

CAPE1330 MASS AND ENERGY BALANCES

HEAT OF REACTION

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General procedures

1. **Perform** all the required mass balance calculations.

2. **Use** the appropriate form of the energy balances:

closed system: $Q + W = m\Delta\hat{U} + m\Delta\hat{E}_k + m\Delta\hat{E}_p$

open system: $\dot{Q} + \dot{W}_s = \dot{n}\Delta\hat{H} + \dot{n}\Delta\hat{E}_k + \dot{n}\Delta\hat{E}_p$

3. **Choose** a reference state (phase, temperature and pressure) for each species involved in the process.

4. **Calculate** all the required values of m , \dot{n} , \hat{U}_i , or \hat{H}_i .

5. **Solve** the mass and energy balances for unknown variables.

Objectives

1. Determine a heat of reaction from heats of formation or heats of combustion using Hess's law.
2. Write and solve an energy balance on a chemical reactor using either the heat of reaction method or the heat of formation method.
3. Solve reactive system energy balance problems for
 - a the heat transfer required for specified inlet and outlet conditions,
 - b the outlet temperature corresponding to a specified heat input,
 - c the product composition corresponding to a specified heat input and a specified outlet temperature.

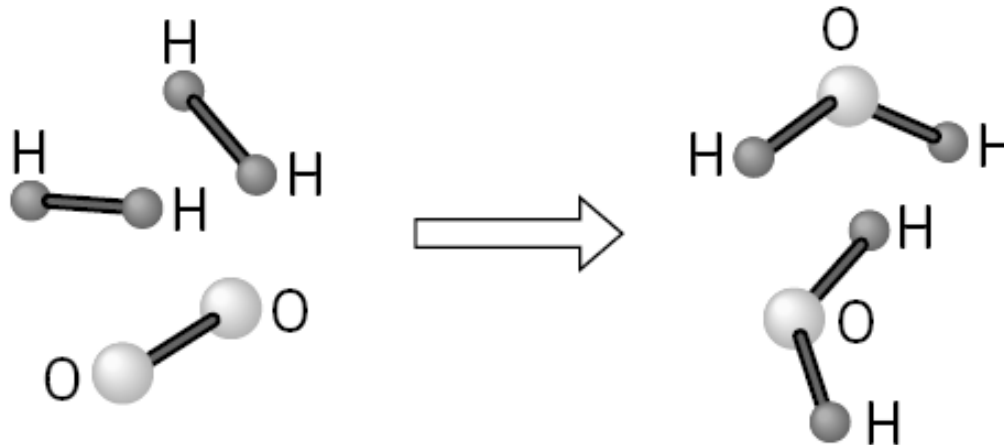
Heat of reaction

An energy balance on a reactor tells the process engineer how much heating or cooling the reactor requires in order to operate at the desired conditions. We will show

1. how enthalpy changes that accompany chemical reactions are determined from tabulated physical properties of the reactants and products.
2. how calculated enthalpies of reaction are incorporated in energy balances on reactive processes.

Reactive systems

Consider the reaction in which water is formed from hydrogen and oxygen: $2H_2(g) + O_2(g) \rightarrow 2H_2O(v)$. On the molecular level, the reaction might be depicted as



Each time this reaction takes place, three chemical bonds are broken (two between hydrogen atoms and one between oxygen atoms) and four bonds are formed among the atoms of the two water molecules.

Heat of reaction

In any reaction between stable molecules, energy is required to break the reactant chemical bonds and energy is released when the product bonds form.

If the first process absorbs less energy than the second process releases, the reaction is **exothermic**: the product molecules at a given temperature and pressure have lower internal energies than the reactant molecules at the same temperature and pressure. The **heat of reaction** is the net energy released which must be transferred from the reactor as heat or work, or else the system temperature increases.

