousseau. Notice that the equation for the molar higher heating value was divided by the molecular weight of the fuel constituent. This is because the result must be obtained per unit of mass.

In a similar way, we can determine the higher heating value of butane:

$$HHV_{C_4H_{10}} = LHV_{C_4H_{10}} + n\Delta\hat{H}_v$$

$$\mathrm{HHV}_{\mathrm{C_4H_{10}}}=\left[\underline{\qquad\quad}\,\frac{\mathrm{kJ}}{\mathrm{mol\ C_4H_{10}}}+\frac{\underline{\quad}\ \mathrm{mol\ H_2O}}{1\ \mathrm{mol\ C_4H_{10}}}\left(44.013\,\frac{\mathrm{kJ}}{\mathrm{mol\ H_2O}}\right)\right]\left(\frac{1\ \mathrm{mol\ C_4H_{10}}}{\underline{\quad}\ \mathrm{g\ C_4H_{10}}}\right)$$

$$\mathrm{HHV}_{\mathrm{C_4H_{10}}}=\underline{\qquad\quad}\,\frac{\mathrm{kJ}}{\mathrm{g\ C_4H_{10}}}$$

Now we can enter the individual higher heating values and the mass fraction of each component of the fuel into the equation for the higher heating value of a mixture:

$$\mathrm{HHV}_{\mathrm{m}}=\left(0.80\,\frac{\mathrm{g\ C_3H_8}}{\mathrm{g\ fuel}}\right)\left(\underline{\qquad\quad}\,\frac{\mathrm{kJ}}{\mathrm{g\ C_3H_8}}\right)+\left(\underline{\qquad}\,\frac{\mathrm{g\ C_4H_{10}}}{\mathrm{g\ fuel}}\right)\left(\underline{\qquad\quad}\,\frac{\mathrm{kJ}}{\mathrm{g\ C_4H_{10}}}\right)$$

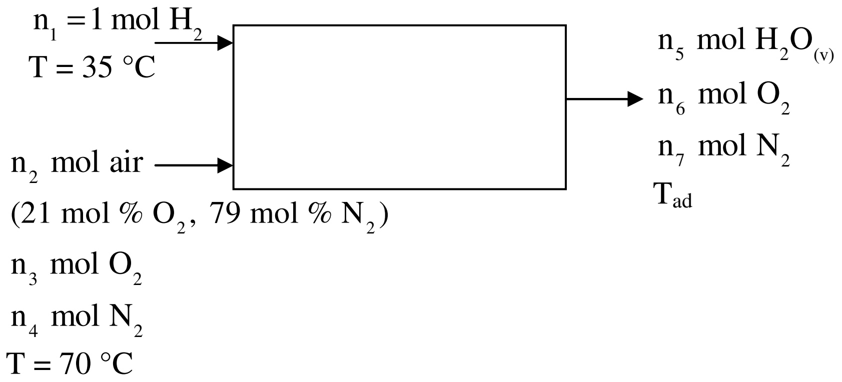
$$\boxed{\mathrm{HHV}_{\mathrm{m}}=\underline{\qquad\quad}\,\frac{\mathrm{kJ}}{\mathrm{g\ fuel}}}$$

9.6-2 Calculation of an Adiabatic Flame Temperature

Determine the adiabatic flame temperature of hydrogen for polymer-electrolyte membrane fuel cells, if it burns with 60 % excess air.

This calculation is useful when designing a furnace. The material selected for the furnace walls must withstand the adiabatic flame temperature. Following is the chemical reaction and the process flow chart of the combustion process of hydrogen:

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O_{(v)} \qquad \Delta\hat{H}_c^o = -241.8 \frac{kJ}{mol}$$



Strategy

An energy balance in the reactor at adiabatic operating conditions will allow us to determine the adiabatic flame temperature of hydrogen.

Solution

The energy balance equation applied to the conditions in the reactor will be given by:

$$Q = \Delta H = 0$$

For this problem, the change in enthalpy will be given by:

$$\Delta H = \sum_{out} n_i \hat{H}_i - \sum_{in} n_i \hat{H}_i + n_f \Delta\hat{H}_c^o = 0$$

where:

n_f = number of moles fuel being consumed by the reaction.

