Introduction to Chemical Engineering

Solutions to Problem Sheet 9 – Week 12 – December 05, 2025

Goal:

The purpose of this session is to deepen your understanding of **combined mass and energy balances on reactive systems**, with applications spanning industrial chemical processes, combustion, hydrogenation, biochemical reactions, and absorption units. By working through the five problems, you will:

- Apply **Hess's Law**, standard heats of formation, and standard heats of combustion to compute reaction enthalpies.
- Analyze how reaction pathways (e.g., multistep chlorination/dehydrochlorination) influence overall heat effects.
- Perform **reactive energy balances** for combustion, hydrogenation, and oxidation systems.
- Interpret biochemical stoichiometry and evaluate the heat released or required during **citric acid fermentation**.
- Determine heat requirements for **gas absorption** and **solution formation** processes.
- Evaluate coupled reactions (steam reforming + water–gas shift) and perform energy balances for high-temperature catalytic reactors.
- Use systematic problem-solving tools (flowcharts, stoichiometric tables, and degree-of-freedom analysis) to organize and solve complex reactive systems.

By the end of the session, you should feel more confident setting up and solving **full mass-and-energy balances** for reactive processes involving combustion, hydrogenation, fermentation, absorption, and catalytic reforming, including evaluating heat loads and process energetics.

Problem 1: Hess's Law (Energy Balance – Reactive)

Trichloroethylene, a widely used degreasing solvent for machine parts, is produced in a two-step reaction sequence. Ethylene is first chlorinated to yield tetrachloroethane, which is dehydrochlorinated to form trichloroethylene.

$$C_2H_4\,(g) + 2\,Cl_2\,(g) \rightarrow C_2H_2Cl_4\,(l) + H_2\,(g): \quad \Delta H°_r = -385.76 \text{ kJ/mol}$$

$$C_2H_2Cl_4\,(l) \rightarrow C_2HCl_3\,(l) + HCl\,(g)$$

The standard heat of formation of liquid trichloroethylene is –276.2 kJ/mol.

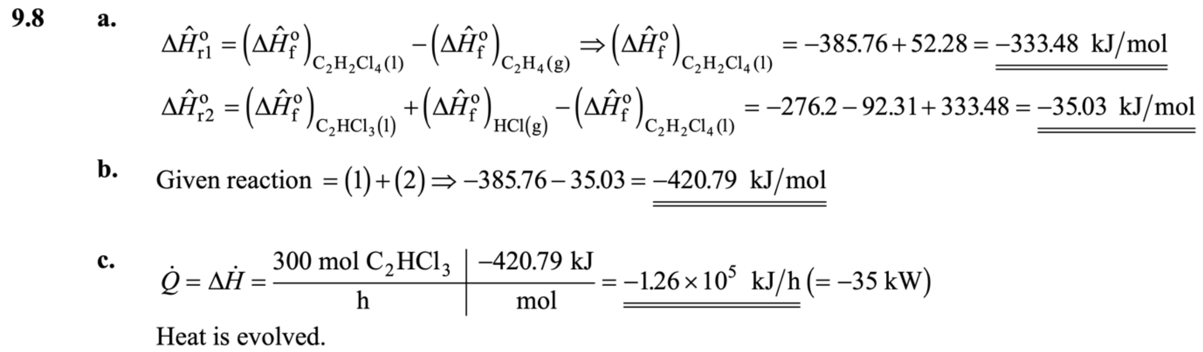
(a) Use the given data and tabulated standard heats of formation of ethylene and hydrogen chloride to calculate the standard heat of formation of tetrachloroethane and the standard heat of the second reaction.

(b) Use Hess's law to calculate the standard heat of the reaction

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

(c) If 300 mol/h of $C_2HCl_3(l)$ is produced in the reaction of part (b) and the reactants and products are all at 25°C and 1 atm, how much heat is evolved or absorbed in the process? (Assume $\dot{Q} = \Delta\dot{H}$)

Solution 1



9.8 **a.**

$$\Delta\hat{H}^o_{r1} = \left(\Delta\hat{H}^o_f\right)_{C_2H_2Cl_4(l)} - \left(\Delta\hat{H}^o_f\right)_{C_2H_4(g)} \Rightarrow \left(\Delta\hat{H}^o_f\right)_{C_2H_2Cl_4(l)} = -385.76 + 52.28 = \underline{\underline{-333.48\ \text{kJ/mol}}}$$

$$\Delta\hat{H}^o_{r2} = \left(\Delta\hat{H}^o_f\right)_{C_2HCl_3(l)} + \left(\Delta\hat{H}^o_f\right)_{HCl(g)} - \left(\Delta\hat{H}^o_f\right)_{C_2H_2Cl_4(l)} = -276.2 - 92.31 + 333.48 = \underline{\underline{-35.03\ \text{kJ/mol}}}$$

b. Given reaction $= (1) + (2) \Rightarrow -385.76 - 35.03 = \underline{\underline{-420.79\ \text{kJ/mol}}}$

c.

