Republic of Iraq

Ministry of Higher Education

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Al-Mustaqbal University College

Chemical Engineering and Petroleum Industries Department

Subject: Energy and Energy Balances

2nd Class

Lecture seven

2.4 Energy Balance for Reactive Processes

For energy balances with reaction, we have two methods for solving these types of problems: the heat of reaction method (extent of reaction) and the heat of formation method (element balance). These two methods differ in the choice of the reference state [2, 3].

2.4.1 Heat of Reaction Method

The heat of reaction method is ideal when there is a single reaction for which $\Delta H Rxo$ is known. This method requires calculation of the extent of reaction, ξ. The extent of reaction can be obtained by performing material balance for any reactant or product for which the feed and product flow rates are known. The reference state is such that all reactant and product species are at 25o C and 1 atm in the states for which the heat of reaction is known (Figure 2.1).
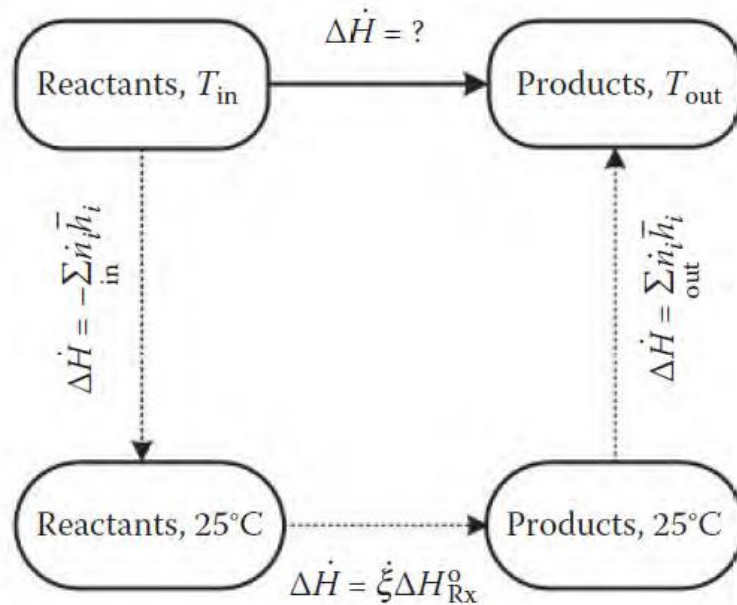
FIGURE 2.1 Rate of change in enthalpy for a reactive process.

For a single reaction at a reference state of 25oC and 1 atm while reactant and product are at different inlet and exit temperatures [4],

$$\Delta \dot{H} = \dot{\xi}\Delta H_{Rx}^{o} + \sum_{out} \dot{n}_i \bar{h}_i - \sum_{in} \dot{n}_i \bar{h}_i$$

where h_i(J/mol) is the specific molar enthalpy of a definite component. For multiple reactions, where the reference state is 25o C and 1 atm and the inlet and exit streams are at temperatures other than the reference states,

$$\Delta \dot{H} = \sum_{\text{reactions}} \dot{\xi}_j \Delta H^o_{Rx,j} + \sum_{\text{out}} \dot{n}_i \overline{h}_i - \sum_{\text{in}} \dot{n}_i \overline{h}_i$$

A reference temperature other than 25o C can be considered in this case, and the heat of reaction should be calculated at the new reference state:

$$\Delta \dot{H} = \sum_{\text{reactions}} \dot{\xi}_j \Delta H_{Rx,j} + \sum_{\text{out}} \dot{n}_i \overline{h}_i - \sum_{\text{in}} \dot{n}_i \overline{h}_i$$

