Introduction to Chemical Engineering

Solution to Problem Sheet 8 – Week 10 – November 21, 2025

<u>Goal</u>:

The purpose of this session is to help you strengthen your ability to carry out combined mass and energy balances on reactive systems, with a particular focus on combustion and oxidation reactor problems. By working through the two exercises, you will:

- Apply stoichiometry, conversion, extent of reaction, and excess air concepts to real chemical processes.
- Learn how to build and use inlet–outlet enthalpy tables for systems with reactions.
- Use the first law of thermodynamics to determine heat transfer in furnaces and reactors.
- Analyze how changes in process variables (temperature, excess air, selectivity, etc.) affect the system's performance.
- Size the cooling-water flow rate needed to remove heat from an exothermic reactor.
- Practice systematic problem-solving using flowcharts and degree-of-freedom analysis.

By the end of the session, you should feel more confident setting up and solving full mass-and-energy balance problems for chemical processes involving reactions and heat exchange.

Problem 1: Energy Balance, Reactive System

INSTRUCTIONS:

Methane at 25°C is burned in a boiler furnace with 10.0% excess air preheated to 100°C. Ninety percent of the methane fed is consumed, the product gas contains 10.0 mol CO_2/mol CO, and the combustion products leave the furnace at 400°C. One **cannot** assume complete combustion of methane.

QUESTIONS:

(a) Calculate the heat transferred from the furnace, $-\dot{Q}$ (kW), for a basis of 1000 mol CH_4 fed/s. (The greater the value of $-\dot{Q}$, the more steam is produced in the boiler.)

(b) Would the following changes increase or decrease the rate of steam production? (Assume the fuel feed rate and fractional conversion of methane remain constant.) Briefly explain your answers.

i. Increasing the temperature of the inlet air.
ii. Increasing the percent excess air for a given stack gas temperature.
iii. Increasing the selectivity of CO_2 to CO formation in the furnace.
iv. Increasing the stack gas temperature.

ASSUMPTIONS:

(1) We assume that air is composed of 79% N_2 and 21% O_2.

(2) For a complete combustion reaction from a hydrocarbon to CO2 and H2O, we use:

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow x\, CO_2 + \frac{y}{2} H_2O$$

(3) For an uncomplete combustion reaction from a hydrocarbon to CO and H2O, we use:

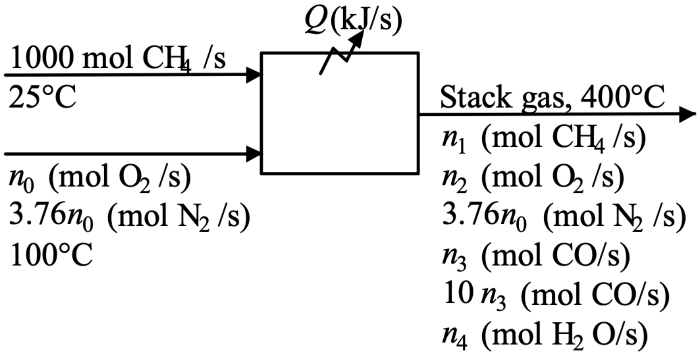
$$C_xH_y + \left(\frac{x}{2} + \frac{y}{4}\right) O_2 \rightarrow x\, CO + \frac{y}{2} H_2O$$

Solution to Problem 1: Energy Balance, Reactive System

Question a) Heat transfer calculations

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\quad\quad$ $CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O$

Basis: 1000 mol CH_4/h fed



90% combustion $\Rightarrow \dot{n}_1 = 0.10(1000) = 100 \text{ mol } CH_4/s$

Theoretical O_2 required = 2000 mol/s

10% excess O_2 $\Rightarrow O_2$ fed=1.1(2000 mol/s)=2200 mol/s

C balance:

$$(1000 \text{ mol } CH_4/s)(1 \text{ mol C/mol } CH_4) = (100)(1) + \dot{n}_3(1) + 10\dot{n}_3(1) \Rightarrow \dot{n}_3 = 81.8 \text{ mol CO/s}$$

$$\Rightarrow 10\dot{n}_3 = 818 \text{ mol } CO_2/s$$

H balance: $(1000)(4) = (100)(4) + 2\dot{n}_4 \Rightarrow \dot{n}_4 = 1800 \text{ mol } H_2O/s$