$$\dot{Q} = \Delta\dot{H} = \frac{300 \text{ mol } C_2HCl_3}{\text{h}}\bigg|\frac{-420.79 \text{ kJ}}{\text{mol}} = \underline{\underline{-1.26 \times 10^5\ \text{kJ/h}}}\,(= -35 \text{ kW})$$

Heat is evolved.

Problem 2: Heat of Combustion (Energy Balance – Reactive)

The standard heat of combustion of gaseous acetylene is listed in Table B.1 as: -1299.6 kJ/mol.

(a) In your own words, briefly explain what that means. (Your explanation should mention the reference states used to define the tabulated heats of combustion.)

(b) Use tabulated heats of formation to verify the given value of ΔH°c.

(c) Calculate the standard heat of the acetylene hydrogenation reaction

C2H2(g) + 2 H2(g) → C2H6(g)

using (i) tabulated heats of formation and (ii) tabulated heats of combustion

$$\Delta\hat{H}^{\circ}_{r} = -\sum_{i} \nu_i (\Delta\hat{H}^{\circ}_{c})_i = \sum_{reactants} |\nu_i| (\Delta\hat{H}^{\circ}_{c})_i - \sum_{products} |\nu_i| (\Delta\hat{H}^{\circ}_{c})_i$$

(d) Write the stoichiometric equations for the combustion reactions of acetylene, hydrogen, and ethane, and use Hess's law to derive the formula you used in part (c-ii).

Solution 2

a.

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l) \qquad \Delta\hat{H}^{o}_{c} = -1299.6 \text{ kJ/mol}$$

The enthalpy change when 1 g-mole of $C_2H_2(g)$ and 2.5 g-moles of $O_2(g)$ at 25°C and 1 atm react to form 2 g-moles of $CO_2(g)$ and 1 g-mole of $H_2O(l)$ at 25°C and 1 atm is -1299.6 kJ.

b.

$$\Delta\hat{H}^{o}_{c} = 2\left(\Delta\hat{H}^{o}_{f}\right)_{CO_2(g)} + \left(\Delta\hat{H}^{o}_{f}\right)_{H_2O(l)} - \left(\Delta\hat{H}^{o}_{f}\right)_{C_2H_2(g)}$$

$$\overset{\substack{\text{Table B.1}\\ \downarrow}}{=} \left[2(-393.5) + (-285.84) - (226.75)\right]\frac{\text{kJ}}{\text{mol}} = \underline{\underline{-1299.6 \ \frac{\text{kJ}}{\text{mol}}}}$$

c.

(i) $$\Delta\hat{H}^{o}_{r} = \left(\Delta\hat{H}^{o}_{f}\right)_{C_2H_6(g)} - \left(\Delta\hat{H}^{o}_{f}\right)_{C_2H_2(g)}$$

$$\overset{\substack{\text{Table B.1}\\ \downarrow}}{=} \left[(-84.67) - (226.75)\right]\frac{\text{kJ}}{\text{mol}} = \underline{\underline{-311.4 \ \frac{\text{kJ}}{\text{mol}}}}$$

(ii) $$\Delta\hat{H}^{o}_{r} = \left(\Delta\hat{H}^{o}_{c}\right)_{C_2H_2(g)} + 2\left(\Delta\hat{H}^{o}_{c}\right)_{H_2(g)} - \left(\Delta\hat{H}^{o}_{c}\right)_{C_2H_6(g)}$$

$$\overset{\substack{\text{Table B.1}\\ \downarrow}}{=} \left[(-1299.6) + 2(-285.84) - (-1559.9)\right]\frac{\text{kJ}}{\text{mol}} = \underline{\underline{-311.4 \ \frac{\text{kJ}}{\text{mol}}}}$$

d.

