Laboratory of
Computational
Systems
Biotechnology

EPFL

Introduction to Chemical Engineering

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Fridays, 14h15 - 17h00
2024-2025

(Updated) Course Schedule

Date	Subject
13-Sep	**1. Fundamentals of Material Balances** 1.1. Process definition and classification 1.2. Material balance calculations
20-Sep	1.3. Balances on multiple-unit processes
27-Sep	**Review on Mass Balances (non-reactive)**
04-Oct	1.4. Chemical reaction stoichiometry **1.5.1 Balances on reactive processes (part 1)**
11-Oct	**1.5.2 Balances on reactive processes (part 2)** **1.6. Balances on multiple unit reactive processes** **Review on Mass Balances (non-reactive & reactive)**
18-Oct	**2. Fundamentals of Energy and Energy Balances** 2.1. Energy balances on closed systems 2.2. Open systems at steady state **3. Balances on Non-Reactive Processes** 3.1. Energy balance calculation 3.2. Changes in Pressure, Temperature, Phases
01-Nov	**4. Balances on Reactive Processes** 4.1. Introduction to the Enthalpy of Reaction 4.2. Heat of Reaction Method 4.3. Heat of Formation Method 4.4 General Procedure to solve energy balance in reactive systems
08-Nov	**Review on Balances on Non-Reactive Processes** Problems: Mass and Energy Balances on non-Reactive Systems
15-Nov	**Midterm Exam: Mass & Energy Balances non-Reactive Systems**
22-Nov	**Review Midterm**

Date	Subject
29-Nov	Review on Heat of Reaction vs Heat of Formation Methods 4.5 Hess's Law to compute the Heat of Reaction 4.6 Heat of Combustion
06-Dec	**5. Energy balances on mixing processes** **5.1 Distinction between ideal and real solutions** **5.2 Heat of Solution**
13-Dec	Review and Study Session • Summing up with Mass and Energy Balances on Reactive Systems with Recycle

Recommended textbook:
Elementary Principles of Chemical Processes,
Richard M. Felder & Ronald W. Rousseau

Session VII: Friday 29 November 2024

After studying this session you will be able to:

1. Understand and apply Hess's Law

   Perform Energy Balances on Reactive Systems with the Heat of Reaction Method !

2. Work with Heats of Combustion

Review: How to calculate $\Delta\hat{H}_r$

Review: Methods to calculate $\Delta\hat{H}_r$

Heat of reaction $\Delta\hat{H}_r(T,P)$: enthalpy change for a process in which stoichiometric ratios of reactants at a **given T and P** are completely consumed and converted to products at the **same T and P.**

WHAT ARE THE TWO METHODS TO CALCULATE IT?

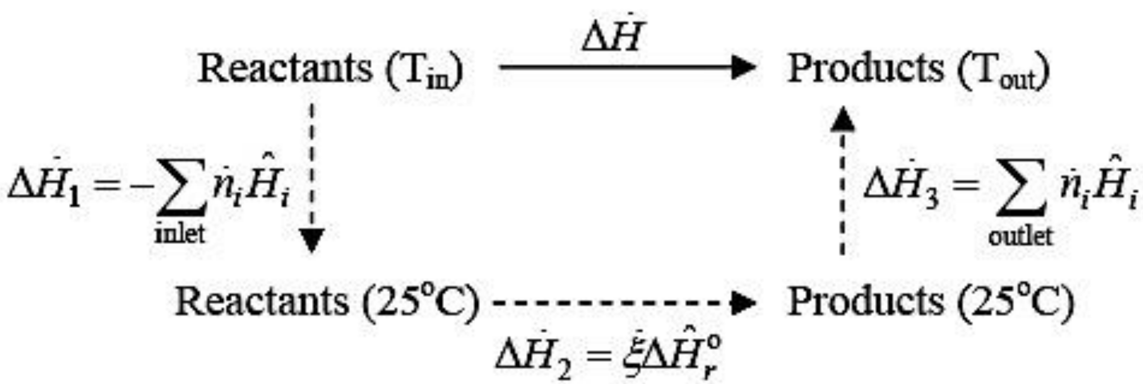
HEAT OF REACTION METHOD : when there is only a single reaction for which $\Delta H°_r$ is known

HEAT OF FORMATION METHOD : problems that have multiple reactions occurring simultaneously or if $\Delta H°_r$ is not know.

Review: Heat of reaction method

- Bring reactants from inlet conditions to 25°C
- react them at 25°C to make products at 25°C and
- then take the products to outlet conditions.