The heat of reaction at any temperature

$$\Delta H_{Rx} = \Delta H^o_{Rx} (25°C) + \int_{25°C} \Delta C_p dT$$

where $\Delta C_p = \sum v_i C_{p,i}$
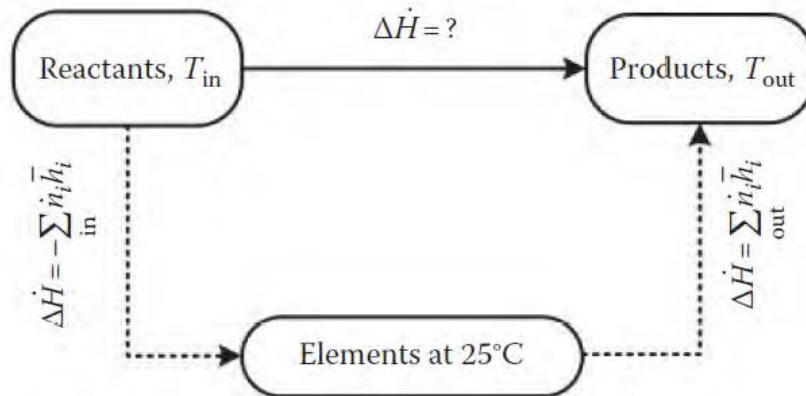
2.4.2 Heat of Formation or Element Balance Method

In the heat of formation method, the heats of reaction terms (ΔHrxno) are not required as they are implicitly included when heats of formation of the reactants are subtracted from the products [5]. For single and multiple reactions,

$$\Delta \dot{H} = \sum_{\text{out}} \dot{n}_i \overline{h}_i - \sum_{\text{in}} \dot{n}_i \overline{h}_i$$

where h_i accounts for the change in molar enthalpy with T and phase $+\Delta H_f$ o (Figure 2.2). In this case we find the enthalpy of all of the compounds relative to the elements at 25o C. No heat of reaction needs to be calculated at all. We then plug these enthalpies directly into the energy balance expression. In the absence of kinetic and potential energy, the energy balance equation is

$$Q - W = \Delta\dot{H} = \sum_{\text{out}} \dot{n}_i \overline{h}_i - \sum_{\text{in}} \dot{n}_i \overline{h}_i$$

FIGURE 2.2 Heat of formation or element balance method.

where the specific molar enthalpy of component i in the inlet streams is

$$\overline{h}_{i,\text{in}} = \int_{25}^{T_{\text{in}}} C_{\text{p},i}\,dT + \Delta H_{\text{f},i}^{\text{o}}$$

Specific molar enthalpy of component i in the exit streams is

$$\overline{h}_{i,\text{out}} = \int_{25}^{T_{\text{out}}} C_{\text{p},i}\,dT + \Delta H_{\text{f},i}^{\text{o}}$$

2.5 Simultaneous Material and Energy Balances

Material balances could be written on either compound that requires the extent of reaction or their elements, which requires only balances without generation terms for each element. Similarly, we can also write down energy balances using either compounds or elements. From material balances with reaction that we had discussed, there are three methods of analyzing these types of reactive processes: atomic species balances, extents of reaction, and component balances. For energy balances with reaction, we have two methods for solving these types of problems: the heat of reaction method and the heat of formation method or element balance method.

Example 2.7 Gas Phase Reaction

Gas phase reaction is taking place in a continuous reactor. Stoichiometric proportions of CO_2 and H_2 are fed to the reactor at 400o C. The reaction proceeds to 80% completion. Given 1 mol of carbon dioxide, estimate the heat that must be provided or removed, if the gas exit steams are to be kept at 500°C. Perform the energy balance using the heat of reaction method at two reference temperatures (500°C and 25°C) and the heat of formation method.

Solution

Known quantities: Inlet and exit temperatures, percent conversion, inlet flow rate of carbon dioxide and hydrogen.

Find: The amount of heat added or removed.

Analysis: The schematic diagram is shown in Example Figure 2.7.1.

Basis: 1 mol of CO_2 and 4 mol of H_2. The process flow diagram is shown in Example Figure 2.7.1.