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l) \qquad (1) \quad \Delta\hat{H}^{o}_{c1} = -1299.6 \text{ kJ/mol}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad (2) \quad \Delta\hat{H}^{o}_{c2} = -285.84 \text{ kJ/mol}$$

$$C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad (3) \quad \Delta\hat{H}^{o}_{c3} = -1559.9 \text{ kJ/mol}$$

Problem 3: Chemical Engineering for Biological Process (Energy Balance – Reactive)

Citric acid is a well-known compound that occurs in living cells for both plants and animals. The citric acid cycle is a series of chemical reactions occurring in a living cell that is essential for the oxidation of glucose, a major source of energy for the cells. The reaction scheme is far too complicated to show here, but from a macroscopic (overall) viewpoint, for the commercial production of citric acid in a batch process, three different phases occur for which the stoichiometries are slightly different:

Early idophase (occurs between 80 and 120 hours), the initial reaction:

1g mol glucose + 1.5 g mol O_2 (g) → 3.81 g mol biomass + 0.62 g mol citric acid + 0.76 g mol CO_2 (g)

Medium idophase (occurs between 120 and 180 hours), additional glucose consumed:

1g mol glucose + 2.4 g mol O_2 (g) → 1.54 g mol biomass + 0.74 g mol citric acid + 1.33 g mol CO_2 (g)

Late idophase (occurs between 180 and 220 hours), additional glucose consumed:

1g mol glucose + 3.91 g mol O_2 (g) → 0.86 g mol biomass + 0.74 g mol citric acid + 2.41 g mol CO_2 (g)

In an aerobic (the presence of air) batch process, a 30% glucose solution at 25°C is introduced into a fermenter. Citric acid is to be produced by using the fungus *Aspergillus niger*. Stochiometric sterile air is mixed with the culture solution by a 100-horsepower aerator. Only 60% overall of the glucose supplied is expected to be converted to citric acid. The early phase is run at 32°C, the middle phase at 35°C, and the late phase at 25°C.

Based on the given data, how much heat must be added or removed from the fermenter during the production of a batch of 10,000 kg of citric acid? Ignore any slight effects of solution on the value of the heat of formation.

Data

	MW (g/mol)	$-\Delta\widehat{H}^{\circ}_{f}$ (kJ/g mol)
Glucose	180.16	1266
Citric acid	192.12	1544.8
Dry cells (biomass)	28.6	91.4

Solution 3

Preliminary remarks

The goal of this exercise is to demonstrate the connection between chemical engineering principles and biological processes, as well as their application in industrial settings. By studying the commercial production of citric acid in a batch process, you will explore how fundamental concepts such as material balances, energy balances, and stoichiometry are applied to biological systems.
This problem is intentionally designed to be more open-ended, reflecting the complexity and variability often encountered in real-world scenarios. To arrive at a solution, you must make reasonable assumptions based on the provided data. This approach highlights a critical aspect of chemical engineering practice: the need to balance theoretical calculations with practical considerations and constraints.
While we present one possible method to solve this problem, alternative solutions may also be valid depending on the assumptions made.

Step 1: Problem analysis

Assumption 1: the fermenter contents (glucose solution, fungus, and dissolved oxygen) are considered the "system," while everything outside (the aerator, the motor, the environment) is considered the "surroundings."
Assumption 2: We will assume that the oxygen and nitrogen drawn into the system and the CO_2 and nitrogen leaving the system are deemed to be part of the initial state of the system and the final state, respectively, to maintain a closed system. The system is closed as it is a batch process. Therefore, we will have to use the appropriate energy balance equation later:

$$\Delta U + \Delta E_k + \Delta E_p = Q - W$$

Step 2: Determine the Time-Weighted Average Stoichiometric Coefficients

Assumption 3: We assume that the consumption of glucose is constant throughout the process. To obtain the total net reaction in g mol the weighted average is computed:
Glucose:

$$\text{Weighted average} = \frac{1*40h+1*60h+1*40h}{140h} = 1$$

Oxygen:

$$\text{Weighted average} = \frac{1.5*40h+2.4*60h+3.91*40h}{140h} = \frac{60+144+156.4}{140} = 2.574$$

Biomass:

$$\text{Weighted average} = \frac{3.81*40h+1.54*60h+0.86*40h}{140h} = 1.994$$

Citric acid:

$$\text{Weighted average} = \frac{0.62*40h+0.74*60h+0.74*40h}{140h} = 0.706$$

Carboxylic acid:

$$\text{Weighted average} = \frac{0.76*40h+1.33*60h+2.41*40h}{140h} = 1.476$$

Thus the overall reaction becomes:

1 Glc + 2.574 O_2→ 1.994 BM + 0.706 CA + 1.476 CO_2

Step 3: Material Balance for 10,000 kg of Citric Acid

Basis: 10 000 kg CA produced.