Since we need the temperature of the product stream to obtain the enthalpy of each one of the products, we can solve this equation for the enthalpies of the product stream as shown in the next step:

$$\sum_{out} n_i \hat{H}_i = \sum_{in} n_i \hat{H}_i - n_f \Delta \hat{H}_c^o \qquad (1)$$

The right hand side of this equation can be calculated as follows:

$$\sum_{in} n_i \hat{H}_i - n_f \Delta \hat{H}_c^o = n_1 \hat{H}_1 + n_2 \hat{H}_2 - n_f \Delta \hat{H}_c^o$$

The number of moles of each species can be obtained by their stoichiometric amounts as shown in the calculations below:

$$n_{O_2,\text{theoretical}} = 0.5 \text{ moles}$$

Since there is 60 % excess air, the amount of oxygen fed into the furnace will be given by:

$$n_3 = n_{O_2,\text{theoretical}} + 0.6\left(n_{O_2,\text{theoretical}}\right) = \_\_\_\_\_(0.5 \text{ moles})$$

$$n_3 = \_\_\_\_\_ \text{ moles}$$

The number of moles of nitrogen entering the reactor can be calculated as follows (assuming a composition of 21 mol % oxygen and 79 mol % nitrogen):

$$n_4 = n_3\left(\frac{1 \text{ mol air}}{\_\_\_\_\_ \text{ moles } O_2}\right)\left(\frac{0.79 \text{ moles } N_2}{1 \text{ mol air}}\right) = \_\_\_\_\_ \text{ moles } O_2\left(\frac{0.79 \text{ moles } N_2}{\_\_\_\_ \text{ moles } O_2}\right)$$

$$n_4 = \_\_\_\_\_\_ \text{ moles } N_2$$

The amount of air entering the system can be obtained by adding the number of moles its constituents: nitrogen and oxygen.

$$n_2 = n_3 + n_4 = \_\_\_\_\_ \text{ moles } O_2 + \_\_\_\_\_ \text{ moles } N_2$$

$$n_2 = 3.81 \text{ moles air}$$

The stoichiometric coefficients of water and hydrogen in the chemical reaction equation are the same. Thus, the amount of water being produced in the reactor will be equal to the amount of hydrogen fed:

$$n_1 = n_5 = 1 \text{ mol } H_2O$$

Since there is an amount of excess air entering the furnace, there will be some oxygen exiting in the product stream. This amount of oxygen can be obtained by the following material balance equation:

O_2 Balance

$$\text{Input} = \text{Output} + \text{Consumption}$$

Notice that since there is a chemical reaction in this process, the consumption term is now included in the material balance equation.

$$n_3 = n_6 + n_{O_2,\text{theoretical}}$$

Substituting the corresponding numerical values into this equation and solving for n_4, we have:

$$n_6 = n_3 - n_{O_2,\text{theoretical}} = \_\_\_\_\_\ \text{moles} - 0.5\ \text{moles}$$

$$n_6 = \_\_\_\_\_\ \text{moles}$$

The amount of nitrogen exiting in the product stream can be also determined by a material balance. Since the nitrogen is not being consumed nor generated by the combustion of hydrogen, all the nitrogen fed into the reactor will exit as a product:

$$n_4 = n_7 = \_\_\_\_\_\_\ \text{mol } N_2$$

Now we can proceed to determine the enthalpies of all the species entering and exiting the furnace. To do this, the reference states selected are shown below:

Air, $H_{2(g)}$, $H_2O_{(l)}$ @ T = 25ºC

The enthalpies of the gases in the inlet stream can be obtained from Table B.8 of Felder & Rousseau by linear interpolation for the temperature of 70ºC:

Air

T (°C)	$\hat{H}\left(\frac{kJ}{mol}\right)$
25	0
70	______
100	2.190

H_2

T (°C)	$\hat{H}\left(\frac{kJ}{mol}\right)$
25	0
35	_______
100	_______

The linear interpolation is set as:

