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:

$$aA + bB = cC + dD$$

The standard heat of reaction (ΔH°_{Rx}) 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,

$$\begin{aligned}\Delta H^{o}_{Rx}[\mathrm{kJ/mol}] &= H_{\text{products}} - H_{\text{reactants}} \\ &= c\Delta H^{o}_{f,C} + d\Delta H^{o}_{f,D} - a\Delta H^{o}_{f,A} - b\Delta H^{o}_{f,B} \\ &= \sum \nu_i \Delta H^{o}_{i}\end{aligned}$$

where ΔH°_f is the standard heat of formation. The reported ΔH_{Rx} applies to stoichiometric quantities of each species. Consider the following example:

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$$A + 2B \rightarrow 3C, \quad \Delta H_{Rx}(100°C, 1\ atm) = -150\ kJ/mol$$

The enthalpy change for the given reaction is

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

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

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

If ΔH_{Rx} (T) is negative, the reaction is exothermic; that is, energy must be removed from the reactor to prevent the temperature from increasing. If ΔH_{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 (ΔH_{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 ($\Delta H°_{Rx}$) can be calculated from the standard heat of formation ($\Delta H°_f$). 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 $\Delta H°_f$ for many compounds can be obtained from tabulated data (Table A.2). The standard heat of reaction ($\Delta H°_{Rx}$) from the heat of formation ($\Delta H°_{f,i}$) of any reaction can be calculated as

$$\Delta H^{o}_{Rx} = \sum_i v_i \Delta H^{o}_{f,i}$$

where
v_i is the stoichiometric coefficient of reactant or product species i $\Delta H°_{f,i}$, 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 ($\lim_{x \to \infty} \Delta H°_{Rx}$) of any reaction involving only oxygen and a combustible species can be calculated as

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$$\Delta H^o_{Rx} = -\sum_i v_i(\Delta H^o_c)_i$$

This is the reverse of determining the heat of reaction from heats of formation, where *vi* is the stoichiometric coefficient of reactant or product species *i*. (ΔH°_c) is the standard heat of combustion of species *i*. If any reactants or products are combustion products (i.e., CO_2, H_2O, SO_2), their heats of combustion are equal to zero. For many substances, it is much easier to measure the standard heat of combustion ($\Delta H^\circ c$) than measuring the standard heat of formation (ΔH°_f). Consider the formation of pentane:

$$5C\,(s) + 6H_2\,(g) \rightarrow C_5H_{12}\,(l) \quad \Delta H^o_{Rx} = ?$$

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

$$\Delta H^o_{Rx} = 5\Delta H^o_{c,C(s)} + 6\Delta H^o_{c,H_2(g)} - \Delta H^o_{c,C_5H_{12}(l)}$$

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*, $\Delta H^\circ_{c,i}$, 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 CO_2 (g), all the hydrogen forms H_2O (l), all the sulfur forms SO_2 (g), and all the nitrogen forms NO_2 (g). The same value of standard heat of reaction can be used to measure the standard heat of formation of pentane:

$$\Delta H^o_{Rx} = \Delta H^o_{f,C_5H_{12}(l)} - 5\Delta H^o_{f,C(s)} - 6\Delta H^o_{f,H_2(g)}$$

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

$$\Delta H^o_{Rx} = \Delta H^o_{f,C_5H_{12}(l)} - 0 - 0$$

Example 9.1 Heat of Reaction from Heats of Formation

Problem

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

$$C_2H_5OH\,(l) + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 3H_2O\,(l)$$

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

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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.

$$\Delta H^o_{Rx} = 3\Delta H^o_{f,\,H_2O\,(l)} + 2\Delta H^o_{f,\,CO_2} - 0 - \Delta H^o_{f,\,C_2H_5OH\,(l)}$$

Substitute the values of the standard heat of formation:

$$\Delta H^o_{Rx}(\mathrm{kJ/mol}) = 3(-285.84) + 2(-393.51) - 0 - (-277.63) = -1366.9\ \mathrm{kJ/mol}$$

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

$$\Delta H^o_{Rx} = \Delta H^o_{c,\,C_2H_5OH\,(l)} + 3\Delta H^o_{c,\,O_2} - 3\Delta H^o_{c,\,H_2O\,(l)} - 2\Delta H^o_{c,\,CO_2\,(g)}$$

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:

$$\Delta H^o_{Rx}(\mathrm{kJ/mol}) = -1366.91 + 0 - 0 - 0 = -1366.9\ \mathrm{kJ/mol}$$

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,

$$2C_4H_{10(g)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(l)}$$

what is the standard rate of change in enthalpy?

Solution

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

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Find: Standard rate of change in enthalpy.

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

$$\Delta H^{o}_{Rx}\ (25°C, 1\ atm) = \sum v_i \Delta H^{o}_{f,i}$$

The heat of reaction is given by

$$\Delta H^{o}_{Rx}\ (25°C, 1\ atm) = 10\Delta H^{o}_{f,\,H_2O\,(l)} + 8\Delta H^{o}_{f,\,CO_2} - 2\Delta H^{o}_{f,\,C_4H_{10}} - 13\Delta H^{o}_{f,\,O_2}$$

$$\Delta H^{o}_{Rx}\ (25°C, 1\ atm) = 10(-285.84) + 8(-393.5) - 2(-124.7) - 13(0)$$

$$\Delta H^{o}_{Rx}\ (25°C, 1\ atm) = -5757\ kJ/mol$$

The extent of reaction is calculated using the mole balance of CO_2; note that no carbon dioxide is present in the feed stream before the reaction takes place:

$$n_{CO_2} = 0 + 8\xi = 240 = 0 + 8\xi$$

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

The change in enthalpy transfer rate is

$$\Delta \dot{H} = \xi \times \Delta H^{o}_{Rx} = 30 \times -5757\ kJ/mol = -1.727 \times 10^{5}\ kJ/s$$

Example 9.3 Butane Combustion

Problem

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

$$C_4H_{10}(g) + \frac{13}{2} O_2\ (g) \rightarrow 4CO_2\ (g) + 5H_2O\ (l),\ \Delta H^{o}_{Rx} = -2900\ kJ/mol$$

Assume that 40 mol/s of CO_2 is produced in this reaction and the reactants and products are all at 25°C. The fresh feed to the reactor contains 20 mol/s of CO_2. Calculate the rate of change in enthalpy *ΔH°(kJ/s)*.

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Solution

Known quantities: Inlet and exit CO_2 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 $\Delta\dot{H} = \dot{\xi}\Delta H^{o}_{\mathrm{Rx}}(T, P)$ at 25°C, $\Delta\dot{H} = \dot{\xi}\Delta H^{o}_{\mathrm{Rx}}$, where $\Delta H^{o}_{\mathrm{Rx}}$ is the standard heat of reaction.

The extent of reaction is calculated using the mole balance of CO_2:

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

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

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

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

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

$$\Delta\dot{H} = \dot{\xi}\Delta H^{o}_{\mathrm{Rx}} = \left(5\,\frac{\mathrm{mol}}{\mathrm{s}}\right)\left(\frac{-2900\ \mathrm{kJ}}{\mathrm{mol}}\right) = -1.45\times10^{4}\ \mathrm{kJ/s}$$