

Calculation of Enthalpy Changes



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14.1 Heat Capacity Equations

As shown previously, the change in enthalpy can be calculated using the heat capacity C_P .

$$\Delta H = \int C_P dT$$

To give the heat capacity some physical meaning, C_P represents the amount of energy required to increase the temperature of a given amount of substance by 1 degree.

Common units for C_P :

$$\frac{\text{kJ}}{\text{kmol} \cdot \text{K}}$$

$$\frac{\text{Btu}}{\text{lbmol} \cdot ^\circ \text{F}}$$

14.1 Heat Capacity Equations

Heat Capacities of Ideal Gases

Type of Molecule	High Temperature	Low Temperature
Monoatomic	$5R/2$	$5R/2$
Polyatomic, linear	$(3n - 3/2)R$	$7R/2$
Polyatomic, nonlinear	$(3n - 2)R$	$4R$

n = number of atoms per molecule ; R = ideal gas constant ; $C_V = C_P - R$

14.1 Heat Capacity Equations

For gas mixtures, the C_P of the mixture is the mole weighted average of the heat capacities of the components:

$$(C_P)_{\text{avg}} = \sum_{i=1}^N x_i C_{Pi}$$

If C_P is not constant for the given temperature range, it may be expressed as a function of temperature in a power series such as:

$$C_P = \alpha + \beta T + \gamma T^2$$

where α , β , and γ are constants specific to a particular substance (**Appendix E.1**, Basic Principles and Calculations in Chemical Engineering, 6th edition, by David M. Himmelblau)

Example 14–1. Calculation of ΔH for a Gas Mixture

An economic feasibility study indicates that solid municipal waste can be burned to a gas of the following composition (on a dry basis):

CO₂	9.2%
CO	1.5%
O₂	7.3%
N₂	82.0%

What is the enthalpy difference for this gas per lbmol between the bottom and the top of the stack if the temperature at the bottom of the stack is 550⁰F and the temperature at the top is 200⁰F.

Example 14-1. Calculation of ΔH for a Gas Mixture

The heat capacity equations for the gases are:

[T in $^{\circ}\text{F}$; C_P in $\text{Btu}/(\text{lbmol})(^{\circ}\text{F})$]

$$\text{N}_2: \quad C_P = 6.895 + 0.7624 \times 10^{-3}T - 0.7009 \times 10^{-7}T^2$$

$$\text{O}_2: \quad C_P = 7.104 + 0.7851 \times 10^{-3}T - 0.5528 \times 10^{-7}T^2$$

$$\text{CO}: \quad C_P = 6.865 + 0.8024 \times 10^{-3}T - 0.7367 \times 10^{-7}T^2$$

$$\text{CO}_2: \quad C_P = 8.448 + 5.757 \times 10^{-3}T - 21.59 \times 10^{-7}T^2 \\ + 3.059 \times 10^{-10}T^3$$

Example 14–1. Calculation of ΔH for a Gas Mixture

Basis: 1.00 lbmol of gas mixture

The enthalpy difference (ΔH) is calculated as:

$$\Delta H = \int C_P dT$$

The C_P of the gas mixture is determined from the equation:

$$(C_P)_{\text{avg}} = \sum_{i=1}^N x_i C_{Pi}$$

$$(C_P)_{\text{avg}} = x_{\text{N}_2} C_{P_{\text{N}_2}} + x_{\text{O}_2} C_{P_{\text{O}_2}} + x_{\text{CO}_2} C_{P_{\text{CO}_2}} + x_{\text{CO}} C_{P_{\text{CO}}}$$

Example 14-1. Calculation of ΔH for a Gas Mixture

$$x_{\text{N}_2} C_{P_{\text{N}_2}} = (0.82)(6.895 + \dots)$$

$$x_{\text{O}_2} C_{P_{\text{O}_2}} = (0.073)(7.104 + \dots)$$

$$x_{\text{CO}_2} C_{P_{\text{CO}_2}} = (0.092)(8.448 + \dots)$$

$$x_{\text{CO}} C_{P_{\text{CO}}} = (0.015)(6.865 + \dots)$$

Obtaining $\sum x_i C_{Pi}$:

$$\begin{aligned} (C_P)_{\text{avg}} = & 7.053 + 1.2242 \times 10^{-3} T - 2.6124 \times 10^{-7} T^2 \\ & + 0.2814 \times 10^{-10} T^3 \end{aligned}$$

Example 14-1. Calculation of ΔH for a Gas Mixture

Solving for ΔH :

$$\Delta H = \int_{550}^{200} \left(7.053 + 1.2242 \times 10^{-3} T - 2.6124 \times 10^{-7} T^2 + 0.2814 \times 10^{-10} T^3 \right) dT$$

$$\Delta H = 7.053(200 - 550) + \frac{1.2242 \times 10^{-3}}{2} (200^2 - 550^2) - \frac{2.6124 \times 10^{-7}}{3} (200^3 - 550^3) + \frac{0.2814 \times 10^{-10}}{4} (200^4 - 550^4)$$

$$\Delta H = -2616 \text{ Btu / lbmol}$$

14.2 Tables of Enthalpy Values

Enthalpies at various temperatures can also be obtained from tables.