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

Solving this equation for the unknown enthalpy $\hat{H}_i$ gives:

$$\hat{H}_i = \left(\frac{T_{mid} - T_{low}}{T_{high} - T_{low}}\right)\left(\hat{H}_{T_{high}} - \hat{H}_{T_{low}}\right) + \hat{H}_{T_{low}}$$

Substituting the tabulated values into this equation, we have:

$$\hat{H}_1 = \left(\frac{\_\_\_\_°\text{C} - \_\_\_\_°\text{C}}{100°\text{C} - \_\_\_\_°\text{C}}\right)\left(\_\_\_\_\_\frac{\text{kJ}}{\text{mol}}\right) = \_\_\_\_\_\_\_\frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}_2 = \left(\frac{\_\_\_\_°\text{C} - \_\_\_\_°\text{C}}{100°\text{C} - \_\_\_\_°\text{C}}\right)\left(2.19\frac{\text{kJ}}{\text{mol}}\right) = \_\_\_\_\_\_\_\_\frac{\text{kJ}}{\text{mol}}$$

The results we have obtained so far can be entered in the right hand side of Equation (1), to get:

$$\sum_{in} n_i\hat{H}_i - n_f\Delta\hat{H}_c^o = \left(1 \text{ mol H}_2\right)\left(\_\_\_\_\_\_\frac{\text{kJ}}{\text{mol H}_2}\right) + (\_\_\_\_\_ \text{ mol air})\left(\_\_\_\_\_\_\frac{\text{kJ}}{\text{mol air}}\right)$$
$$-\left(1 \text{ mol H}_2\right)\left(-241.8\frac{\text{kJ}}{\text{mol H}_2}\right)$$

$$\sum_{in} n_i\hat{H}_i - n_f\Delta\hat{H}_c^o = \_\_\_\_\_\_\_\_ \text{ kJ}$$

Recalling the definition of enthalpy:

$$\hat{H}_i\left(\frac{\text{kJ}}{\text{mol}}\right) = \int_{T_{ref}}^{T} C_{p,i}(T)dT$$

The heat capacities of the product gases in $\frac{\text{kJ}}{\text{mol}\cdot°\text{C}}$ can be obtained from Table B.2 of Felder & Rousseau to be:

$$C_{p,5}\left(\frac{\text{kJ}}{\text{mol}\cdot°\text{C}}\right) = \left(3.346\times10^{-2}\right) + (\_\_\_\_\_\_\_\_\_\_\_\_)T + \left(7.604\times10^{-9}\right)T^2 - \left(3.593\times10^{-12}\right)T^3$$

$$C_{p,6}\left(\frac{\text{kJ}}{\text{mol}\cdot°\text{C}}\right) = \left(2.91\times10^{-2}\right) + (\_\_\_\_\_\_\_\_\_\_\_\_)T - (\_\_\_\_\_\_\_\_\_\_\_\_)T^2 + \left(1.311\times10^{-12}\right)T^3$$

$$C_{p,7}\left(\frac{\text{kJ}}{\text{mol}\cdot°\text{C}}\right) = (\_\_\_\_\_\_\_\_\_\_\_\_) + (\_\_\_\_\_\_\_\_\_\_\_\_)T + \left(5.723\times10^{-9}\right)T^2 - (\_\_\_\_\_\_\_\_\_\_\_\_)T^3$$

To calculate the enthalpies of each gas in the product stream, these equations have to be integrated from the reference temperature to the adiabatic temperature, T_{ad} and substituted into the left hand side of Equation (1). However, the calculations may be simplified by multiplying the Cp equations by the corresponding number of moles and summing these expressions before integrating. Thus, we get:

$$\begin{aligned}\sum_{out} n_i C_{p,i} = {} & (1 \text{ mol } H_2O)\left[(3.346\times10^{-2}) + (\underline{\qquad\qquad})T + (7.604\times10^{-9})T^2 - (3.593\times10^{-12})T^3\right] \\ & + (\underline{\quad\;} \text{ mol } O_2)\left[(2.91\times10^{-2}) + (\underline{\qquad\qquad})T - (\underline{\qquad\qquad})T^2 + (1.311\times10^{-12})T^3\right] \\ & + (\underline{\quad\;} \text{ mol } N_2)\left[(\underline{\qquad\qquad}) + (\underline{\qquad\qquad})T + (5.723\times10^{-9})T^2 \right. \\ & \left. - (\underline{\qquad\qquad})T^3\right]\end{aligned}$$

$$\sum_{out} n_i C_{p,i} = -(\underline{\qquad\qquad})T^3 + (\underline{\qquad\qquad})T^2 + (\underline{\qquad\qquad})T + 0.1295$$

