

Example.3.10. 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):($\text{CO}_2=9.2\%$, $\text{CO}=1.5\%$, $\text{O}_2=7.3\%$, $\text{N}_2= 82\%$)

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 550°F and the temperature at the top is 200°F .

The heat capacity equations for the gases are: (T in $^\circ\text{F}$; C_P in $\text{Btu}/(\text{lbmol})(^\circ\text{F})$)

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

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

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

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

Solution:-

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

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

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

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

Obtaining $\sum x_i C_{P_i}$:

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

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:

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

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

Solving for ΔH :

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

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

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

Energy Balances: How to Account for Chemical Reaction

The Standard Heat (Enthalpy) of Formation:

-The observed heat transfer that occurs to or from a closed isothermal system in which a reaction takes place represents the energy change associated with the rearrangement of the bonds holding together the atoms of the reacting molecules.

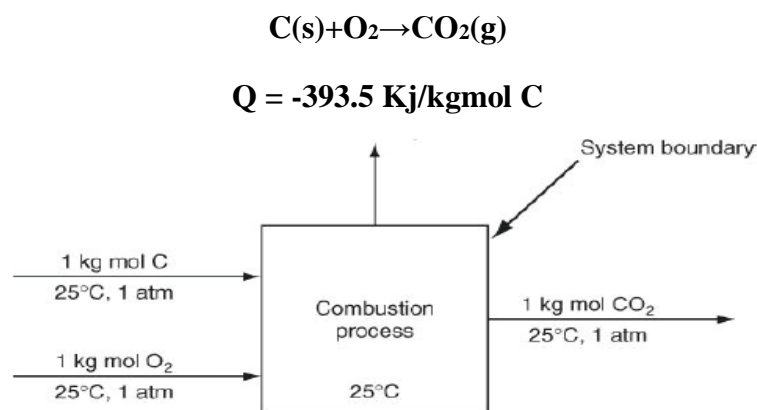
- For an exothermic reaction, heat is removed from the process in order to maintain a fixed system temperature; that is, energy is produced by the reaction to maintain isothermal conditions. The reverse is true of an endothermic reaction, in which heat is added to the system.

-To include energy changes caused by a reaction in the energy balance, we make use of a quantity called the standard heat (really enthalpy) of **formation**, often called just the heat of formation, denoted by the symbol $\Delta\hat{H}_f^\circ$. The superscript ($^\circ$) denotes the **standard state** (reference state) for reaction of 25°C and 1 atm, and the subscript **f** denotes “formation.” In this chapter the overlay caret (^) will usually denote that the value is per mole.

-**the standard heat of formation** is the name given to the special enthalpy change associated with the formation of 1 mol of a compound from its constituent elements and products in their standard state of 25°C and 1 atm.

the heat of formation as zero in the standard state for each stable (e.g., N₂ versus N) element.

-An example is the enthalpy change that occurs for the reaction of carbon and oxygen to form carbon dioxide at 25°C and 1 atm,



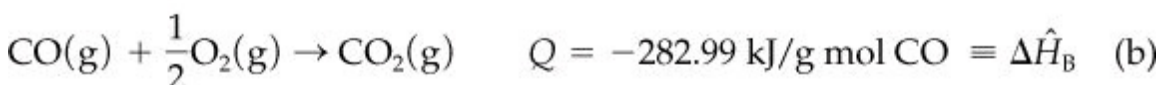
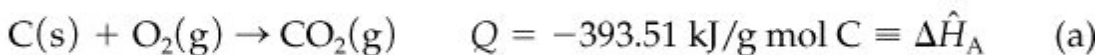
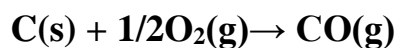
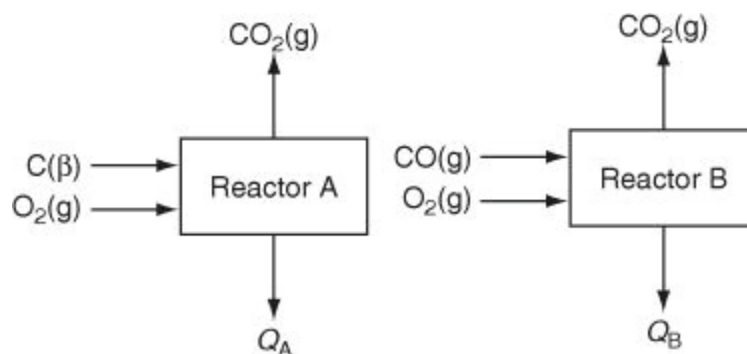
If you simplify the general energy balance, for the isothermal process in Figure (steady-state, flow, no KE or PE, etc.), you get the standard heat of formation of CO₂, calculated from

$$\begin{aligned}
 -393.5 \text{ kJ/kg mol CO}_2 = Q = \Delta H &= (1)\Delta\hat{H}_{f,\text{CO}_2}^\circ - (1)\Delta\hat{H}_{f,\text{C}}^\circ - (1)\Delta\hat{H}_{f,\text{O}_2}^\circ \\
 &= (1)\Delta\hat{H}_{f,\text{CO}_2}^\circ - 0 - 0 = \Delta\hat{H}_{f,\text{CO}_2}^\circ
 \end{aligned}$$

-it is possible to design a system to express the heats of formation for all compounds at 25°C and 1 atm.

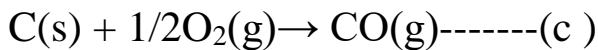
Example.4.1. Use of Heat Transfer Measurements to Get a Heat of Formation:

Suppose that you want to find the **standard heat of formation of CO** from experimental data. Can you prepare pure CO from the reaction of C and O₂ and measure the heat transfer? This would be far too difficult. It would be easier experimentally to find first the heat of reaction at standard conditions for the two reactions shown below for the flow process as shown in Figure below (assuming you had some pure CO to start with).