From Basic Principles and Calculations in Chemical Engineering by David M. Himmelblau (6th edition):

Table D.2 Enthalpies of Paraffinic Hydrocarbons (C₁ – C₆)

Table D.3 Enthalpies of Other Hydrocarbons (ethylene, propylene, butene, acetylene, benzene)

Table D.4 Enthalpies of Nitrogen and Some of its Oxides

Table D.5 Enthalpies of Sulfur Compounds

Table D.6 Enthalpies of Combustion Gases

14.3 Enthalpy Calculations from Standard Heat of Formation

The enthalpy from a standard reference state is given by

$$H = H_f^\circ + \int_{T_R}^T C_P dT$$

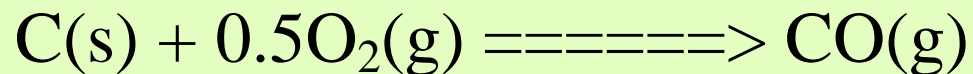
where H_f° is the standard heat of formation and T_R is the reference temperature.

For a mixture,

$$H_{mixture} = \sum_{i=1}^N \left(H_f^\circ + \int_{T_R}^T C_P dT \right)$$

14.3 Enthalpy Calculations from Standard Heat of Formation

The standard heat of formation (ΔH_f°) is the special enthalpy for the formation of 1 mole of a compound from its constituent elements, for example



The reactants and products must be at 25⁰C and 1 atm.

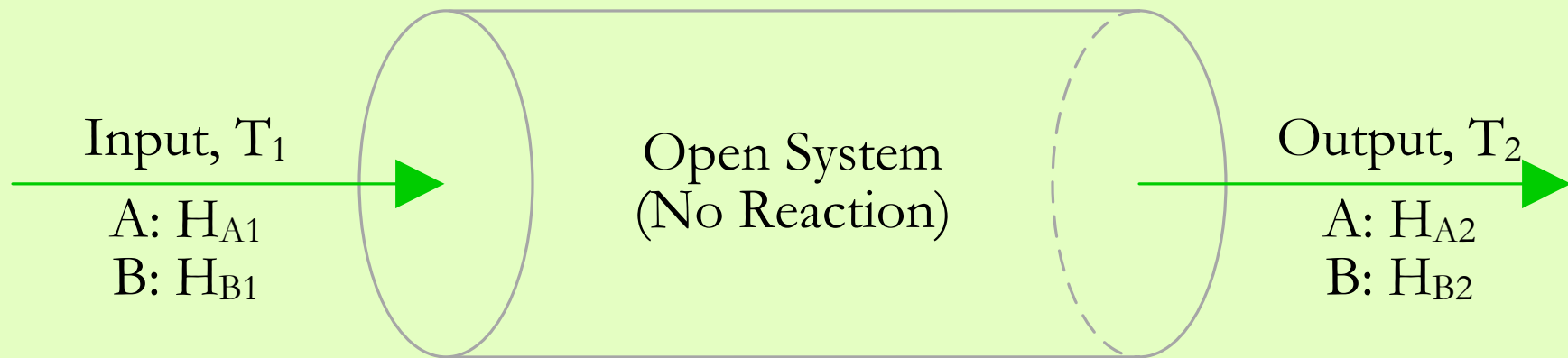
The reaction may not represent a real reaction. By definition, the heat of formation for the elements is zero in the standard state.

From Basic Principles and Calculations in Chemical Engineering by David M. Himmelblau (6th edition):

Table F.1 Heats of Formation and Combustion

14.3 Enthalpy Calculations from Standard Heat of Formation

Consider an open system with no chemical reaction:



The enthalpy difference between inlet and outlet will be

$$\Delta H = H_{\text{out}} - H_{\text{in}} = (H_{A2} + H_{B2}) - (H_{A1} + H_{B1})$$

