



## Energy balance with reaction

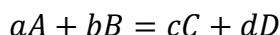
The large changes in enthalpy and internal energy throughout a chemical reaction require significant heat transfer (heating or cooling) from the reactor in order to eventually maintain the reactor under optimum operating conditions. This chapter demonstrates how to calculate the heat of reaction at a specific temperature and illustrates how to estimate the heat of reaction from the heat of formation. The energy balances for a reacting system using two methods are defined. Problems that involve the application of combined material and energy balances are addressed. Finally, a few applications, specifically, combustion, bioprocesses, and membrane reactors, are discussed at length to practice the concepts further. The following items outline the principal learning objectives of this chapter

### Learning Objectives

1. Calculate the heat of reaction (Section 9.1).
2. Estimate the heat of reaction from heats of formation (Section 9.2).
3. Establish the energy balance for a reacting system (Section 9.3).
4. Write simultaneous material and energy balances for a reacting system (Section 9.4).
5. Write the appropriate balances for combustion processes (Section 9.5).
6. Apply the energy balance to bioprocesses (Section 9.6).
7. Perform material and energy balances for a membrane reactor system (Section 9.7)

### 9.1 Heat of Reaction

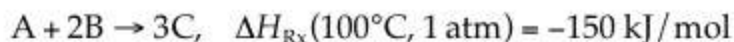
The heat of reaction,  $\Delta H_{Rx}(T, P)$ , is the enthalpy change for a process in which stoichiometric quantities of reactants at temperature  $T$  and pressure  $P$  react completely to form products at the same temperature and pressure. Consider the following reaction:



The standard heat of reaction ( $\Delta H_{Rx}^{\circ}$ ) is calculated as the difference between the product and reactant enthalpies when both reactants and products are at standard conditions, that is, at 25°C and 1 atm [1]. The symbol “o” denotes standard conditions. Therefore,

$$\begin{aligned}\Delta H_{Rx}^{\circ} [\text{kJ/mol}] &= H_{\text{products}} - H_{\text{reactants}} \\ &= c\Delta H_{f,C}^{\circ} + d\Delta H_{f,D}^{\circ} - a\Delta H_{f,A}^{\circ} - b\Delta H_{f,B}^{\circ} \\ &= \sum v_i \Delta H_i^{\circ}\end{aligned}$$

where  $\Delta H_f^{\circ}$  is the standard heat of formation. The reported  $\Delta H_{Rx}$  applies to stoichiometric quantities of each species. Consider the following example:



The enthalpy change for the given reaction is

$$\frac{-150 \text{ kJ}}{1 \text{ mol A consumed}} = \frac{-150 \text{ kJ}}{2 \text{ mol B consumed}} = \frac{-150 \text{ kJ}}{3 \text{ mol C generated}}$$

If 150 mol/s of C was generated at 100°C and 1 atm, then

$$\Delta \dot{H} = \left( \frac{-150 \text{ kJ}}{3 \text{ mol C generated}} \right) \left( \frac{150 \text{ mol C generated}}{\text{s}} \right) = -7500 \text{ kJ/s}$$

If  $\Delta H_{Rx}(T)$  is negative, the reaction is exothermic; that is, energy must be removed from the reactor to prevent the temperature from increasing. If  $\Delta H_{Rx}(T)$  is positive, the reaction is endothermic; that is, energy must be added to the reactor to prevent the temperature from decreasing. The heat of reaction ( $\Delta H_{Rx}(T, P)$ ) is nearly independent of pressure. The value of the heat of reaction depends on how the stoichiometric equation is written and on the phase of the reactants and products.

## 9.2 Heats of formation and heat of combustion

The standard heat of reaction ( $\Delta H^\circ_{Rx}$ ) can be calculated from the standard heat of formation ( $\Delta H^\circ_f$ ). The standard heat of formation is the enthalpy change associated with the formation of 1 mol of the compound at 25°C and 1 atm. The values of  $\Delta H^\circ_f$  for many compounds can be obtained from tabulated data (Table A.2). The standard heat of reaction ( $\Delta H^\circ_{Rx}$ ) from the heat of formation ( $\Delta H^\circ_{f,i}$ ) of any reaction can be calculated as

$$\Delta H^\circ_{Rx} = \sum_i \nu_i \Delta H^\circ_{f,i}$$

where

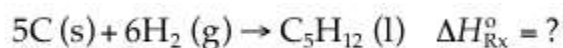
$\nu_i$  is the stoichiometric coefficient of reactant or product species  $i$   $\Delta H^\circ_{f,i}$  is the standard heat of formation of species  $i$