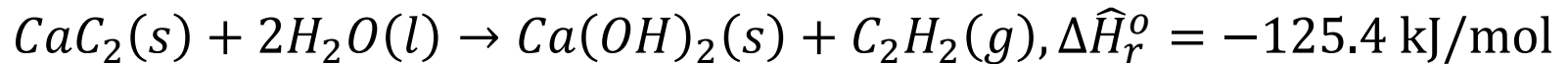
If less energy is released when the product bonds form than it took to break the reactant bonds, the reaction is **endothermic**: energy must be added to the reactor as heat or work to keep the temperature from decreasing.

Test yourself 1

In an exothermic reaction, the products are at a lower energy level than the reactants. However, if the reactor is not cooled, the products are hotter than the reactants, which means they must be at a higher energy level than the reactants.

Heat of reaction

Consider the reaction between solid calcium carbide and liquid water to form solid calcium hydroxide and gaseous acetylene:



The heat of reaction, $\Delta \hat{H}_r(T, P)$, is the enthalpy change for a process in which **stoichiometric quantities** of reactants at temperature T and pressure P react **completely** in a **single reaction** to form products at the **same temperature and pressure**.

i.e. if 1 mol of solid calcium carbide reacts completely with 2 mols of liquid water to form 1 mol solid calcium hydroxide and 1 mol of gaseous acetylene, and the initial and final temperature and pressures are both at 25°C and 1 atm. The $H_{\text{products}} - H_{\text{reactants}} = -125.4 \text{ kJ}$.

Example 1

Consider the reaction between A and B to form C :



means that the enthalpy change for the given reaction is

$$\frac{-50 \text{ KJ}}{2 \text{ mols A consumed}} = \frac{-50 \text{ KJ}}{1 \text{ mol B consumed}} = \frac{-50 \text{ KJ}}{3 \text{ mols C generated}}$$

Therefore, if 150 mols/s of C was generated in the given reaction at 100°C and 1atm , the associated enthalpy change is

$$\Delta \dot{H} = \frac{-50 \text{ KJ}}{3 \text{ mols C generated}} \times \frac{150 \text{ mols C generated}}{\text{s}} = -2,500 \text{ kJ/s}$$

Heat of reaction

More generally, if ν_A is the stoichiometric coefficient of a reactant or product A and $n_{A,r}$ moles of A are consumed or generated at T_o and P_o , then the associated enthalpy change is

$$\Delta H = \frac{\Delta \hat{H}_r(T_o, P_o)}{\nu_A} n_{A,r}$$

If we define the extent of reaction, ξ , as a measure of how far a reaction has proceeded at T_o and P_o , then

$$\xi = \frac{|n_{A,out} - n_{A,in}|}{\nu_A} = \frac{n_{A,r}}{\nu_A}$$

Therefore $\Delta H = \xi \Delta \hat{H}_r(T_o, P_o)$

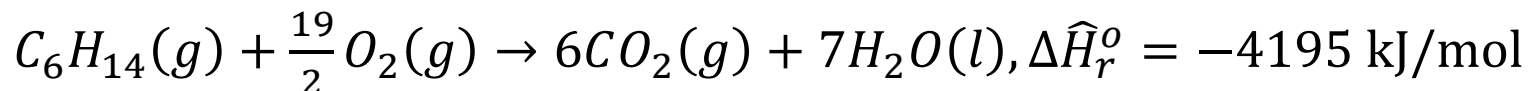
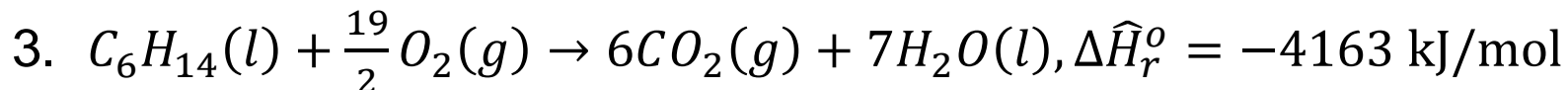
Heat of reaction