From the definition of enthalpy, the left hand side of Equation (1) can be obtained using the following equation:

$$\sum_{out} n_i \hat{H}_i = n_5\left(\Delta\hat{H}_{v,H_2O}\right) + \int_{T_{ref}}^{T_{ad}} \sum_{out} n_i C_{p,i}(T)dT$$

Since the reference state of water is in the liquid phase at 25°C, we are including the change in enthalpy due to the phase change of water from liquid to vapor.

Substituting the heat of vaporization of water (from Table B.1) and integrating the equation for $\sum_{out} n_i C_{p,i}$ yields:

$$\sum_{out} n_i \hat{H}_i = (\underline{\qquad\qquad})T^4 + (\underline{\qquad\qquad})T^2 + (\underline{\qquad\qquad})T + 0.1295\Big|_{T_{ref}}^{T_{ad}} + (1 \text{ mol } H_2O)\left(44.013\frac{\text{kJ}}{\text{mol } H_2O}\right)$$

Evaluating the integral, we have:

$$\begin{aligned}\sum_{out} n_i \hat{H}_i = {} & -(\underline{\qquad\qquad})\left[(T_{ad}{}^4) - (\underline{\quad\;}\text{°C})^4\right] + (\underline{\qquad\qquad})\left[(T_{ad}{}^3) - (\underline{\quad\;}\text{°C})^3\right] \\ & + (\underline{\qquad\qquad})\left[(T_{ad}{}^2) - (\underline{\quad\;}\text{°C})^2\right] + 0.1295\left[T_{ad} - \underline{\quad\;}\text{°C}\right] + 44.013\text{kJ}\end{aligned}$$

$$\sum_{out} n_i \hat{H}_i = (\underline{\qquad\qquad})T_{ad}{}^4 + (\underline{\qquad\qquad})T_{ad}{}^3 + (\underline{\qquad\qquad})T_{ad}{}^2 + 0.1295T_{ad} + \underline{\qquad}$$

Now we will have to solve this fourth-order equation to determine the adiabatic flame temperature T_{ad}. To do this, we substitute this expression we just obtained into Equation (1) as follows:

$$(\underline{\hspace{3cm}})T_{ad}^{4}+(\underline{\hspace{3cm}})T_{ad}^{3}+(\underline{\hspace{3cm}})T_{ad}^{2}+0.1295T_{ad}+\underline{\hspace{2cm}}=247.09$$

Reducing this equation, we get:

$$(\underline{\hspace{3cm}})T_{ad}^{4}+(\underline{\hspace{3cm}})T_{ad}^{3}+(\underline{\hspace{3cm}})T_{ad}^{2}+0.1295T_{ad}-\underline{\hspace{2cm}}=0$$

This equation can be solved for T_{ad} using computer software or numerical methods. After making calculations, we find the adiabatic flame temperature to be:

$$\boxed{T_{ad}=\underline{\hspace{2cm}}\ ^{\circ}C}$$

9.6-3 Ignition Temperature and Flammability Limits

Hydrogen is a very flammable gas which poses an immediate fire and explosive hazard at very low concentrations. This concentration is known as the lower or lean flammability limit.

Determine the lower and upper flammability limits and ignition temperature of hydrogen.

Strategy

This problem may be solved by looking for tabulated values of flammability limits and ignition temperature.

Solution

Looking at Table 26-10 of *Perry's Chemical Engineers' Handbook*, 7th Edition, we find that the flammability properties for hydrogen are:

Minimum mol % of H_2 for combustion = ____ %
Maximum mol % of H_2 for combustion = _____%
Ignition temperature = ______ ºC