The standard heats of formation of all elemental species are zero ( $H_2$ ,  $O_2$ ,  $N_2$ ). The standard heat of reaction ( $\lim_{x \rightarrow \infty} \Delta H^\circ_{Rx}$ ) of any reaction involving only oxygen and a combustible species can be calculated as



$$\Delta H_{R_x}^{\circ} = - \sum_i \nu_i (\Delta H_c^{\circ})_i$$

This is the reverse of determining the heat of reaction from heats of formation, where  $\nu_i$  is the stoichiometric coefficient of reactant or product species  $i$ . ( $\Delta H_c^{\circ}$ ) is the standard heat of combustion of species  $i$ . If any reactants or products are combustion products (i.e.,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ ), their heats of combustion are equal to zero. For many substances, it is much easier to measure the standard heat of combustion ( $\Delta H_c^{\circ}$ ) than measuring the standard heat of formation ( $\Delta H_f^{\circ}$ ). Consider the formation of pentane:



Carbon, hydrogen, and pentane can all be burned, and their standard heats of combustion can be determined experimentally. Therefore,

$$\Delta H_{R_x}^{\circ} = 5\Delta H_{c,\text{C}(\text{s})}^{\circ} + 6\Delta H_{c,\text{H}_2(\text{g})}^{\circ} - \Delta H_{c,\text{C}_5\text{H}_{12}(\text{l})}^{\circ}$$

The standard enthalpy of combustion is the enthalpy change when 1 mol of a reactant completely burns in excess oxygen under standard thermodynamic conditions. The standard heat of combustion of a species  $i$ ,  $\Delta H_{c,i}^{\circ}$ , is the enthalpy change associated with the complete combustion of 1 mol of species  $i$  with oxygen at 25°C and 1 atm such that all the carbon forms  $\text{CO}_2(\text{g})$ , all the hydrogen forms  $\text{H}_2\text{O}(\text{l})$ , all the sulfur forms  $\text{SO}_2(\text{g})$ , and all the nitrogen forms  $\text{NO}_2(\text{g})$ . The same value of standard heat of reaction can be used to measure the standard heat of formation of pentane:

$$\Delta H_{R_x}^{\circ} = \Delta H_{f,\text{C}_5\text{H}_{12}(\text{l})}^{\circ} - 5\Delta H_{f,\text{C}(\text{s})}^{\circ} - 6\Delta H_{f,\text{H}_2(\text{g})}^{\circ}$$

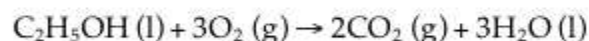
Since carbon and hydrogen are atoms, the magnitude of their standard heats of formation is zero. Accordingly,

$$\Delta H_{R_x}^{\circ} = \Delta H_{f,\text{C}_5\text{H}_{12}(\text{l})}^{\circ} - 0 - 0$$

### Example 9.1 Heat of Reaction from Heats of Formation

#### Problem

Consider the combustion of liquid ethanol as shown in the following reaction scheme:



Use heat of formation and heat of combustion to determine the standard heat of reaction.



### Solution

**Known quantities:** Reaction stoichiometry.

**Find:** Standard heat of reaction.

**Analysis:** Values for standard heat of combustion and standard heat of formation are available in the appendix.

$$\Delta H_{R_x}^{\circ} = 3\Delta H_{f, H_2O(l)}^{\circ} + 2\Delta H_{f, CO_2}^{\circ} - 0 - \Delta H_{f, C_2H_5OH(l)}^{\circ}$$

Substitute the values of the standard heat of formation:

$$\Delta H_{R_x}^{\circ} (\text{kJ/mol}) = 3(-285.84) + 2(-393.51) - 0 - (-277.63) = -1366.9 \text{ kJ/mol}$$

The standard heat of reaction is calculated from the standard heat of combustion as

$$\Delta H_{R_x}^{\circ} = \Delta H_{c, C_2H_5OH(l)}^{\circ} + 3\Delta H_{c, O_2}^{\circ} - 3\Delta H_{c, H_2O(l)}^{\circ} - 2\Delta H_{c, CO_2(g)}^{\circ}$$

Substitute the values of the standard heat of combustion, knowing that the magnitudes of the standard heat of combustion of oxygen, water, and carbon dioxide are zero:

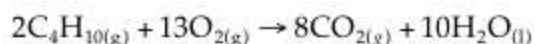
$$\Delta H_{R_x}^{\circ} (\text{kJ/mol}) = -1366.91 + 0 - 0 - 0 = -1366.9 \text{ kJ/mol}$$

Results reveal that both values of standard heat of reactions are identical.