1. The reaction is **exothermic** at T and P when $\Delta\hat{H}_r(T, P)$ is negative, and the reaction is **endothermic** at T and P when $\Delta\hat{H}_r(T, P)$ is positive.
2. At low and moderate pressures, $\Delta\hat{H}_r(T, P)$ is nearly independent of pressure. So that $\Delta\hat{H}_r(T, P) = \Delta\hat{H}_r(T)$.
3. The value of the heat of reaction depends on how the stoichiometric equation is written.
4. The value of a heat of reaction depends on the states of aggregation of the reactants and products.
5. The standard heat of reaction, $\Delta\hat{H}_r^o$, is the heat of reaction when both the reactants and products are at a specified reference temperature and pressure, usually 25°C and 1atm.

Test yourself 2

1. What is a heat of reaction? A standard heat of reaction?
2. Suppose $\Delta \hat{H}_r^o$ is -40 kJ/mol for the reaction $2A \rightarrow B$.
 - a What is the value of the ratio kJ/mol A reacted?
 - b Is the reaction exothermic or endothermic at 25°C and 1atm?
 - c If the reactants and products are at the same temperature, must heat be added to or withdrawn from the reactor? (Assume that the energy balance reduces to $Q = \Delta H$.)
 - d If the reactor is adiabatic ($Q = 0$), would the products leave at a higher or a lower temperature than that of the entering reactants?

Test yourself 2



The standard state for the heats of reaction is 25°C and 1atm. What is the physical significance of the difference between the two given values of $\Delta \hat{H}_r^o$?

Heat of reaction method

The heat of reaction method is generally preferable when there is a single reaction for which $\Delta\hat{H}_r^o$ is known.

1. Complete the mass balance calculations on the reactor to the greatest extent possible.
2. Choose reference states for specific enthalpy calculations. The best choices are generally reactant and product species at 25°C and 1atm in the states for which the heat of reaction is known and nonreacting species at any convenient temperature.
3. Calculate the extents of reactions from any known flow rates of reactants or products at reactor inlet and outlet corresponding to the rates of consumption or generation.