O balance: $(2200)(2) = 2\dot{n}_2 + (81.8)(1) + (818)(2) + (1800)(1) \Rightarrow \dot{n}_2 = 441 \text{ mol } O_2/s$

References : C(s), $H_2(g)$, $O_2(g)$, $N_2(g)$ at 25°C

Substance	$\dot{n}_{\text{in}}$ (mol/s)	$\hat{H}_{\text{in}}$ (kJ/mol)	$\dot{n}_{\text{out}}$ (mol/s)	$\hat{H}_{\text{out}}$ (kJ/mol)
CH_4	1000	−74.85	100	−57.62
O_2	2200	2.24	441	11.72
N_2	8272	2.19	8272	11.15
CO	–	–	81.8	−99.27
CO_2	–	–	818	−377.2
H_2O	–	–	1800	−228.63

$$\hat{H} = \overset{\substack{\text{Table B.1} \\ \downarrow}}{\Delta \hat{H}_f^o} + \int_{25}^{T} \overset{\substack{\text{Table B.2} \\ \downarrow}}{C_p}\, dT \text{ for } CH_4$$

$$= \Delta \hat{H}_f^o + \overset{\substack{\text{Table B.8} \\ \downarrow}}{\hat{H}_i(T)} \text{ for others}$$

Energy balance: $\dot{Q} = \Delta \dot{H} = \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i = \underline{\underline{-5.85 \times 10^5 \text{ kJ/s (kW)}}}$

Question b) Consequences of Variables Change

(i) $T_{air} \uparrow$ (increases) $\Rightarrow -\dot{Q}\uparrow$

(ii) %XS $\uparrow \Rightarrow -\dot{Q}\downarrow$ (more energy required to heat additional O_2 and N_2 to 400°C, therefore less energy transferred.)

(iii) $S_{CO_2/CO}\uparrow \Rightarrow -\dot{Q}\uparrow$ (reaction to form CO2 has a greater heat of combustion and so releases more thermal energy)

(iv) $T_{stack}\uparrow \Rightarrow -\dot{Q}\downarrow$ (more energy required to heat combustion products)

Problem 2: Energy Balance, Reactive System

INSTRUCTIONS:

Sulfur dioxide (SO_2) is oxidized to sulfur trioxide (SO_3) in a small pilot-plant reactor. SO_2 and 100% excess air are fed to the reactor at 450°C. The reaction proceeds to a 65% SO_2 conversion, and the products emerge from the reactor at 550°C. The production rate of SO_3 is 1.00×10^2 kg/min. The reactor is surrounded by a water jacket into which water at 25°C is fed.

QUESTIONS:

(a) Calculate the feed rates (standard cubic meters per second) of the SO_2 and air feed streams and the extent of reaction, ξ (kmol/s).

(b) Calculate the standard heat of the SO_2 oxidation reaction, ΔH°_r (kJ/mol). Then, taking molecular species at 25°C as references, prepare and fill in an inlet–outlet enthalpy table and write an energy balance to calculate the heat (kW) that must be transferred from the reactor to the cooling water.

(c) Calculate the minimum flow rate of the cooling water if its temperature rise is to be kept below 15°C.

(d) Briefly state what would have been different in your calculations and results if you had taken elemental species as references in part (b).