### Example 9.2 Standard Rate of Change in Enthalpy

#### Problem

If 240 mol/s of  $CO_2$  is produced in the following reaction where reactants and products are all at 25°C, and no  $CO_2$  is present in the feed stream,



what is the standard rate of change in enthalpy?

#### Solution

**Known quantities:** Molar flow rate of effluent  $CO_2$  and reaction temperature.



**Find:** Standard rate of change in enthalpy.

**Analysis:** The standard heat of reaction from the heat of formation is as follows:

$$\Delta H_{R_x}^{\circ} (25^{\circ}\text{C}, 1 \text{ atm}) = \sum v_i \Delta H_{f,i}^{\circ}$$

The heat of reaction is given by

$$\Delta H_{R_x}^{\circ} (25^{\circ}\text{C}, 1 \text{ atm}) = 10\Delta H_{f, \text{H}_2\text{O}(l)}^{\circ} + 8\Delta H_{f, \text{CO}_2}^{\circ} - 2\Delta H_{f, \text{C}_4\text{H}_{10}}^{\circ} - 13\Delta H_{f, \text{O}_2}^{\circ}$$

$$\Delta H_{R_x}^{\circ} (25^{\circ}\text{C}, 1 \text{ atm}) = 10(-285.84) + 8(-393.5) - 2(-124.7) - 13(0)$$

$$\Delta H_{R_x}^{\circ} (25^{\circ}\text{C}, 1 \text{ atm}) = -5757 \text{ kJ/mol}$$

The extent of reaction is calculated using the mole balance of  $\text{CO}_2$ ; note that no carbon dioxide is present in the feed stream before the reaction takes place:

$$n_{\text{CO}_2} = 0 + 8\xi = 240 = 0 + 8\xi$$

$$\xi = \frac{240}{8} = 30 \text{ mol/s}$$

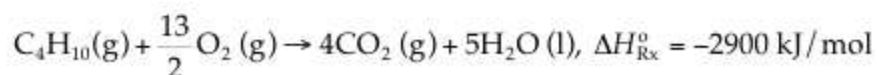
The change in enthalpy transfer rate is

$$\dot{\Delta H} = \xi \times \Delta H_{R_x}^{\circ} = 30 \times -5757 \text{ kJ/mol} = -1.727 \times 10^5 \text{ kJ/s}$$

### Example 9.3 Butane Combustion

#### Problem

The reaction stoichiometry and standard heat of the reaction on *n*-butane vapor is shown here:



Assume that 40 mol/s of  $\text{CO}_2$  is produced in this reaction and the reactants and products are all at  $25^{\circ}\text{C}$ . The fresh feed to the reactor contains 20 mol/s of  $\text{CO}_2$ . Calculate the rate of change in enthalpy  $\dot{\Delta H}^{\circ}(\text{kJ/s})$ .





### Solution

**Known quantities:** Inlet and exit CO<sub>2</sub> molar flow rate and reaction temperature.

**Find:** The rate of change in enthalpy.

**Analysis:** Since inlet and exit streams' temperature is equal, the change in the sensible heat is irrelevant. Accordingly, the rate of change in enthalpy is only due to heat of reaction and is calculated as

$\Delta \dot{H} = \xi \Delta H_{R_x}^0(T, P)$  at 25°C,  $\Delta \dot{H} = \xi \Delta H_{R_x}^0$ , where  $\Delta H_{R_x}^0$  is the standard heat of reaction.

The extent of reaction is calculated using the mole balance of CO<sub>2</sub>:

$$\dot{n}_{CO_2} = \dot{n}_{CO_2, feed} + 4\dot{\xi}$$

Substitute the values of inlet and exit molar flow rates of carbon dioxide:

$$40 = 20 + 4\dot{\xi}$$

The extent of reaction is  $\dot{\xi} = \frac{40 - 20}{4} = \frac{20}{4} = 5 \text{ mol/s}$

The standard rate of change in enthalpy,  $\Delta \dot{H}$  is

$$\Delta \dot{H} = \xi \Delta H_{R_x}^0 = \left( 5 \frac{\text{mol}}{\text{s}} \right) \left( \frac{-2900 \text{ kJ}}{\text{mol}} \right) = -1.45 \times 10^4 \text{ kJ/s}$$