Material balance (Extent of reaction method)

$$CO_2 + 4H_2 \rightarrow 2H_2O + CH_4 \quad \xi$$
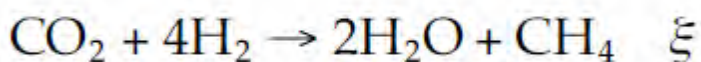
Component balance is calculated using the extent of reaction method as follows:

$$CO_2: \ n_{CO_2} = 1 - \xi$$

$$H_2: \ n_{H_2} = 4 - 4\xi$$

$$CH_4: \ n_{CH_4} = 0 + \xi$$
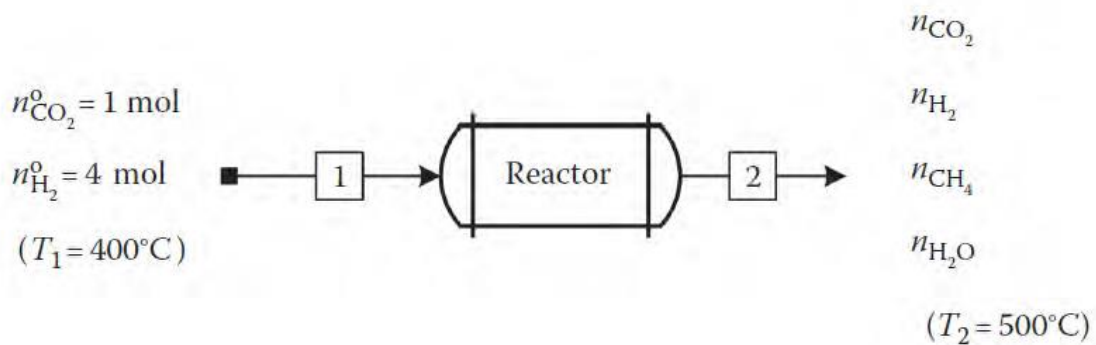
$$H_2O: \ n_{H_2O} = 0 + 2\xi$$

From the fractional conversion of CO2,

$$f = \frac{n^o_{CO_2} - n_{CO_2}}{n^o_{CO_2}}$$

$$0.8 = \frac{1.0 - n_{CO_2}}{1.0}$$

$$n_{CO_2} = 1.0 - 0.8 = 0.2 \text{ mol}$$

$n^o_{CO_2} = 1$ mol

$n^o_{H_2} = 4$ mol   [1] → Reactor → [2]

$(T_1 = 400°C)$

n_{CO_2}

n_{H_2}

n_{CH_4}

n_{H_2O}

$(T_2 = 500°C)$

EXAMPLE FIGURE 2.7.1 Process flow diagram of gas phase reaction.

Accordingly, the number of moles of carbon dioxide leaving the reactor is $n_{CO_2} = 0.2$ mol. The extent of reaction, ξ, is calculated by substituting $n_{CO_2} = 0.2$ mol in the CO_2 mole balance equation: $0.2 = 1 - \xi$.

Solving for the extent of reaction, $\xi = 0.8$.

To calculate moles of exit components, substitute values of the extent of reaction in the mole component balance equations given earlier. The following results are obtained:

$n_{H_2} = 0.8$, $n_{CH_4} = 0.8$, $n_{H_2O} = 1.6$

Energy balance (Heat of reaction method)

The energy balance is performed at two reference temperatures; exit stream temperature (500° C) and at the standard heat of reaction temperature (25° C). First, prepare the following data table using the polynomial form of the specific heat capacity:

$Cp(J/mol°C) = a + bT + cT2$

The standard heats of formation at 25°C can be obtained from Table A.2 (Appendix A.1). Components of heat capacity (Appendix A.2) and heats of formation (Table A.2):

Components	v_i	a	b	c	ΔH_f°
CO_2	-1	36.11	0.04233	-2.887×10^{-5}	-393.5
H_2	-4	28.84	0.0000765	0.3288×10^{-5}	00.00
H_2O	2	33.46	0.006880	0.7604×10^{-5}	-241.83
CH_4	1	34.31	0.054690	0.3661×10^{-5}	-74.85
Δ		-50.24	0.025810	3.4600×10^{-5}	-165.00

Note: $\Delta = CH_4 + 2H_2O - 4H_2 - CO_2$

The ΔH_f^o in the last column is for the heats of formation. The Δ in the last row is the difference between the product and reactants based on the stoichiometric coefficient; for example, the Δa is calculated as

$$\Delta a = \sum v_i a = -1 \times 36.11 - 4 \times 28.84 + 2 \times 33.46 + 34.31 = -50.24$$

The same method is used for calculating the values of Δb, Δc, and ΔH_f^o.

