

Republic of Iraq

Ministry of Higher Education

and Scientific Research

Al-Mustaqbal University College

Chemical Engineering and Petroleum Industries Department



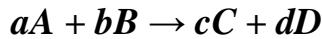
Subject: Energy and Energy Balances

2nd Class

Lecture Six

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 (ΔH_{Rx}^o) 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,

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

where ΔH_{fo} is the standard heat of formation. The reported ΔH_{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.

2. Heats of Formation and Heat of Combustion

The standard heat of reaction (ΔH_{Rxo}) can be calculated from the standard heat of formation (ΔH_{fo}). 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 ΔH_{fo} for many compounds can be obtained from tabulated data (Table A.2). The standard heat of reaction (ΔH_{Rxo}) from the heat of formation ($\Delta H_{fo, i}$) of any reaction can be calculated as

$$\Delta H_{Rxo}^{\circ} = \sum_i v_i \Delta H_{f,i}^{\circ}$$

where

v_i is the stoichiometric coefficient of reactant or product species i

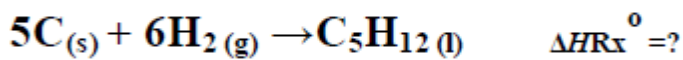
$\Delta H_{fo,i}$ is the standard heat of formation of species i

The standard heats of formation of all elemental species are zero (H₂, O₂, N₂).

The standard heat of reaction (ΔH_{Rxo}°) of any reaction involving only oxygen and a combustible species can be calculated as

$$\Delta H_{Rxo}^{\circ} = - \sum_i v_i (\Delta H_{c,i}^{\circ})$$

This is the reverse of determining the heat of reaction from heats of formation, where v_i is the stoichiometric coefficient of reactant or product species i . ($\Delta H_{c,i}$) is the standard heat of combustion of species i . If any reactants or products are combustion products (i.e., CO₂, H₂O, SO₂), their heats of combustion are equal to zero. For many substances, it is much easier to measure the standard heat of combustion ($\Delta H_{c,o}$) than measuring the standard heat of formation (ΔH_{fo}). Consider the formation of pentane:



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

$$\Delta H_{Rxo}^{\circ} = 5\Delta H_{c,C(s)}^{\circ} + 6\Delta H_{c,H_2(g)}^{\circ} - \Delta H_{c,C_5H_{12(l)}}^{\circ}$$

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 , $\Delta H_{c,i}$, 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 CO₂ (g), all the hydrogen forms H₂O (l), all the sulfur forms SO₂ (g), and all the nitrogen forms NO₂ (g). The same value of standard heat of reaction can be used to measure the standard heat of formation of pentane:

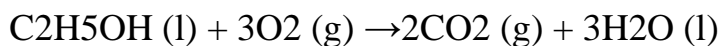
$$\Delta H_{R_x}^{\circ} = \Delta H_{f,C_5H_{12}}^{\circ}(l) - 5\Delta H_{f,C(s)}^{\circ} - 6\Delta H_{f,H_2(g)}^{\circ}$$

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

$$\Delta H_{R_x}^{\circ} = \Delta H_{f,C_5H_{12}}^{\circ}(l) - 0 - 0$$

Example 1 :Heat of Reaction from Heats of Formation

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:

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

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

2.1 :Extent of Reaction

If n_A is the moles of A generated or consumed by a reaction at a temperature T and pressure P , and ν_A is the stoichiometric coefficient of the reactant or product, the associated enthalpy change is

$$\Delta \dot{H} = \dot{\xi} \Delta H_{\text{Rx}}(T, P)$$

The extent of reaction, ξ , is a measure of how far a reaction has proceeded:

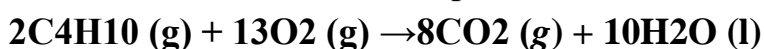
$$(\dot{n}_i)_{\text{out}} = (\dot{n}_i)_{\text{in}} + \nu_i \dot{\xi}$$

Rearranging, the extent of reaction is expressed as

$$\dot{\xi} = \frac{(\dot{n}_i)_{\text{out}} - (\dot{n}_i)_{\text{in}}}{\nu_i}$$

Example 2:

If 240 mol/s of CO₂ is produced in the following reaction where reactants and products are all at 25C, and no CO₂ is present in the feed stream,



what is the standard rate of change in enthalpy?

Solution

Known quantities: Molar flow rate of effluent CO₂ and reaction temperature.

Find: Standard rate of change in enthalpy.

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

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

The heat of reaction is given by

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

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

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

The extent of reaction is calculated using the mole balance of CO₂; note that no carbon dioxide is present in the feed stream before the reaction takes place:

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

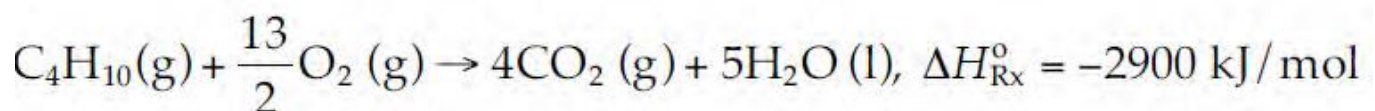
$$\xi = \frac{240}{8} = 30 \text{ mol/s}$$

The change in enthalpy transfer rate is

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

Example 3: Butane Combustion

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



Assume that 40 mol/s of CO₂ 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 CO₂. Calculate the rate of change in enthalpy ΔHR_{xo} (kJ/s).