ASSUMPTIONS:

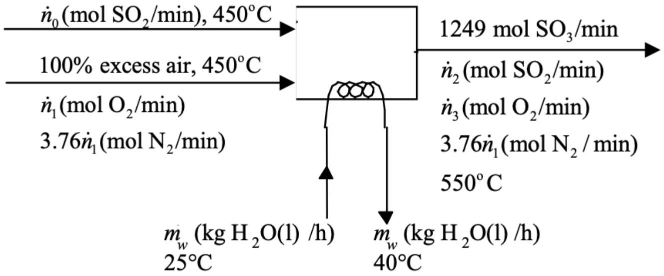
(1) We assume that air is composed of 79% N_2 and 21% O_2.

(2) Assume two separate input streams, one for SO_2, one for air.

Solution to Problem 2: Energy Balance, Reactive System

a. $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$

$$\underline{\text{Basis}}: \begin{array}{c|c|} \text{100 kg SO}_3 & 10^3 \text{ mol SO}_3 \\ \hline \text{min} & 80.07 \text{ kg SO}_3 \end{array} = 1249 \text{ mol SO}_3/\text{min}$$



Assume low enough pressure for $\hat{H}$ to be independent of *P*.

$$\underset{\text{(Generation=output)}}{\text{SO}_3 \text{ balance}}: \begin{array}{c|c|c} \dot n_0 \text{ (mol SO}_2\text{ fed)} & 0.65 \text{ mol SO}_2 \text{ react} & 1 \text{ mol SO}_3 \text{ produced} \\ \hline \text{min} & 1 \text{ mol SO}_2 \text{ fed} & 1 \text{ mol SO}_2 \text{ react} \end{array} = 1249 \frac{\text{mol SO}_3}{\text{min}}$$

$$\Rightarrow \dot n_0 = \underline{\underline{1922 \text{ mol SO}_2 \text{ / min fed}}}$$

$$\underline{\text{100\% excess air}}: \; \dot n_1 = \begin{array}{c|c|c} 1922 \text{ mol SO}_2 & 0.5 \text{ mol O}_2 \text{ reqd} & (1+1) \text{ mol O}_2 \text{ fed} \\ \hline \text{min} & 1 \text{ mol SO}_2 & 1 \text{ mol O}_2 \text{ reqd} \end{array} = \underline{\underline{1922 \text{ mol O}_2/\text{min fed}}}$$

$$\underline{\text{N}_2 \text{ balance}}: 3.76(1922) = \underline{\underline{7227 \text{ mol/min (in \& out)}}}$$

$$\underline{\text{65\% conversion}}: \; \dot n_2 = 1922(1-0.65) \text{ mol/s} = \underline{\underline{673 \text{ mol SO}_2/\text{min out}}}$$

$$\underline{\text{O balance:}} \; (2)(1922)+(2)(1922) = (3)(1249)+(2)(673)+2\dot n_3 \Rightarrow \dot n_3 = 1298 \text{ mol/min out}$$

b.

$$\underline{\text{Extent of reaction}}: \; \dot\xi = \frac{\left|(\dot n_{SO_2})_{out} - (\dot n_{SO_2})_{in}\right|}{\left|\nu_{SO_2}\right|} = \frac{|673-1922|}{|1|} = \underline{\underline{1249 \text{ mol / min}}}$$

$$\Delta\hat{H}_r^o = (\Delta\hat{H}_f^o)_{SO_3(g)} - (\Delta\hat{H}_f^o)_{SO_2(g)} \overset{\substack{\text{Table B.1}\\ \downarrow}}{=} -395.18-(-296.9) = \underline{\underline{-99.28 \text{ kJ / mol}}}$$

$\underline{\text{References}}$: $SO_2(g)$, $O_2(g)$, $N_2(g)$, $SO_3(g)$ at 25°C