<u>Add the enthalpy changes in 3 steps.</u>

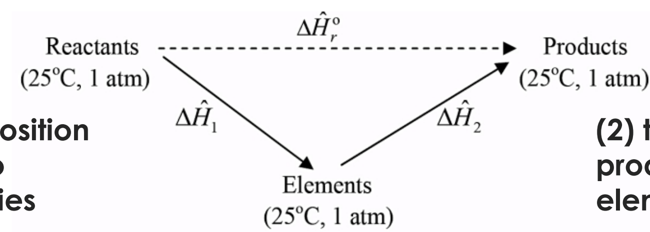


Review: Heat of formation method

- Bring reactants from inlet conditions
  to their constituent elements at 25°C and
- take the elements at 25°C to the outlet conditions.

<u>Add the enthalpy changes in 4 steps.</u>

(1) the decomposition of reactants into elemental species



(2) the formation of products from the elemental species

Hess' Law

Hess's Law

Application

To solve energy balances on reactive systems with the Heat of Reaction method!

Previously, we said: you can only apply the Heat of Reaction method, when you know the standard enthalpy of reaction ($\Delta\hat{H}_r°$)

This is PARTIALLY TRUE! We have to know $\Delta\hat{H}°_r$ but we do not need to have it as a data in the problem → WE CAN CALCULATE IT with HESS's LAW

HOW? We can calculate $\Delta\hat{H}_r°$ with the $\Delta\hat{H}°_r$ of other reactions (values that would be known)

Principles of Hess's Law

Hess's Law directly relates the heat of reaction ($\Delta\hat{H}_r°$) with the heats of formation of the reactants and products ($\Delta\hat{H}°_f$)

Definition: If the stoichiometric equation for a reaction 1 can be obtained by algebraic operations on stoichiometric equations for reactions 2, 3,… (which are independent reactions) then:

the heat of reaction $\Delta\hat{H}_{r1}°$ can be obtained by performing the same operations on the heats of reactions $\Delta\hat{H}_{r2}°$, $\Delta\hat{H}_{r3}°$,…

LOOK OUT! All reactions should be carried out at the same *T* and *P*

Algebraic operations : multiplication by constants, addition and subtraction

Example 1: Calculation of heats of reaction with Hess's Law

Given $\Delta\hat{H}^\circ_r$ for the reactions R1 and R2, calculate $\Delta\hat{H}^\circ_r$ for R3

R1: $A + B \rightarrow 2C$ $\quad \Delta\hat{H}^\circ_{r1} = -40$ kJ/mol

R2: $C \rightarrow D + B$ $\quad \Delta\hat{H}^\circ_{r2} = 100$ kJ/mol

R3: $A \rightarrow B + 2D$ $\quad \Delta\hat{H}^\circ_{r3} = ?$

We want to determine the heat of the reaction of R3, but we cannot carry out that reaction experimentally! What to do?

Calculate it using Hess's Law!

- R1: $A + B \rightarrow 2C$
- 2xR2: $2C \rightarrow 2B + 2D$
- R3=R1+2xR2: $A + B + 2C \rightarrow 2C + 2B + 2D$

$A \rightarrow B + 2D$ (R3)

Therefore:

$\Delta\hat{H}^\circ_{r3} = \Delta\hat{H}^\circ_{r1} + 2\Delta\hat{H}^\circ_{r2} = -40 + 2(100) = 160$ kJ/mol ☺

Example 2: Calculation of heats of reaction with Hess's Law

HANDS ON IT! Given $\Delta\hat{H}^\circ_r$ for the reactions R1 and R2, calculate $\Delta\hat{H}^\circ_r$ for R3

R1: $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta\hat{H}^\circ_{r1} = -393.51$ kJ/mol

R2: $CO(g) + ½\ O_2(g) \rightarrow CO_2(g)$ $\Delta\hat{H}^\circ_{r2} = -282.99$ kJ/mol

R3: $C(s) + 1/2O_2(g) \rightarrow CO(g)$ $\Delta\hat{H}^\circ_{r3} = ?$

R3 = R1 – R2 $C(s) + O_2(g) + CO_2(g) \rightarrow CO(g) + ½\ O_2(g) + CO_2(g)$

$C(s) + 1/2O_2(g) \rightarrow CO(g)$

$\Delta\hat{H}^\circ_{r3} = -110{,}52$ kJ/mol

NOTE: What kind of heat is $\Delta\hat{H}^\circ_{r1}$?

