Introduction to Chemical Engineering

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.

$$C2H4\ (g) + 2\ Cl2\ (g) \rightarrow C2H2Cl4\ (l) + H2\ (g): \quad \Delta H°r = -385.76\ kJ/mol$$

$$C2H2Cl4\ (l) \rightarrow C2HCl3\ (l) + HCl\ (g)$$

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

$$C2H4(g) + 2\ Cl2(g) \rightarrow C2HCl3(l) + H2(g) + HCl(g)$$

(c) If 300 mol/h of C2HCl3(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 $\dot{Q} = \Delta\dot{H}$)

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

$$C_2H_2(g) + 2\,H_2(g) \rightarrow C_2H_6(g)$$

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).

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.

For the commercial production of citric acid in a batch fermenter, a 30 wt% aqueous glucose solution at 25 °C is introduced and inoculated with the fungus Aspergillus niger. The batch is run aerobically (in the presence of air). From a macroscopic viewpoint, three idophases occur with different stoichiometries (per 1 g mol of glucose consumed):

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

$$1 \text{ Glucose} + 1.5\ O_2(g) \rightarrow 3.81 \text{ biomass} + 0.62 \text{ citric acid} + 0.76\ CO_2(g)$$

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

$$1 \text{ Glucose} + 2.4\ O_2(g) \rightarrow 1.54 \text{ biomass} + 0.74 \text{ citric acid} + 1.33\ CO_2(g)$$

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

$$1 \text{ Glucose} + 3.91\ O_2(g) \rightarrow 0.86 \text{ biomass} + 0.74 \text{ citric acid} + 2.41\ CO_2(g)$$

A 100-horsepower aerator is used to supply stochiometric sterile air and to mix the broth. Over the full batch, only 60 % of the glucose fed is actually consumed (overall glucose conversion of 60 %); the remaining 40 % leaves as unreacted glucose.

You may assume that:

1. The system is the fermenter contents (glucose solution, water, dissolved O_2, biomass, citric acid, CO_2); everything else (aerator, motor, environment) is the surroundings.
2. The batch behaves as a closed system for the energy balance: oxygen and nitrogen entering with air, and CO_2 and nitrogen leaving, can be treated as part of the initial and final states, respectively.
3. Glucose consumption rate is constant during the productive period (80–220 h). Use a time-weighted average of the three stoichiometries to obtain a single overall reaction per mole of glucose consumed.

4. Nitrogen is inert and may be neglected in the stoichiometric and energy calculations.
5. The reference temperature for enthalpies is 25 °C. The broth is at 25 °C at the beginning and end of the batch; sensible heats and heat of mixing can be neglected (ignore the temperature differences 32 °C / 35 °C / 25 °C for enthalpy calculations).
6. Kinetic and potential energy changes are negligible.
7. You may approximate $\Delta U \approx \Delta H$, i.e. PV work is negligible, and use only standard heats of formation at 25 °C.
8. The aerator runs at 100 hp for the entire 220 h of operation, and this is treated as shaft work into the system. Use 1 hp = 745.7 W.

Data:

Species	**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
CO2(g)	44.01	393.51
O2(g)	32.00	0

Ignore any effects of solution on the heats of formation and any heat capacity effects.

Task: Based on the above data and assumptions, **determine the total amount of heat that must be added to or removed from the fermenter** during the production of a batch of **10 000 kg of citric acid**. State clearly whether heat must be supplied to or removed from the fermenter.

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)?

<u>Note</u>: The heat capacity (C_p) for the HCl solution is equal to 0.557 kJ / (mol HCl * °C)

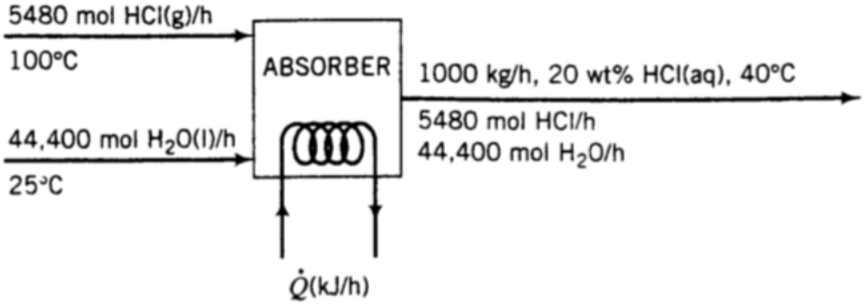


Table B.11 Integral Heats of Solution and Mixing at 25°C

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.

Problem 5: El Classico (Energy Balance – Reactive)

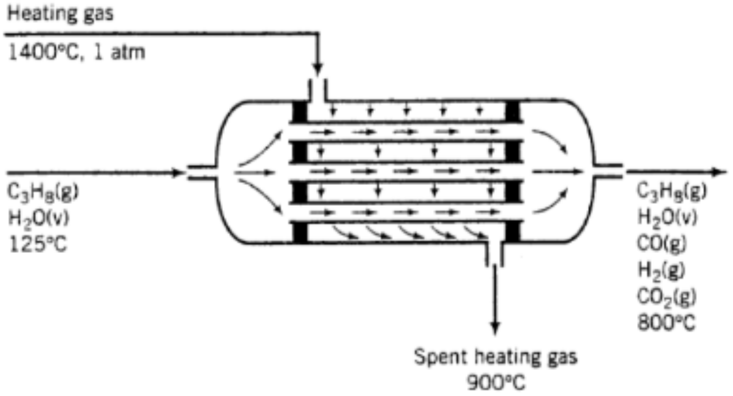
Hydrogen is produced in the steam reforming of propane:

$$C3H8(g) + 3\ H2O(v) \rightarrow 3\ CO(g) + 7\ H2(g)$$

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

$$CO(g) + H2O(v) \rightarrow CO2(g) + H2(g)$$

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).