Moles of Citric Acid (CA) Produced:

$$\frac{10000 kg\ CA}{} * \frac{1 kmol\ CA}{192.12\ kg\ CA} * \frac{1000\ mol\ CA}{1\ kmol\ CA} = 52\ 500\ mol\ CA\ produced$$

Glucose Required (Considering 60% Efficiency):

$$\frac{52'050\ g\ mol\ CA}{} * \frac{1\ mol\ \mathrm{Glc}}{0.706\ mol\ CA} = 73'725\ mol\ of\ \mathrm{Glc}\ needed$$

Since only 60% of the glucose is converted:

$$\frac{73'725\ mol\ \mathrm{Glc}\ consumed}{} * \frac{1.00\ mol\ \mathrm{Glc}\ fed}{0.60\ mol\ \mathrm{Glc}\ consumed} = 122'875\ moles\ of\ \mathrm{Glc}\ fed$$

Oxygen Consumed:

$$\frac{73'725\ mol\ \mathrm{Glc}\ consumed}{} * \frac{2.54\ mol\ O_2\ consumed}{1\ mol\ \mathrm{Glc}\ consumed} = 189'755\ moles\ O_2$$

Biomass Produced:

$$\frac{73'725\ mol\ \mathrm{Glc}\ consumed}{} * \frac{1.994\ mol\ BM\ produced}{1\ mol\ \mathrm{Glc}\ consumed} = 147'000\ moles\ BM$$

Carbon Dioxide Produced:

$$\frac{73'725\ mol\ \mathrm{Glc}\ consumed}{} * \frac{1.476\ mol\ CO_2\ produced}{1\ mol\ \mathrm{Glc}\ consumed} = 108'800\ moles\ CO_2$$

The water serves as a culture medium and does not enter the overall stoichiometry.
Summary of the material balances:

Component	Initial (mol)	Final (mol)
Glucose	122 875	49 150
BM	0	147 000
CA	0	52 500
O_2 (accumulated)	316 280	126 525
CO_2 (accumulated)	0	108 800

Step 3: Energy Balance (ΔH Calculation)

As mentioned in the first step, the equation that we should use to perform the energy balance is the following:

$$\Delta U + \Delta E_k + \Delta E_p = Q - W$$

As there is no mention of variation of kinetic energy nor potential energy, the equation reduces to the following:

$$\Delta U = Q - W$$

Where:

- Q is positive when it is **<u>transferred from the surroundings to the system</u>**
- W is positive when it is done **<u>by the system on the surroundings</u>**[1]

However, one quickly notices that we are only provided the specific enthalpies, and there is no mention of internal energy U in the problem. We should therefore look if we can express the internal energy as a function of the enthalpy.
We know that:

$$\Delta H = \Delta U + \Delta(PV)$$

Assumption 4: Changes in volume and pressure are negligible, there: $\Delta U \approx \Delta H$
Hence, we now have to solve the following energy balance:

$$\Delta H = Q - W$$

This can be recasted as follows:

$$\mathrm{Q} = \Delta H + W$$

Where:

- Q is positive when it is **<u>transferred from the surroundings to the system</u>**
- W is positive when it is **<u>done by the system on the surroundings</u>**
- ΔH is positive when heat is absorbed, meaning the system requires heat input **from the surroundings.**

Enthalpy change calculations:
The reference temperature will be 25°C. The initial state is 25°C and the final state is also 25°C so that the sensible heats are zero. We will omit including the nitrogen in equals the nitrogen out.
This means that we only have to consider the specific enthalpies of formation in our calculations:

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[1] The opposite sign convention is sometimes used. The choice is arbitrary, as long as it is used consistently.

	Component	**mol**	$\Delta\widehat{H}^{\circ}{}_f$ **(kJ/mol)**	ΔH **(kJ)**
Initial	Glucose	122 875	-1266	-155.566 x 10^6
	O2	316 280	0	0
	Total			-155.566 x 10^6
Final	Glucose	49 150	-1266	-62.224 x 10^6
	BM	147 000	-91.4	-13.44x 10^6
	CA	52 500	-1544.8	-80.407 x 10^6
	CO2	108 800	-393.51	-42.814 x 10^6
	O2	126 525	0	0
	Total			**- 198.885 x 10^6**

So, we finally obtain:

$$\Delta H = H_{out} - H_{in} = -43.320 \times 10^{6}\, kJ < 0$$

The reaction is hence exothermic, indicating that heat is released from the system to the surrounding.

Work calculation

Based on assumption 1, the aerator which provides work is an external device powered by a motor. It provides mechanical energy to the broth inside the fermenter, effectively stirring and ensuring proper mixing and oxygen transfer. This mechanical energy originates in the surroundings (e.g., electricity running the motor, which is not part of the system).