Reference temperature = 500°C

In this approach, we perform the energy balance using the heat of reaction method at the reference temperature of 500°C: $T_{ref} = 500o$ C. This requires knowledge of the heat of reaction at 500o C. The energy balance for this process includes the sensible heat to change the temperature of everything in the inlet stream from 500o C to 400o C and the heat of reaction at 500o C times the extent of reaction. Recall that the heat of reaction was expressed in kilojoules per mole, where the mole basis was per molar extent of reaction:

$$Q = \xi \Delta H_{Rx}(T_{ref}) + H_{out} - H_{in}$$

For multiple input and exit components,

$$Q = \int_{500°C}^{500°C} \sum_{out} n_i C_{p_i}\, dT - \int_{500°C}^{400°C} \sum_{in} n_i^o C_{p_i}\, dT + \xi\, \Delta H_{Rx}\Big|_{500°C}$$

Substituting the proper values,

$$Q = 0 + \int_{400°C}^{500°C} \sum_i n_i^o C_{pi} dT + \xi \Delta H_{Rx}\big|_{500°C}$$

The heat of reaction at 500°C is then

$$\Delta H_{Rx}\big|_{500°C} = \Delta H_{Rx}^o + \int_{25°C}^{500°C} \Delta C_p \, dT = \Delta H_{Rx}^o + \int_{25}^{500} \left(\Delta a + \Delta b T + \Delta c T^2\right) dT$$

The ΔCp for the reaction is immediately obtained from the Δ row for use in integration from one temperature to another:

$$\Delta H_{Rx}\big|_{500°C} = -165 \text{ kJ/mol} + [(-50.24)(500 - 25) + \frac{1}{2}(0.02581)(500^2 - 25^2)$$

$$+ \frac{1}{3}(3.46 \times 10^{-5})(500^3 - 25^3)] \frac{J}{mol} \frac{kJ}{1000 J} = -184.6 \text{ kJ/mol}$$

The heat of reaction at 500°C is

$$\Delta H_{Rx}\big|_{500°C} = -184.6 \text{ kJ/mol}$$

Now the sensible heat term (first terms shown in the earlier equation) includes only the moles of those compounds in the inlet stream. This gives
So

$$H_{in} = \int_{500°C}^{400°C} \sum_i n_i^o C_{pi} dT = (1) \int_{500}^{400} C_{p\,CO_2} dT$$

$$+ (4) \int_{500}^{400} C_{p\,H_2} dT = 1(-5) + 4(-2.95) \text{ kJ} = -16.80 \text{ kJ}$$

$$H_{out} = \int_{500°C}^{500°C} \sum_i \dot{n}_i C_{p_i} dT = 0$$

So finally, substitute estimated inlet, exit enthalpies and heat of reaction in the general energy balance equation shown here:

$$Q = \xi \Delta H_{Rx}(T_{ref}) + H_{out} - H_{in}$$

$$Q = (0.8 \text{ mol}) (-184.6 \text{ kJ/mol}) + 0 - (-16.80 \text{ kJ}) = -131 \text{ kJ}$$

Reference temperature = 25o C

The energy balance for this process at this reference temperature includes the sensible heat to change the temperature of everything in the inlet stream from 25o C to 400o C and also to change everything in the product stream from 25o C to 500o C. Again, the 16

heat of reaction at 25o C must be multiplied by the extent of reaction. The heat of the process at 25o C is

$$Q = H_{out} - H_{in} + \xi \Delta H_{Rx}^o = \int_{25°C}^{500°C} \sum_{out} n_i C_{p_i} dT - \int_{25°C}^{400°C} \sum_{in} n_i^o C_{p_i} dT + \xi \Delta H_{Rx}^o$$

The enthalpy of inlet stream relative to reference temperature (25o C) is

$$H_{in} = \int_{25°C}^{400°C} \sum_i n_i^o C_{p_i} dT = (1 \text{ mol}) \int_{25°C}^{400°C} C_{pCO_2} dT$$

$$+ (4 \text{ mol}) \int_{25°C}^{400°C} C_{pH_2} dT = 16.35 + 43.54 = 59.89 \text{ kJ}$$