YES, $\Delta\hat{H}^\circ_{f,CO(g)}$!!!!! So, with Hess's Law we can calculate $\Delta\hat{H}^\circ_r$ with $\Delta\hat{H}^\circ_{f,i}$

Heat of combustion

Heats of combustion

- The **standard heat of combustion** $\Delta \hat{H}^\circ_c$ of a substance:
  - The heat of reaction when 1 mole of the substance is fully reacted with O_2(g) to yield the products CO_2(g) and H_2O**(l)**, with the combustion reaction carried out at 25°C and 1 atm.
  - Combustion is always exothermic, $\Delta \hat{H}^\circ_c$ is negative

- Heats of combustion are relatively easy to determine experimentally

- **The heats of other reactions can be easily calculated from the heats of combustion of the reactants and products**

- Heats of combustion are large compared with heats of reaction

General term:

$$\Delta \hat{H}^\circ_r = -\sum_i \nu_i (\Delta \hat{H}^\circ_c)_i = \sum_{reactants} |\nu_i| (\Delta \hat{H}^\circ_C)_i - \sum_{products} |\nu_i| (\Delta \hat{H}^\circ_C)_i$$

Example 3: Calculate the heat of reaction ($\Delta\hat{H}r°$) with the heats of combustion ($\Delta\hat{H}c°$) of species using two methods

Calculate the standard heat of reaction ($\Delta\hat{H}_r°$) for the following reaction (R5): the hydrogenation of benzene to cyclohexane.

R5: $C_6H_6(g) + 3H_2(g) \rightarrow C_6H_{12}(g)$

R1: $C_6H_6(g) + 15/2\ O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$ $\qquad \Delta\hat{H}_C = -3287.4$ kJ/mol

R2: $C_6H_{12}(g) + 9O_2 \rightarrow 6CO_2(g) + 6H_2O(l)$ $\qquad \Delta\hat{H}_C = -3949.2$ kJ/mol

R3: $C(s) + O_2(g) \rightarrow CO_2(g)$ $\qquad \Delta\hat{H}_C = -393.12$ kJ/mol

R4: $H_2(g) + ½\ O_2(g) \rightarrow H_2O(l)$ $\qquad \Delta\hat{H}_C = -285.58$ kJ/mol

- **LOOK OUT!:** unlike heats of formation, the standard state of water for heats of combustion is liquid

For heats of combustion standard conditions are normally P and T of 25°C and 1 atm

Example 3: Calculate the heat of reaction ($\Delta\hat{H}r°$) with the heats of combustion ($\Delta\hat{H}c°$) of species using two methods

Method 1: Heat of formation

GOAL: Calculate $\Delta\hat{H}_r°$ for R5: $C_6H_6(g) + 3H_2(g) \rightarrow C_6H_{12}(g)$

We can calculate the enthalpy of formation of C_6H_6 and C_6H_{12}, and with these values we can determine the heat of hydrogenation reaction:

$$\Delta\hat{H}°_r = \sum_{products} |\nu_i|(\Delta\hat{H}°_f)_i - \sum_{reactants} |\nu_i|(\Delta\hat{H}°_f)_i$$

Applying Hess's Law to calculate $\Delta\hat{H}_r°$ for R5

HOW?

Example 3: Calculate the heat of reaction ($\Delta\hat{H}r°$) with the heats of combustion ($\Delta\hat{H}c°$) of species using two methods

<u>Method 1: Heat of formation</u>

Applying Hess's Law to calculate $\Delta\hat{H}_f°$ for $C_6H_6(g)$:

Combine the reactions R1, R3 and R4

R5: $C_6H_6(g) + 3H_2(g) \rightarrow C_6H_{12}(g)$

R1: $C_6H_6(g) + 15/2\ O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$ $\Delta\hat{H}°_c = -3287.4$ kJ/mol

R2: $C_6H_{12}(g) + 9O_2 \rightarrow 6CO_2(g) + 6H_2O(l)$ $\Delta\hat{H}°_c = -3949.2$ kJ/mol

R3: $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta\hat{H}°_c = -393.12$ kJ/mol

R4: $H_2(g) + ½\ O_2(g) \rightarrow H_2O(l)$ $\Delta\hat{H}°_c = -285.58$ kJ/mol

$6C(s) + 3H_2(g) \rightarrow C_6H_6(g)$ $\Delta H°_f(C_6H_6) = ???$

Example 3: Calculate the heat of reaction ($\Delta\hat{H}r°$) with the heats of combustion ($\Delta\hat{H}c°$) of species using two methods

Method 1: Heat of formation

Applying Hess's Law to calculate $\Delta\hat{H}_f°$ for $C_6H_6(g)$:

Combine the reactions R1, R3 and R4

- R1:	$\cancel{6CO_2(g)} + \cancel{3H_2O(l)}$	$\rightarrow$	$C_6H_6(g) + \cancel{15/2\ O_2(g)}$
6xR3:	$6C(s) + \cancel{6O_2(g)}$	$\rightarrow$	$\cancel{6CO_2(g)}$
3xR4:	$3H_2(g) + \cancel{3/2\ O_2(g)}$	$\rightarrow$	$\cancel{3H_2O(l)}$

$$6C(s) + 3H_2(g) \rightarrow C_6H_6(g)$$

Applying Hess's Law:

$$DH°_f(C_6H_6) = -DH°_{C,R1} + 6\times DH°_{C,R3} + 3\times DH°_{C,R4}$$

$$DH°_f(C_6H_6) = -(-3287.4) + 6(-393.12) + 3(-285.58)$$

$$\Rightarrow DH°_f(C_6H_6) = 71.88\ kJ/mol$$

Example 3: Calculate the heat of reaction ($\Delta\hat{H}r°$) with the heats of combustion ($\Delta\hat{H}c°$) of species using two methods

Method 1: Heat of formation

Applying Hess's Law to calculate $\Delta\hat{H}_f°$ for $C_6H_{12}(g)$:

Combine the reactions R2, R3 and R4

- R2: $\cancel{6CO_2}(g) + \cancel{6H_2O}(l) \rightarrow C_6H_{12}(g) + \cancel{9O_2}$

6xR3: $6C(s) + \cancel{6O_2}(g) \rightarrow \cancel{6CO_2}(g)$

6xR4: $6H_2(g) + \cancel{3O_2(g)} \rightarrow \cancel{6H_2O}(l)$

$6C(s) + 6H_2(g) \rightarrow C_6H_{12}(g)$

Note: The enthalpy of formation of O_2 and H_2 is zero

Applying Hess's Law: $\Delta H°_f(C_6H_{12}) = -(-3949{,}2) + 6(-393{,}12) + 6(-285{,}58)$

$$\rightarrow \Delta H°_f(C_6H_{12}) = -123{,}06\ kJ/mol$$

$$\Delta H°_r = \Delta H°_f\,(C_6H_{12}) - \Delta H°_f(C_6H_6) = -123{,}06\ - 71{,}88 = -\ 195\ kJ/mol$$

Example 3: Calculate the heat of reaction ($\Delta\hat{H}r°$) with the heats of combustion ($\Delta\hat{H}c°$) of species using two methods

Method 2: Heat of combustion

GOAL: Calculate $\Delta\hat{H}_r°$ for R5: $C_6H_6(g) + 3H_2(g) \rightarrow C_6H_{12}(g)$

We can determine the heat of hydrogenation reaction with the heat of combustions of the species participating in the reaction R5:

$$\Delta\hat{H}°_r = \sum_{reactants} |\nu_i| (\Delta\hat{H}°_C)_i - \sum_{products} |\nu_i| (\Delta\hat{H}°_C)_i$$

Example 3: Calculate the heat of reaction ($\Delta\hat{H}r°$) with the heats of combustion ($\Delta\hat{H}c°$) of species using two methods

Method 2: Heat of combustion

GOAL: Calculate $\Delta\hat{H}_r°$ for R5: $C_6H_6(g) + 3H_2(g) \rightarrow C_6H_{12}(g)$

We can determine the heat of hydrogenation reaction with the heat of combustions of the species participating in the reaction R5:

1x R1:	$C_6H_6(g) + \cancel{15/2\ O_2}(g) \rightarrow \cancel{6\ CO_2}(g) + \cancel{3H_2O}(l)$	$\Delta\hat{H}°_c$ = -3287.4 kJ
-R2:	$\cancel{6CO_2}(g) + \cancel{6H_2O}(l) \rightarrow C_6H_{12}(g) + \cancel{9O_2}$	$\Delta\hat{H}°_c$ = -3949.2 kJ
3 x R4:	$3\ H_2(g) + \cancel{3/2\ O_2}(g) \rightarrow \cancel{3H_2O}(l)$	$\Delta\hat{H}°_c$ = -285.58 kJ

R5: $\mathbf{C_6H_6(g) + 3H_2(g) \rightarrow C_6H_{12}(g)}$

$$\Delta H°_r = (\Delta H°_C(C_6H_6) + 3\Delta H°_C(H_2)) - \Delta H°_c(C_6H_{12})$$

$$= (-3287.4 + 3(-285.88)) - (-3949.2)$$

$$\Rightarrow \Delta H°_r = 196\ kJ/mol$$