Hence, he direction of work flow is from the surroundings into the system. In other words, the work **is done by the surroundings on the system**. Based on the convention noted above, this means that **the work done by the system on the surroundings is negative.**

The work done is :

$$W = -\frac{100hp}{} * \frac{745.7J}{1(hp)(s)} * \frac{220hr}{} * \frac{3600s}{1hr} * \frac{1kJ}{1000J} = -59{,}6 * 10^{6}kJ$$

Note on the choice of 220 hr instead of 140 hr:

In thermodynamics and process engineering, “work” refers to the transfer of energy that involves a force acting over a distance. In this fermentation scenario, the 100-horsepower aerator introduces mechanical energy into the fermenter’s contents. This mechanical input, which helps maintain proper mixing, oxygen transfer, and temperature distribution, begins as soon as the fermenter is started up.

Even though the key biochemical reactions (notably, citric acid production) may predominantly occur during the defined idophases (with the bulk of reaction-driven changes happening after certain growth phases), the mechanical work of the aerator does not depend on the reaction kinetics. The motor-driven agitator is running and imparting energy to the system from the outset to ensure proper conditions for microbial growth and product formation later on.

While the stoichiometry and citric acid production vary during the early, medium, and late phases—occurring largely between 80 to 220 hours—the mechanical aeration and stirring are present and **continuously doing work from the start (0 hours) through the entire 220-hour period**. The work done from the surroundings is essentially a continuous input required to maintain the environment in which the microorganisms can eventually produce citric acid, **even if the bulk of product formation happens later in the timeline.**

Hence, from a thermodynamic and process viewpoint, the work input is counted from the beginning of the operation (t=0) and persists throughout the entire duration (220 hours).

Heat calculation:

We can finally compute the heat exchanged:

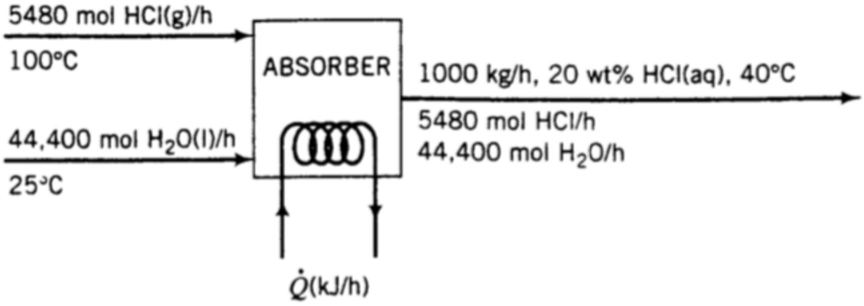
$$Q = \Delta H + W$$

$$Q = (-43.32 - 59.6) \times 10^6 \ kJ = \ -102.92 \ \times 10^6 \ kJ$$

As the heat is negative, this means that -102.02 x 10^6 kJ are **transferred from the surroundings to the system.** In other words, 102.02 x 10^6 kJ are transferred from the system to the surroundings, a.k.a **102.02 x 10^6 kJ are removed from the system.**

Problem 4: Heat of Solution (Energy Balance – Reactive)

Hydrochloric acid is produced by absorbing gaseous HCl in water. Calculate the heat that must be transferred to or from an absorption unit if HCl(g) at 100°C and water at 25°C are fed to produce 1000kg/h of 20.0 wt% HCl(aq) at 40°C)?