The heat of reaction term at 25°C is found from the Δ term in the table for the heats of formation. Likewise, we have already found in method 1 that $\xi = 0.8$ mol. Thus, the reaction term is

$$\xi \Delta H_{Rx}^{o} = (0.8 \text{ mol})(-165 \text{ kJ} / \text{mol}) = -132 \text{ kJ}$$

We can now calculate the sensible heat term for heating everything in the outlet stream from 25o C to 500o C. The enthalpy change of the outlet stream with respect to reference temperature (25o C) is

$$H_{out} = \int_{25°C}^{500°C} \sum_{i} n_i C_{p_i} \, dT = (0.2 \text{ mol}) \int_{25}^{500} C_{p\,CO_2} dT + (0.8 \text{ mol}) \int_{25}^{500} C_{p\,H_2} \, dT$$

$$+ (0.8 \text{ mol}) \int_{25}^{500} C_{p\,CH4} \, dT + (1.6 \text{ mol}) \int_{25}^{500} C_{p\,H2O} \, dT$$

Integration of the earlier equation after substitution of components heat capacity yields

$$H_{out} = \int_{25°C}^{500°C} \sum_{i} n_i C_{p_i} \, dT = (4.27 + 11.06 + 18.48 + 27.22) \text{ kJ} = 61.03 \text{ kJ}$$

Finally, we obtain

$$Q = H_{out} - H_{in} + \xi \Delta H_{Rx}^{o} = \sum_{out} n_i \overline{h}_i - \sum_{in} n_i^o \overline{h}_i + \xi \Delta H_{Rx}^{o}$$

$$= 61.03 - 59.89 - 132 = -131 \text{ kJ}$$

The heat transferred from the system is 131 kJ.

Heat of formation method (Element balance)

In this case, no heat of reaction needs to be calculated at all. We write the energy balance as follows:

$$Q = \sum_{out} n_i \overline{h}_i - \sum_{in} n_i \overline{h}_i$$

Next, we compute the enthalpy of each component in each stream relative to their elements. The compound is formed from its elements at 25oC (this is the heat of

formation), and then we raise the temperature of the compound up to the temperature of the stream.

The specific enthalpy of outlet compounds

$$CH_4 : \overline{h}_{CH_4} = \Delta H_f^\circ(25) + \int_{25°C}^{500°C} C_{p,CH_4}\, dT = -74.85 + 23.10 = -51.75 \text{ kJ}/\text{mol}$$

$$H_2O : \overline{h}_{H_2O} = \Delta H_f^\circ(25) + \int_{25°C}^{500°C} C_{p,H_2O}\, dT = -241.83 + 17.01 = -224.8 \text{ kJ}/\text{mol}$$

$$CO_2 : \overline{h}_{CO_2} = \Delta H_f^\circ(25) + \int_{25°C}^{500°C} C_{p,CO_2}\, dT = -393.5 + 21.34 = -372.2 \text{ kJ}/\text{mol}$$

$$H_2 : \overline{h}_{H_2} = 0 + \int_{25°C}^{500°C} C_{p\,H2}\, dT = 13.83 \text{ kJ}/\text{mol}$$

Thus, the sum of all of the outlet specific enthalpies is

$$H_{out} = \sum_{out} n_i h_i = (0.2)(-372.2) + (0.8)(13.83) + (0.8)(-51.75)$$
$$+ (1.6)(-224.8) = -464.5 \text{ kJ}$$

The specific enthalpies of inlet compounds

$$CO_2 : h^o_{CO_2} = \Delta H^o_f + \int_{25°C}^{400°C} C_{p,\,CO_2} dT = -393.5 + 16.35 = -377.2 \text{ kJ/mol}$$

$$H_2 : h^o_{H_2} = 0 + \int_{25°C}^{400°C} C_{p\,H2} dT = 10.89 \text{ kJ/mol}$$

Thus, the sum of all of the inlet enthalpies is

$$H_{in} = \sum_{in} n_i h_i = (1)(-377.2) + (4)(10.89) = -333.6 \text{ kJ}$$

Finally, from the energy balance we obtain

$$Q = H_{out} - H_{in} = -464.5 \text{ kJ} + 333.6 \text{ kJ} = -131 \text{ kJ}$$

The heat calculated using the three methods are equal.