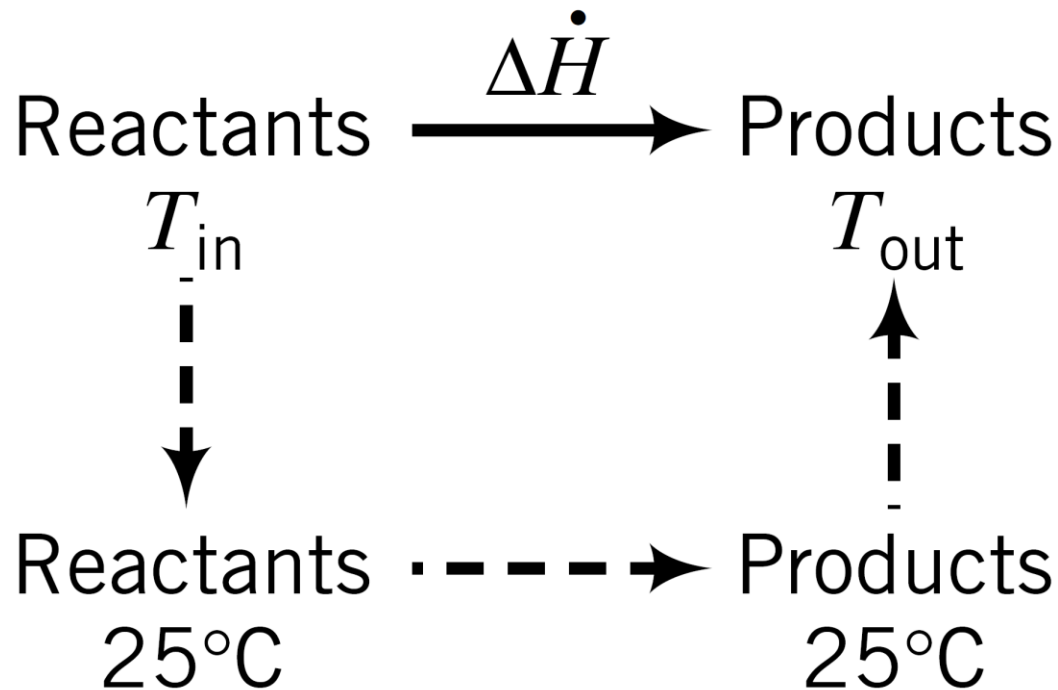
Heat of reaction method

4. Prepare the inlet-outlet enthalpy table, inserting known molar amounts or flow rates for all inlet and outlet stream components.
5. Calculate each unknown stream component enthalpy, \hat{H}_i , as $\Delta\hat{H}$ for the species going from its reference state to the process state, using tabulated physical properties of the reactants and products.
6. For multiple reactions, calculate $\Delta\dot{H}$ for the reactor,

$$\Delta\dot{H} = \sum_{\text{reactions}} \xi_j \Delta\dot{H}_{r,j}^o + \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i$$