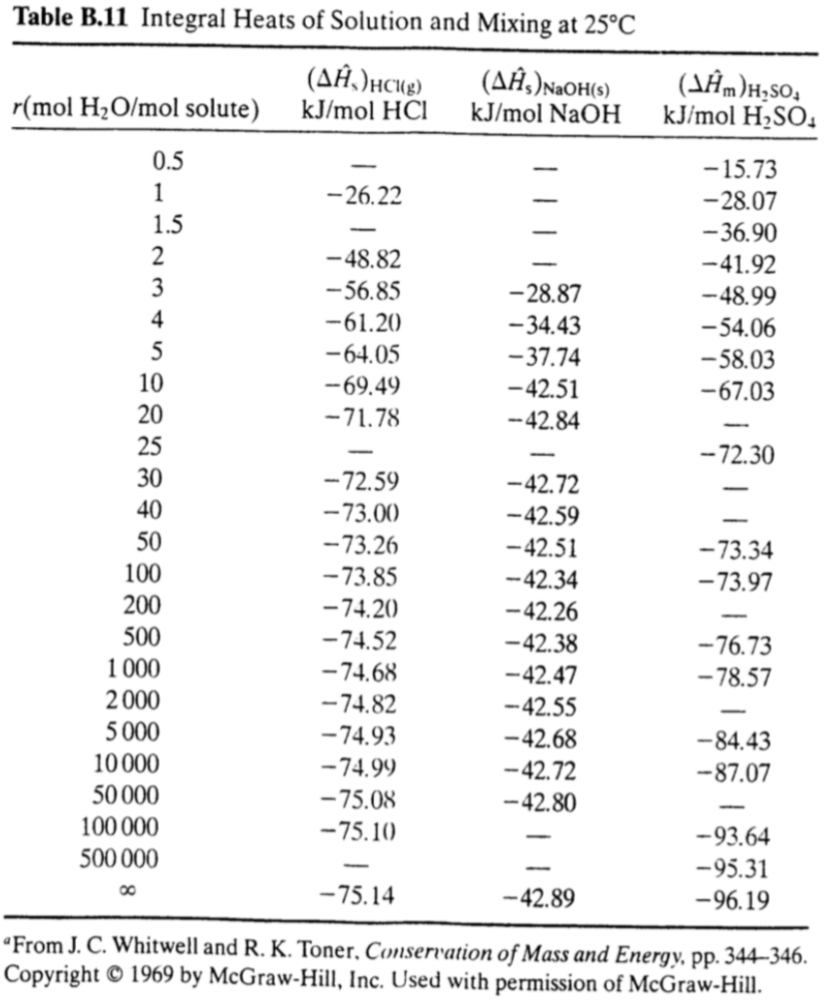


Table B.11 Integral Heats of Solution and Mixing at 25°C

r(mol H_2O/mol solute)	$(\Delta\hat{H}_s)_{HCl(g)}$ kJ/mol HCl	$(\Delta\hat{H}_s)_{NaOH(s)}$ kJ/mol NaOH	$(\Delta\hat{H}_m)_{H_2SO_4}$ kJ/mol H_2SO_4
0.5	—	—	−15.73
1	−26.22	—	−28.07
1.5	—	—	−36.90
2	−48.82	—	−41.92
3	−56.85	−28.87	−48.99
4	−61.20	−34.43	−54.06
5	−64.05	−37.74	−58.03
10	−69.49	−42.51	−67.03
20	−71.78	−42.84	—
25	—	—	−72.30
30	−72.59	−42.72	—
40	−73.00	−42.59	—
50	−73.26	−42.51	−73.34
100	−73.85	−42.34	−73.97
200	−74.20	−42.26	—
500	−74.52	−42.38	−76.73
1 000	−74.68	−42.47	−78.57
2 000	−74.82	−42.55	—
5 000	−74.93	−42.68	−84.43
10 000	−74.99	−42.72	−87.07
50 000	−75.08	−42.80	—
100 000	−75.10	—	−93.64
500 000	—	—	−95.31
∞	−75.14	−42.89	−96.19

[a] From J. C. Whitwell and R. K. Toner, *Conservation of Mass and Energy*, pp. 344–346. Copyright © 1969 by McGraw-Hill, Inc. Used with permission of McGraw-Hill.

Solution 4

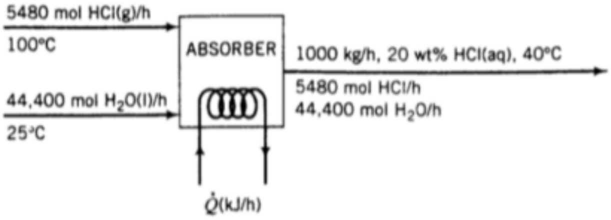
It is advisable to determine the molar amounts or flow rates of the components of all feed and product solutions before drawing and labeling the flowchart. In this case

$$1000\text{ kg/h of }20.0\text{ wt\% HCl(aq)}$$

$$\Downarrow$$

$$\dot{n}_{HCl} = \frac{1000\text{ kg}}{\text{h}}\left|\frac{0.200\text{ kg HCl}}{\text{kg}}\right|\frac{10^3\text{ mol}}{36.5\text{ kg HCl}} = 5480\text{ mol HCl/h}$$

$$\dot{n}_{H_2O} = \frac{1000\text{ kg}}{\text{h}}\left|\frac{0.800\text{ kg }H_2O}{\text{kg}}\right|\frac{10^3\text{ mol}}{18.0\text{ kg }H_2O} = 44{,}400\text{ mol }H_2O\text{/h}$$



The enthalpy table for the process is shown below. As usual, physical property data valid at $P = 1$ atm are used and the effects on enthalpy of any pressure differences that may occur in the process are neglected. Note that the value of $\dot{n}$ for the product solution is the molar flow rate of the *solute* (HCl) rather than the solution, since the enthalpy will be determined in kJ/mol solute.