14.3 Enthalpy Calculations from Standard Heat of Formation

Calculating the enthalpies from standard heat of formation

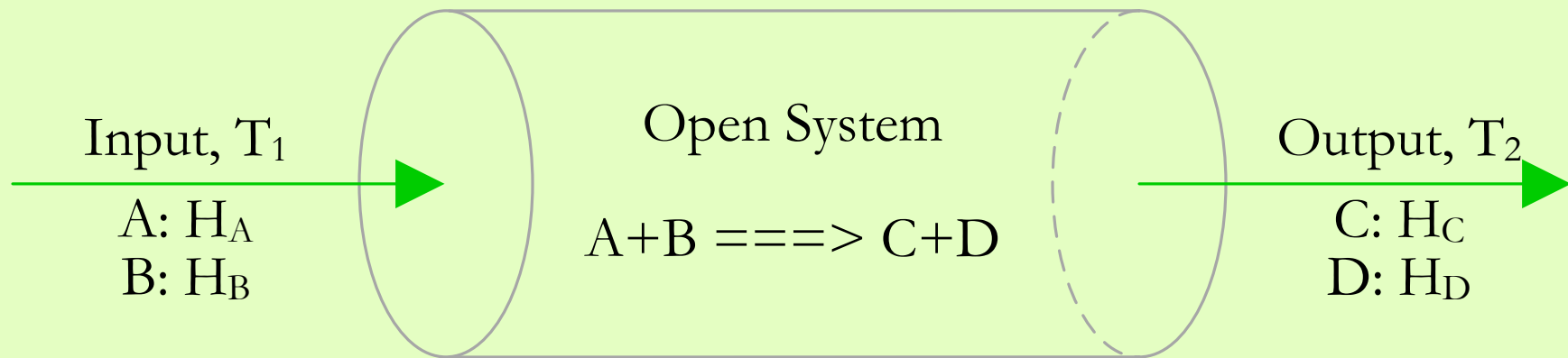
$$\Delta H = \left[\left(H_{fA}^\circ + \int_{T_R}^{T_2} C_{PA} dT \right) + \left(H_{fB}^\circ + \int_{T_R}^{T_2} C_{PB} dT \right) \right] \\ - \left[\left(H_{fA}^\circ + \int_{T_R}^{T_1} C_{PA} dT \right) + \left(H_{fB}^\circ + \int_{T_R}^{T_1} C_{PB} dT \right) \right]$$

Simplifying,

$$\Delta H = \int_{T_1}^{T_2} C_{PA} dT + \int_{T_1}^{T_2} C_{PB} dT$$

14.3 Enthalpy Calculations from Standard Heat of Formation

Consider an open system with chemical reaction:



The enthalpy difference between inlet and outlet will be

$$\Delta H = H_{\text{out}} - H_{\text{in}} = (H_C + H_D) - (H_A + H_B)$$

14.3 Enthalpy Calculations from Standard Heat of Formation

Calculating the enthalpies from standard heat of formation

$$\Delta H = \left[\left(H_{fC}^{\circ} + \int_{T_R}^{T_2} C_{PC} dT \right) + \left(H_{fD}^{\circ} + \int_{T_R}^{T_2} C_{PD} dT \right) \right] \\ - \left[\left(H_{fA}^{\circ} + \int_{T_R}^{T_1} C_{PA} dT \right) + \left(H_{fB}^{\circ} + \int_{T_R}^{T_1} C_{PB} dT \right) \right]$$

Rearranging the terms,

$$\Delta H = \left[\left(H_{fC}^{\circ} + H_{fD}^{\circ} \right) - \left(H_{fA}^{\circ} + H_{fB}^{\circ} \right) \right] + \int_{T_R}^{T_2} C_{PC} dT \\ + \int_{T_R}^{T_2} C_{PD} dT - \int_{T_R}^{T_1} C_{PA} dT - \int_{T_R}^{T_1} C_{PB} dT$$

14.3 Enthalpy Calculations from Standard Heat of Formation

The group of terms involving the standard heats of formation is called the standard heat of reaction, $\Delta H^{\circ}_{\text{R}}$.

In general,

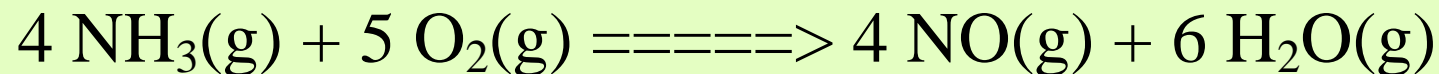
$$\Delta H^{\circ}_{\text{R}} = \sum_{\text{products}} \left(nH^{\circ}_{\text{f}} \right)_i - \sum_{\text{reactants}} \left(nH^{\circ}_{\text{f}} \right)_i$$

The n in the equation is the stoichiometric coefficient of species i in the chemical reaction.

The standard heat of reaction is the difference between the heats of formation of the products and that of the reactants.

Example 14-2. Calculation of Standard Heat of Reaction

Calculate ΔH_R° for the following reaction:



The standard heats of formation of the products and reactants are:



And the standard heat of reaction:

$$\Delta H_R^\circ = [4(90.374) + 6(-241.826)] - [4(-46.191) + 5(0)]$$

$$\Delta H_R^\circ = -904.696 \text{ kJ/4 mol NH}_3$$