Basis: 1 g mol each of C and CO

According to Hess's law, you subtract Reaction (b) from Reaction (a), subtract the corresponding $\Delta\hat{H}_i$, and rearrange the compounds to form the desired chemical equation:



for which the net heat of reaction per gram mole of CO is the heat of formation of CO:

$$\Delta \hat{H}_{f, \text{CO}}^{\circ} = -393.51 - (-282.99) = -110.52 \text{ kJ/g mol CO}$$

Enthalpy Calculations from Standard Heat of Formation:

The enthalpy from a standard reference state is given by:

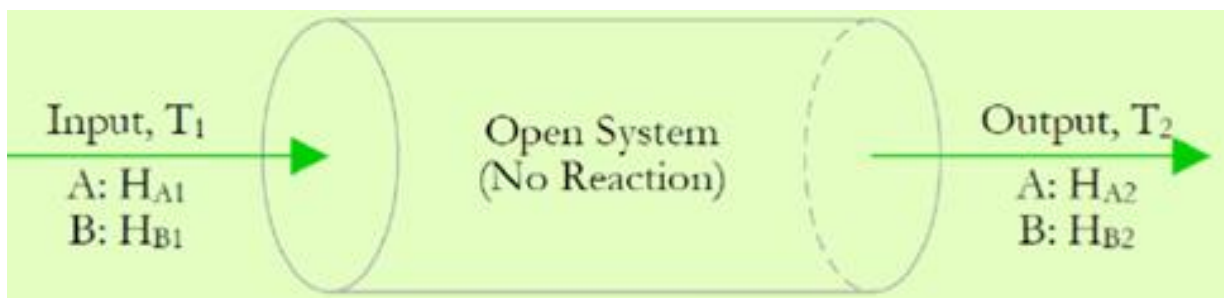
$$H = H_f^{\circ} + \int_{T_R}^T C_P dT$$

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

For a mixture:

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

Consider an open system with no chemical reaction:



The enthalpy difference between inlet and outlet will be:

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

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:

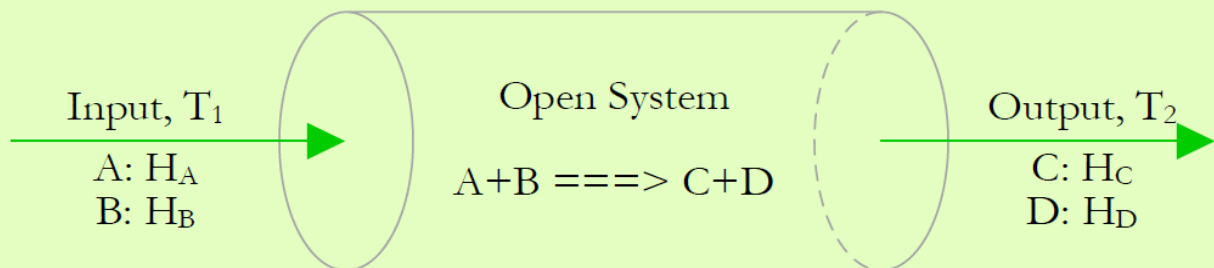
$$\Delta H = \int_{T_1}^{T_2} C_{PA} dT + \int_{T_1}^{T_2} C_{PB} dT$$

The Heat (Enthalpy) of Reaction:-

The heat of reaction (which should be but is only rarely called the enthalpy of reaction) is the enthalpy change that occurs when reactants at various T and p react to form products at some T and p.

The standard heat of reaction (ΔH_{rxn}° or ΔH_R°) is the name given to the heat of reaction when stoichiometric quantities of reactants in the standard state (25°C and 1 atm) react completely to produce products in the standard state.

Consider an open system with chemical reaction:



The enthalpy difference between inlet and outlet will be

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

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,

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

The group of terms involving the standard heats of formation is called the standard heat of reaction, ΔH_R° .

In general,

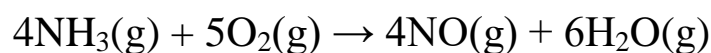
$$\Delta H_R^{\circ} = \sum_{\text{products}} (nH_f^{\circ}) - \sum_{\text{reactants}} (nH_f^{\circ})$$

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.4.2. Calculation of the Standard Heat of Reaction from the Standard Heats of Formation:

Calculate ΔH_{rxn}° or ΔH_R° for the following reaction of 4 g mol of NH₃ and 5 g mol of O₂:



Solution:

Basis: 4 g mol of NH₃

| Tabulated data: | <u>NH₃(g)</u> | <u>O₂(g)</u> | NO(g) | <u>H₂O(g)</u> |
|---|--------------------------|-------------------------|---------|--------------------------|
| $\Delta \hat{H}_f^\circ$ per mol at 25°C and 1 atm } (kJ/g mol) | -46.191 | 0 | +90.374 | -241.826 |

We shall use Equation $\Delta H_R^\circ = \sum_{Products}(nH_f^\circ)_i - \sum_{Reactants}(nH_f^\circ)_i$ to calculate ΔH_R° or ΔH_{rxn}° (25°C, 1 atm) for 4 g mol of NH₃, assuming complete reaction:

$$\Delta H_{rxn}^\circ = [4(90.374) + 6(-241.826)] + [(-5)(0) + (-4)(-46.191)] = -904.696 \text{ kJ}$$

Per gram mole of NH₃, $\Delta \hat{H}_{rxn}^\circ = \frac{904.646 \text{ kJ}}{4 \text{ g mol NH}_3} = -226.174 \text{ kJ/g mol NH}_3$