References: HCl(g), H_2O(l) at 25°C and 1 atm

Substance	$\dot{n}_{in}$	$\hat{H}_{in}$	$\dot{n}_{out}$	$\hat{H}_{out}$
HCl(g)	5480 mol HCl	$\hat{H}_1$ (kJ/mol HCl)	—	—
H_2O(l)	44,400 mol H_2O	0	—	—
HCl(aq)	—	—	5480 mol HCl	$\hat{H}_2$(kJ/mol HCl)

Calculate $\hat{H}_1$ and $\hat{H}_2$

$$\text{HCl(g, 25°C)} \rightarrow \text{HCl(g, 100°C)}$$

$$\hat{H}_1 = \Delta\hat{H} = \int_{25°C}^{100°C} C_p\,dT$$

$$\Big\Downarrow C_p \text{ for HCl(g) from Table B.2}$$

$$\hat{H}_1 = 2.178\text{ kJ/mol}$$

For the product solution,

$$r = (44{,}400\text{ mol }H_2O)/(5480\text{ mol HCl}) = 8.10$$

$$\text{HCl(g, 25°C)} + 8.10\ H_2O(1, 25°C) \xrightarrow{\Delta\hat{H}_a} \text{HCl(aq, 25°C)} \xrightarrow{\Delta\hat{H}_b} \text{HCl(aq, 40°C)}$$

$$\Delta\hat{H}_a = \Delta\hat{H}_s(25°C, r = 8.1) \xRightarrow{\text{Table B.11}} -67.4\text{ kJ/mol HCl}$$

The heat capacities of aqueous hydrochloric acid solutions are listed on p. 2-184 of *Perry's Chemical Engineers' Handbook* (see footnote 5) as a function of the mole fraction of HCl in the solution, which in our problem is

$$\frac{5480 \text{ mol HCl/h}}{(5480 + 44{,}400) \text{ mol/h}} = 0.110 \text{ mol HCl/mol}$$

$$\Downarrow$$

$$C_p = \frac{0.73 \text{ kcal}}{\text{kg}\cdot{}^\circ\text{C}} \left| \frac{1000 \text{ kg solution}}{5480 \text{ mol HCl}} \right| \frac{4.184 \text{ kJ}}{\text{kcal}} = 0.557 \frac{\text{kJ}}{\text{mol HCl}\cdot{}^\circ\text{C}}$$

$$\Delta\hat{H}_b = \int_{25^\circ\text{C}}^{40^\circ\text{C}} C_p \, dT = 8.36 \text{ kJ/mol HCl}$$

$$\Downarrow$$

$$\hat{H}_2 = \Delta\hat{H}_a + \Delta\hat{H}_b = (-67.4 + 8.36) \text{ kJ/mol HCl} = -59.0 \text{ kJ/mol HCl}$$

Energy Balance

$$\begin{aligned}\dot{Q} = \Delta\dot{H} &= \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i \\ &= (5480 \text{ mol HCl/h})(-59.0 \text{ kJ/mol HCl}) - (5480 \text{ mol HCl/h})(2.178 \text{ kJ/mol HCl}) \\ &= \boxed{-3.35 \times 10^5 \text{ kJ/h}}\end{aligned}$$

Heat must be transferred out of the absorber at a rate of 335,000 kJ/h to keep the product temperature from rising above 40°C.

Problem 5: El Classico (Energy Balance – Reactive)

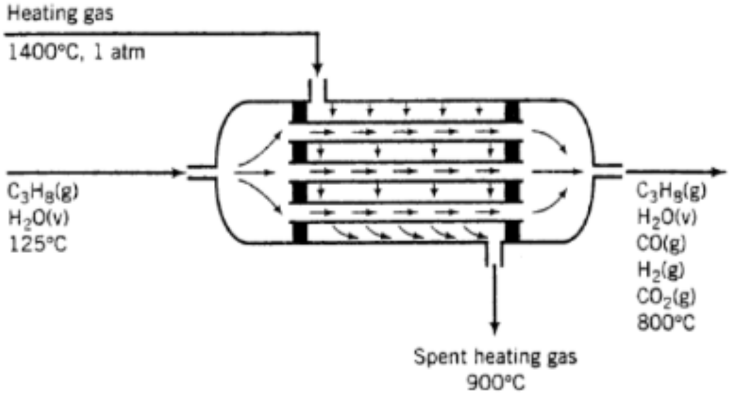
Hydrogen is produced in the steam reforming of propane:

