

Solutions 12 ICE

Exercise 1

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 CO₂ 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 compute:

Glucose:

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

Oxygen:

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

Biomass:

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

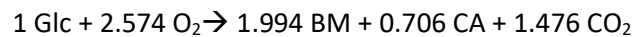
Citric acid:

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

Carboxylic acid:

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

Thus the overall reaction becomes:



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

Basis: 10 000 kg CA produced.

Moles of Citric Acid (CA) Produced:

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

Glucose Required (Considering 60% Efficiency):

$$\frac{52\,500 \text{ g mol CA}}{0.706 \text{ mol CA}} * \frac{1 \text{ mol Glc}}{1 \text{ mol Glc}} = 73\,725 \text{ mol of Glc needed}$$

Since only 60% of the glucose is converted:

$$\frac{73\,725 \text{ mol Glc consumed}}{0.60 \text{ mol Glc consumed}} * \frac{1.00 \text{ mol Glc fed}}{1 \text{ mol Glc consumed}} = 122\,875 \text{ moles of Glc fed}$$

Oxygen Consumed:

$$\frac{73\,725 \text{ mol Glc consumed}}{1 \text{ mol Glc consumed}} * \frac{2.54 \text{ mol O}_2 \text{ consumed}}{1 \text{ mol Glc consumed}} = 189\,755 \text{ moles O}_2$$

Biomass Produced:

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

Carbon Dioxide Produced:

$$\frac{73\,725 \text{ mol Glc consumed}}{1 \text{ mol Glc consumed}} * \frac{1.476 \text{ mol CO}_2 \text{ produced}}{1 \text{ mol Glc consumed}} = 108\,800 \text{ moles CO}_2$$

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 **transferred from the surroundings to the system**
- W is positive when it is done **by the system on the surroundings**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:

$$Q = \Delta H + W$$

Where:

- Q is positive when it is **transferred from the surroundings to the system**
- W is positive when it is **done by the system on the surroundings**

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

- 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:

	Component	mol	$\widehat{\Delta H}_f^\circ$ (kJ/mol)	ΔH (kJ)
Initial	Glucose	122 875	-1266	-155.566 x 10 ⁶
	O ₂	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
	CO ₂	108 800	-393.51	-42.814 x 10 ⁶
	O ₂	126 525	0	0
	Total			- 198.885 x 10 ⁶

So, we finally obtain:

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

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, the 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 :

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

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:

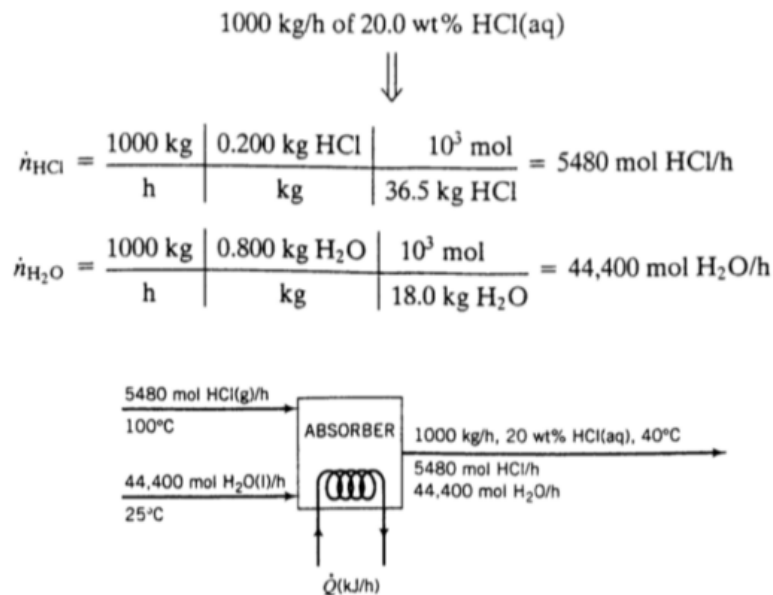
$$Q = \Delta H + W$$

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

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

Exercise 2

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



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), H₂O(l) at 25°C and 1 atm

Substance	$\dot{n}_{\text{in}}$	$\hat{H}_{\text{in}}$	$\dot{n}_{\text{out}}$	$\hat{H}_{\text{out}}$
HCl(g)	5480 mol HCl	$\hat{H}_1$ (kJ/mol HCl)	—	—
H ₂ O(l)	44,400 mol H ₂ O	0	—	—
HCl(aq)	—	—	5480 mol HCl	$\hat{H}_2$ (kJ/mol HCl)