Solution

Known quantities: Inlet and exit CO₂ 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

$$\Delta\dot{H} = \dot{\xi}\Delta H_{R_x}^{\circ}(T, P) \text{ at } 25^{\circ}\text{C}, \Delta\dot{H} = \dot{\xi}\Delta H_{R_x}^{\circ},$$

where $\Delta H_{R_x}^{\circ}$ is the standard heat of reaction.

The extent of reaction is calculated using the mole balance of CO₂:

$$\dot{n}_{\text{CO}_2} = \dot{n}_{\text{CO}_2, \text{feed}} + 4\dot{\xi}$$

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

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

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

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

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

2.2 :Reactions in Closed Processes

If the reaction is taking place in a closed system of constant volume, the change in the internal energy of reaction, ΔU_{R_x} , is given as

$$\Delta U_{R_x} = \Delta H_{R_x} - (\Delta n)RT$$

The change in the number of moles is equivalent to the change in the number of stoichiometric coefficients between the product and the reactant.

Substituting

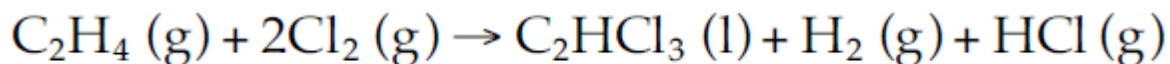
$$\Delta n = \sum_i \nu_i$$

$$\Delta U_{\text{Rx}} = \Delta H_{\text{Rx}} - RT \sum v_i$$

where v_i is the stoichiometric coefficient of the gaseous reactant or product component (+for product, -for reactant).

Example 4: Heat of Reaction from Internal Energy

Calculate the standard heat of the reaction of the following reaction:



The internal energy of reaction at standard conditions (25C, 1 atm) is

$$\Delta U_{\text{Rx}} = -418 \text{ kJ/mol.}$$

Solution

Known quantities: Internal energy of reaction.

Find: The standard heat of reaction.

Analysis: Use the following equation for closed system:

$$\Delta U_{\text{Rx}}(T) = \Delta H_{\text{Rx}}(T) - RT \sum v_i$$

Substitute known quantities:

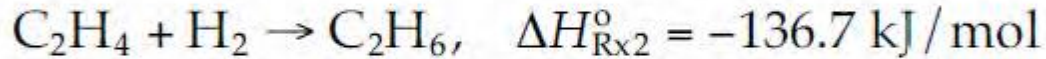
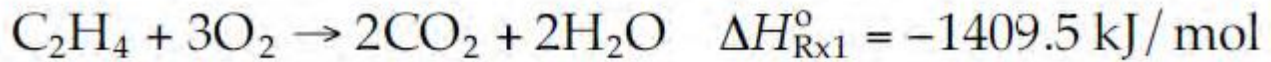
$$-418 \text{ kJ/mol} = \Delta H_{\text{Rx}}^{\circ} - \frac{8.314 \text{ J}}{\text{mol K}} \frac{1 \text{ kJ}}{1000 \text{ J}} \times 298.15 \text{ K} \times (1 + 1 + 0 - 2 - 1)$$

$$\Delta H_{\text{Rx}}^{\circ} = -420.5 \text{ kJ/mol}$$

Note that v_i is the stoichiometric coefficient (+for product, -for reactant) of the gaseous reactant or product component only (not liquids or solids components). If a set of reactions can be manipulated through a series of algebraic operations to yield the desired reaction, then the desired heat of reaction can be obtained by performing the same algebraic operations on the heats of reaction of the manipulated set of reactions (Hess law).

Example 5: Standard Heat of Reaction

Calculate the heat of combustion for C₂H₆ from the following reactions:

**Solution**

Known quantities: Standard heat of reaction.

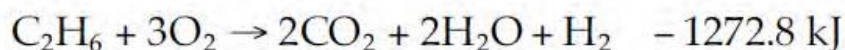
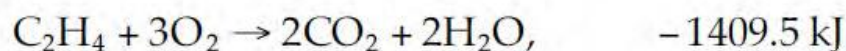
Find: Standard heat of reaction for the combustion of ethane.

Analysis: Use Hess' law.

The reaction for combustion of ethane is as follows:



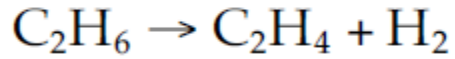
The first reaction minus the second reaction based on one mole reacted



Accordingly, the heat of combustion of C₂H₆ is -1558.3 kJ.

Example 6: Dehydrogenation of Ethane

Calculate the standard heat of reaction from the dehydrogenation of ethane using the standard heats of combustion:

**Solution**

$$\Delta H_{\text{RX}}^{\circ} = \Delta H_{\text{c}, \text{C}_2\text{H}_6}^{\circ} - \Delta H_{\text{c}, \text{C}_2\text{H}_4}^{\circ} - \Delta H_{\text{c}, \text{H}_2}^{\circ}$$

Substituting the values of standard heat of combustion (from the appendix) yields

$$\begin{aligned} HR_{\text{xO}} \text{ (kJ/mol)} &= -1559.9 - (-1410.99) - (-285.84) \\ &= 136.93 \text{ kJ/mol} \end{aligned}$$