Substance	$\dot n_{in}$ (mol / min)	$\hat{H}_{in}$ (kJ / mol)	$\dot n_{out}$ (mol / min)	$\hat{H}_{out}$ (kJ / mol)
SO_2	1922	$\hat{H}_1$	673	$\hat{H}_4$
O_2	1922	$\hat{H}_2$	1298	$\hat{H}_5$
N_2	7227	$\hat{H}_3$	7227	$\hat{H}_6$
SO_3	–	–	1249	$\hat{H}_7$

$$\mathrm{SO_2(g,450^\circ C)}:\ \hat{H}_1 = \int_{25}^{450} \overset{\overset{\text{Table B.2}}{\downarrow}}{C_p}\, dT = \underline{\underline{19.62\ \text{kJ / mol}}}$$

$$\mathrm{O_2(g,450^\circ C)} = \hat{H}_2 = \hat{H}_{\mathrm{O_2}}(450^\circ\mathrm{C}) \overset{\overset{\text{Table B.8}}{\downarrow}}{=} \underline{\underline{13.36\ \text{kJ / mol}}}$$

$$\mathrm{N_2(g,450^\circ C)} = \hat{H}_3 = \hat{H}_{\mathrm{N_2}}(450^\circ\mathrm{C}) \overset{\overset{\text{Table B.8}}{\downarrow}}{=} \underline{\underline{12.69\ \text{kJ / mol}}}$$

<u>Out</u> :

$$\mathrm{SO_2(g,550^\circ C)}:\ \hat{H}_4 = \int_{25}^{550} \overset{\overset{\text{Table B.2}}{\downarrow}}{C_p}\, dT = \underline{\underline{24.79\ \text{kJ/mol}}}$$

$$\mathrm{O_2(g,550^\circ C)} = \hat{H}_5 = \hat{H}_{\mathrm{O_2}}(550^\circ\mathrm{C}) \overset{\overset{\text{Table B.8}}{\downarrow}}{=} \underline{\underline{16.71\ \text{kJ / mol}}}$$

$$\mathrm{N_2(g,550^\circ C)} = \hat{H}_6 = \hat{H}_{\mathrm{N_2}}(550^\circ\mathrm{C}) \overset{\overset{\text{Table B.8}}{\downarrow}}{=} \underline{\underline{15.81\ \text{kJ / mol}}}$$

$$\mathrm{SO_3(g,550^\circ C)}:\ \hat{H}_7 = \int_{25}^{550} \overset{\overset{\text{Table B.2}}{\downarrow}}{C_p}\, dT = \underline{\underline{35.34\ \text{kJ / mol}}}$$

$$\begin{aligned}\dot{Q} = \Delta\dot{H} &= \dot{\xi}\Delta\hat{H}_r^\circ + \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i \\ &= (1249)(-98.28) + (673)(24.796) + (179.8)(16.711) + (7227)(15.808) + (1249)(35.336) - (19 \\ &\quad -1922(13.362) - (7227)(12.691) \\ &= \frac{-8.111\times10^4\ \text{kJ}}{\text{min}}\left|\frac{1\ \text{min}}{60\ \text{s}}\right|\frac{1\ \text{kW}}{1\ \text{kJ/s}} = \underline{\underline{-1350\ \text{kW}}}\end{aligned}$$

c. Assume system is adiabatic, so that $\dot{Q}_{\text{lost from reactor}} = \dot{Q}_{\text{gained by cooling water}}$

$$\dot{Q} = \Delta\dot{H} = \dot{m}_w\left[\underset{\underset{\text{Table B.5}}{\uparrow}}{\hat{H}_w}(1,\ 40^\circ\mathrm{C}) - \hat{H}_w\big(1,\ \underset{\underset{\text{Table B.5}}{\uparrow}}{25^\circ\mathrm{C}}\big)\right]$$

d.

$$\Rightarrow 8.111\times10^4\ \frac{\text{kJ}}{\text{min}} = \dot{m}_w\left(\frac{\text{kg}}{\text{min}}\right)[167.5 - 104.8]\frac{\text{kJ}}{\text{kg}} \Rightarrow \underline{\underline{\dot{m}_w = 1290\ \text{kg/min cooling water}}}$$

If elemental species were taken as references, the heats of formation of each molecular species would have to be taken into account in the enthalpy calculations and the heat of reaction term would not have been included in the calculation of $\Delta\dot{H}$.