7. Substitute the calculated value of $\Delta\dot{H}$ in the energy balance and complete the required calculations.

Heat of reaction method



(a) Process path for heat of reaction method

Example 2

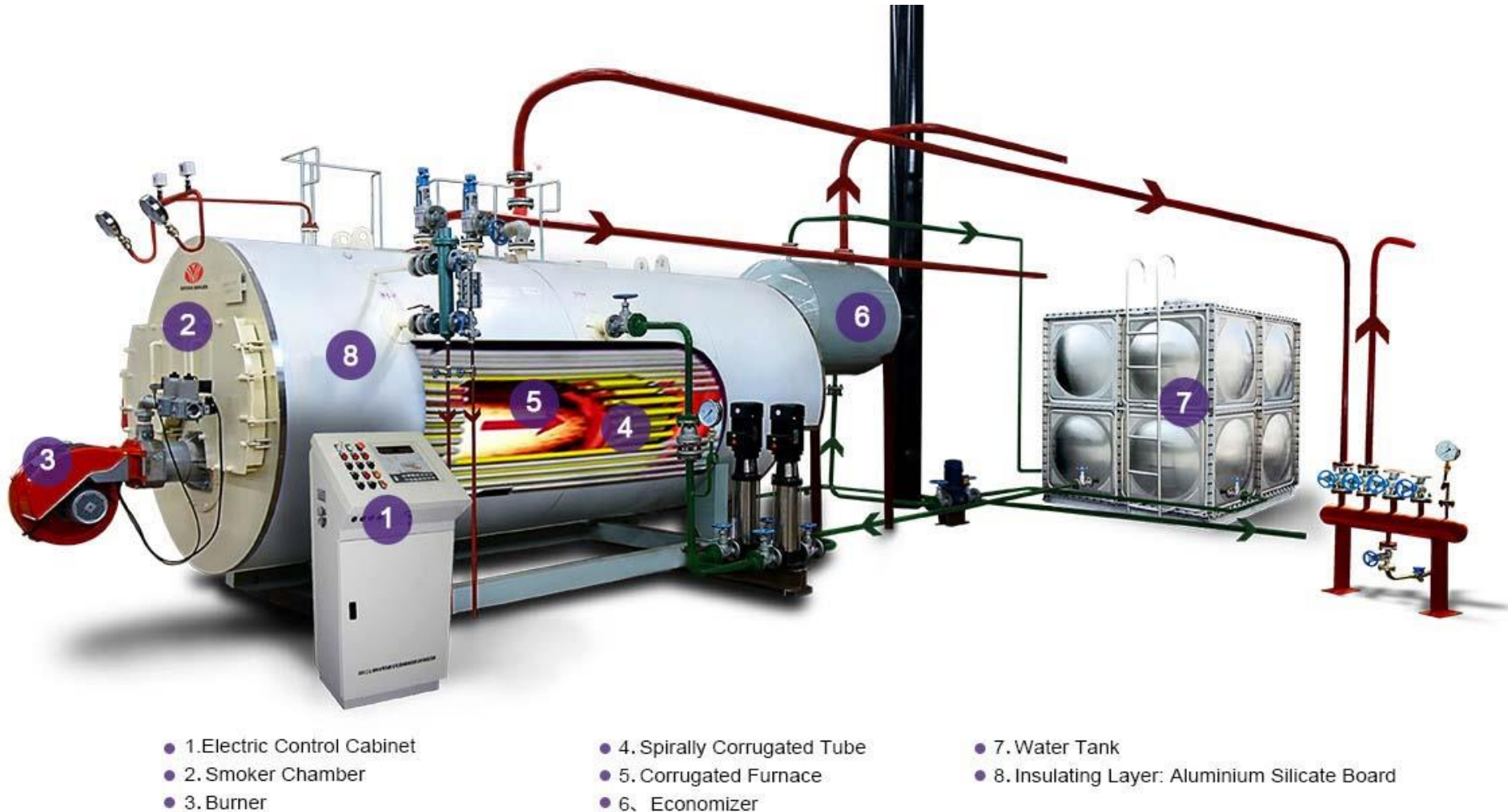
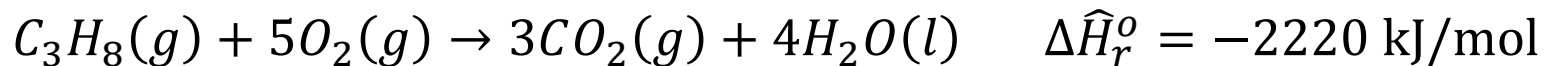
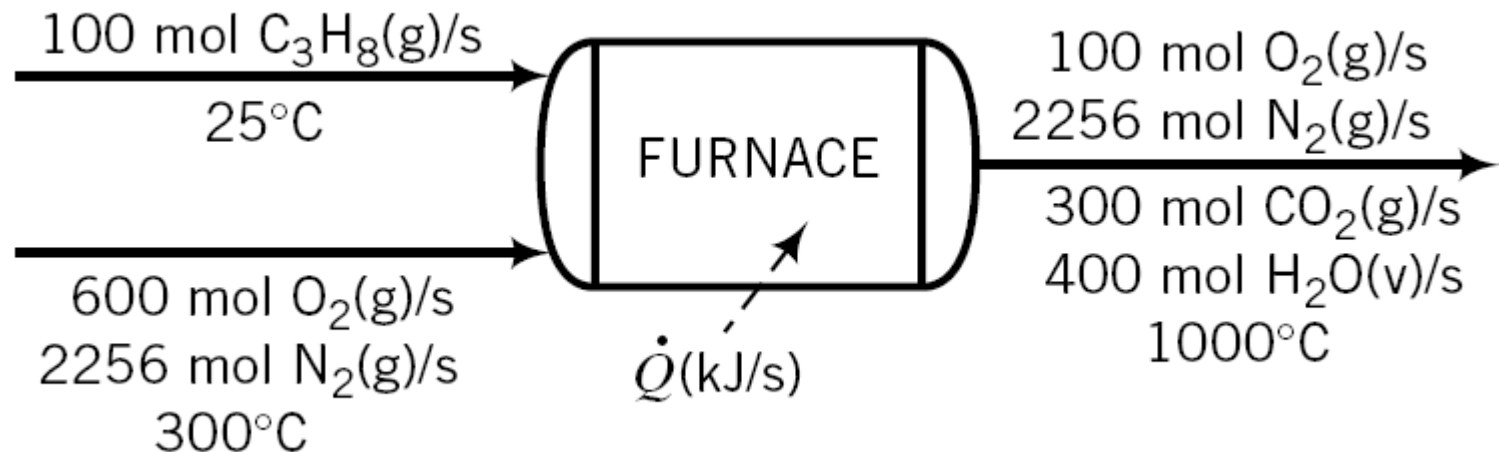


Fig.1 Propane gas fired steam boiler.