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



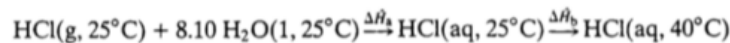
$$\hat{H}_1 = \Delta \hat{H} = \int_{25^\circ\text{C}}^{100^\circ\text{C}} C_p dT$$

↓ C_p for HCl(g) from Table B.2

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

For the product solution,

$$r = (44,400 \text{ mol H}_2\text{O}) / (5480 \text{ mol HCl}) = 8.10$$



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

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

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

⇓

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

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

⇓

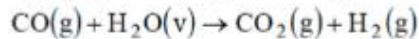
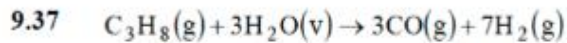
$$\hat{H}_2 = \Delta \hat{H}_a + \Delta \hat{H}_b = (-67.4 + 8.36) \text{ kJ/mol HCl} = -59.0 \text{ kJ/mol HCl}$$

Energy Balance

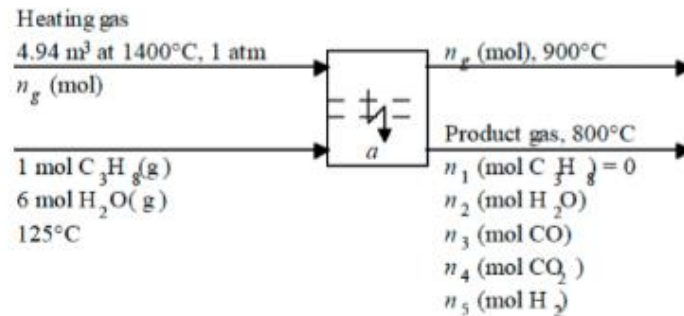
$$\begin{aligned} \dot{Q} = \Delta \dot{H} &= \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i \\ &= (5480 \text{ mol HCl/h})(-59.0 \text{ kJ/mol HCl}) - (5480 \text{ mol HCl/h})(2.178 \text{ kJ/mol HCl}) \\ &= \boxed{-3.35 \times 10^5 \text{ kJ/h}} \end{aligned}$$

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.

Exercise 3



Basis: 1 mol C_3H_8 fed



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

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

$$\begin{aligned} n_1 &= 1 - \xi_1 \Rightarrow \xi_1 = 1 \text{ mol} & n_4 &= \xi_2 \\ n_2 &= 6 - 3\xi_1 - \xi_2 \Rightarrow n_2 = 3 - \xi_2 & n_5 &= 7\xi_1 + \xi_2 \Rightarrow n_5 = 7 + \xi_2 \\ n_3 &= 3\xi_1 - \xi_2 \Rightarrow n_3 = 3 - \xi_2 \end{aligned}$$

References: $\text{C}(\text{s})$, $\text{H}_2(\text{g})$, $\text{O}_2(\text{g})$ at 25°C , heating gas at 900°C

$$\hat{H}_i = \Delta \hat{H}_f^\circ + \int_{25}^T C_{p,i} dT \quad \text{for } \text{C}_3\text{H}_8$$

= Table B.8 for CO_2 , H_2 , H_2O , CO

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

Substance	n_{in} mol	$\hat{H}_{\text{in}}$ kJ/mol	n_{out} mol	$\hat{H}_{\text{out}}$ 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

Energy Balance:

$$\begin{aligned} \sum_{\text{out}} n_i \hat{H}_i - \sum_{\text{in}} n_i \hat{H}_i &= 0 \Rightarrow \xi_2 = 2.00 \text{ mol} \Rightarrow n_2 = 1 \text{ mol } \text{H}_2\text{O}, n_3 = 1 \text{ mol } \text{CO}, \\ n_4 &= 1 \text{ mol } \text{CO}_2, n_5 = 9 \text{ mol } \text{H}_2 \Rightarrow \underline{\underline{7.7 \text{ mol } \% \text{H}_2\text{O}, 7.7\% \text{CO}, 15.4\% \text{CO}_2, 69.2\% \text{H}_2}} \end{aligned}$$