C3H8(g) + 3 H2O(v) → 3 CO(g) + 7 H2(g)

The water-gas shift reaction also takes place in the reactor, leading to the formation of additional hydrogen:

CO(g) + H2O(v) → CO2(g) + H2(g)

The reaction is carried out over a nickel catalyst in the tubes of a shell-and-tube reactor. The feed to the reactor contains steam and propane in a 6:1 molar ratio at 125°C, and the products emerge at 800°C. The excess steam in the feed assures essentially complete consumption of the propane. Heat is added to the reaction mixture by passing a hot gas over the outside of the tubes that contain the catalyst. The gas is fed at 4.94 m^3/mol C3H8, entering the unit at 1400°C and 1 atm and leaving at 900°C. The unit may be considered adiabatic.



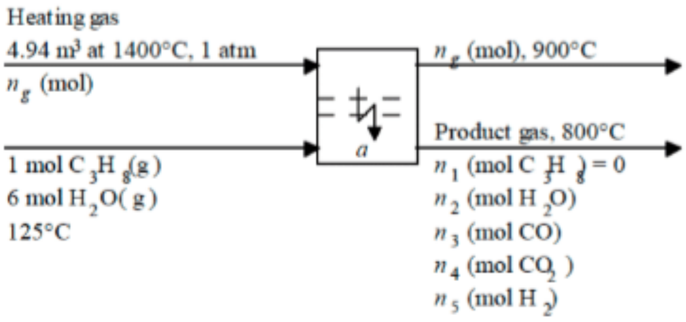
Calculate the molar composition of the product gas, assuming that the heat capacity of the heating gas is 0.040 kJ/(mol·°C).

Solution 5

$C_3H_8(g) + 3H_2O(v) \rightarrow 3CO(g) + 7H_2(g)$

$CO(g) + H_2O(v) \rightarrow CO_2(g) + H_2(g)$

<u>Basis</u>: 1 mol C_3H_8 fed



$$n_g = \frac{4.94\ \text{m}^3}{} \left| \frac{10^3\ \text{L}}{1\ \text{m}^3} \right| \frac{273\ \text{K}}{1673\ \text{K}} \left| \frac{1\ \text{mol}}{22.4\ \text{L}} \right. = 35.99 \text{ mol heating gas}$$

Let ξ_1 and ξ_2 be the extents of the two reactions.

$n_1 = 1 - \xi_1 \overset{n_1=0}{\Rightarrow} \xi_1 = 1 \text{ mol}$ $\qquad$ $n_4 = \xi_2$

$n_2 = 6 - 3\xi_1 - \xi_2 \overset{\xi_1=1}{\Rightarrow} n_2 = 3 - \xi_2$ $\qquad$ $n_5 = 7\xi_1 + \xi_2 \overset{\xi_1=1}{\Rightarrow} n_5 = 7 + \xi_2$

$n_3 = 3\xi_1 - \xi_2 \overset{\xi_1=1}{\Rightarrow} n_3 = 3 - \xi_2$

<u>References</u>: C(s), $H_2(g)$, $O_2(g)$ at 25°C, heating gas at 900°C

$$\hat{H}_i = \Delta\hat{H}^\circ_{fi} + \int_{25}^{T} C_{pi}\,dT \qquad \text{for } C_3H_8$$

$$= \text{Table B.8 for } CO_2, H_2, H_2O, CO$$

$$= \int_{900}^{T} C_p\,dT = C_p(T - 900) \quad \text{for heating gas}$$

Substance	n_{in} mol	$\hat{H}_{in}$ kJ / mol	n_{out} mol	$\hat{H}_{out}$ kJ / mol
C_3H_8	1	−95.39	0	–
H_2O	6	−238.43	$3-\xi_2$	−212.78
CO	–	–	$3-\xi_2$	−86.39
CO_2	–	–	ξ_2	−356.15
H_2	–	–	$7+\xi_2$	22.85
heating gas	35.99	20	35.99	0

<u>Energy Balance</u>:

$$\sum_{out} n_i\hat{H}_i - \sum_{in} n_i\hat{H}_i = 0 \Rightarrow \xi_2 = 2.00 \text{ mol} \Rightarrow n_2 = 1 \text{ mol } H_2O,\ n_3 = 1 \text{ mol CO},$$

$$n_4 = 1 \text{ mol } CO_2, n_5 = 9 \text{ mol } H_2 \Rightarrow \underline{\underline{7.7 \text{ mol \% } H_2O,\ 7.7\% \text{ CO},\ 15.4\% \text{ } CO_2,\ 69.2\% \text{ } H_2}}$$