Example 2

Propane gas at 25°C is burned in a furnace with 20% excess air preheated to 300°C. For a basis of 100 mol C₃H₈ fed/s, assuming complete reaction, the combustion products leave the furnace at 1000°C. Calculate the heat transferred from the furnace.



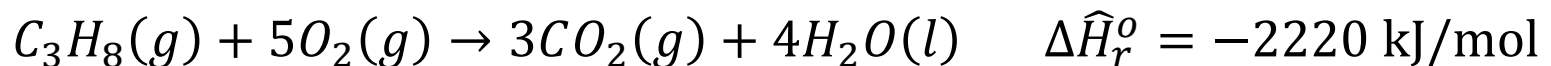
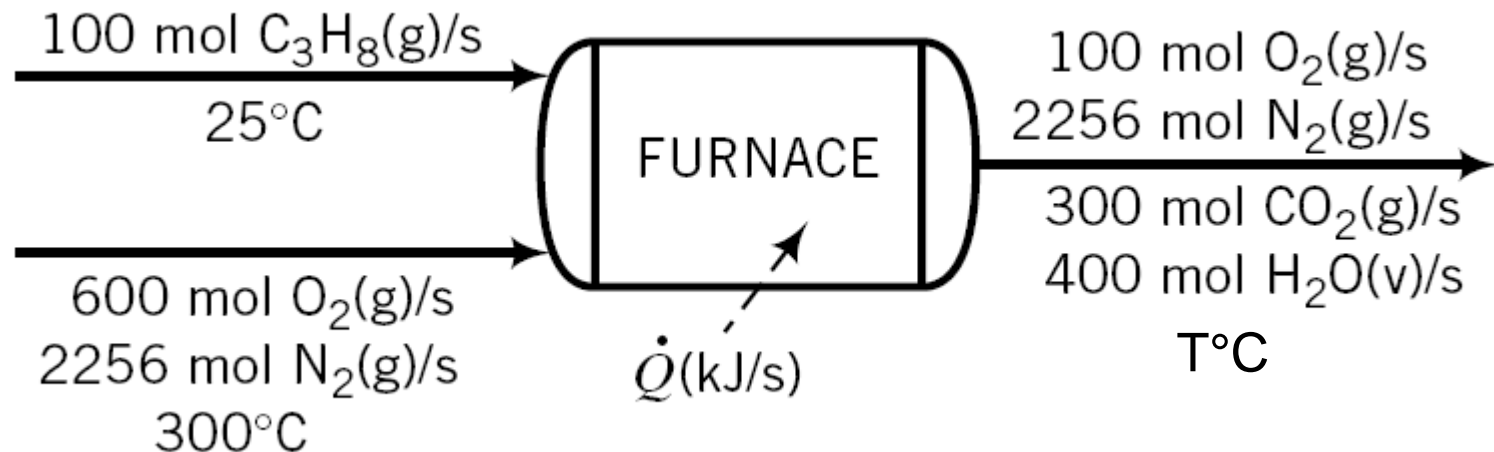
Heat capacities

$c_p = a + bT + cT^2 + dT^3$ kJ/mol°C where T is in °C

Substance	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$	Range (°C)
C ₃ H ₈ (g)	68.032	22.59	−13.11	31.71	0 – 1200
O ₂ (g)	29.10	1.158	−0.6076	1.311	0 – 1500
N ₂ (g)	29.00	0.2199	0.5723	−2.871	0 – 1500
CO ₂ (g)	36.11	4.233	−2.887	7.464	0 – 1500
H ₂ O(v)	33.46	0.6880	0.7604	−3.593	0 – 1500
H ₂ O(l)	75.4	—	—	—	0 – 100

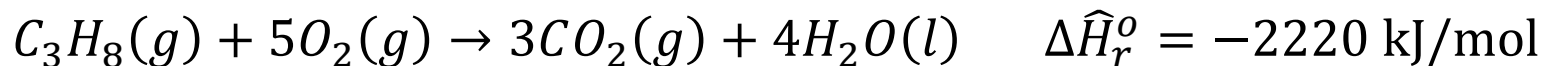
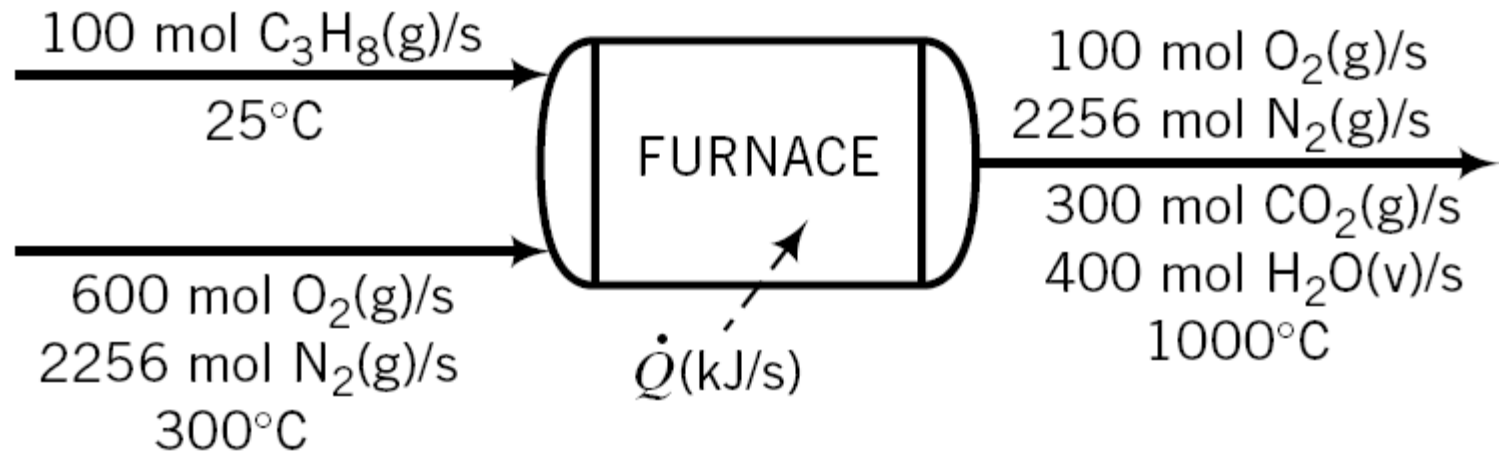
Example 3

Propane gas at 25°C is burned in a furnace with 20% excess air preheated to 300°C. For a basis of 100 mol C₃H₈ fed/s, assuming complete reaction and $\dot{Q} = -126,032.8212$ kJ/s, calculate the temperature of the combustion products leaving the furnace.



Example 4

Propane gas at 25°C is burned in a furnace with 20% excess air preheated to 300°C. For a basis of 100 mol C₃H₈ fed/s, assuming complete reaction, the combustion products leave the furnace at 1000°C. Determine the heat of reaction for propane gas at 1000°C, $\Delta\hat{H}_r(1000^\circ\text{C})$.



Example 5

Propane gas at 25°C is burned in a furnace with 20% excess air preheated to 300°C. For a basis of 100 mol C₃H₈ fed/s, assuming complete reaction, the combustion products leave the furnace at 1000°C. Calculate the heat transferred from the furnace using $\Delta\hat{H}_r(1000^\circ\text{C}) = -2,054.0815 \text{ kJ/mol}$.

