

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
CHEMICAL ENGINEERING DEPARTMENT
CHE 252: CHEMICAL PROCESS CALCULATIONS II
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LECTURE 7: ENERGY BALANCE ON REACTIVE PROCESSES

Learning Objectives

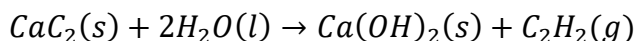
At the end of this lecture the students are expected to do the following:

1. Explain the concepts of heat of reaction; heat of formation; combustion; heat of combustion; standard heats of formation, combustion, and reaction;
2. Calculate the total enthalpy change, given (a) the amount of any reactant consumed or any product generated in a reaction at a given temperature and pressure and (b) the heat of the reaction at that temperature and pressure.
3. Determine a heat of reaction from heats of other reactions using Hess's law. Determine standard enthalpies and internal energies of reaction from known standard heats of formation and heats of combustion.
4. Solve reactive-system energy balance problems for (a) the heat transfer required for specified inlet and outlet conditions, (b) the outlet temperature corresponding to a specified heat input (e.g., for an adiabatic reactor), and (c) the product composition corresponding to a specified heat input and a specified outlet temperature.

8.1 HEATS OF REACTION

The heat of reaction (or enthalpy of reaction), $\Delta\hat{H}_r(T, P)$, is the enthalpy change for a process in which stoichiometric quantities of reactants at temperature T and pressure P react completely in a single reaction to form products at the same temperature and pressure.

Consider the reaction between solid calcium carbide and liquid water to form solid calcium hydroxide and gaseous acetylene,



the heat of reaction for this at 25°C and 1 atm is $\Delta\hat{H}_r(25^\circ\text{C}, 1 \text{ atm}) = -125.4 \text{ kJ/mol}$

From the above it means that if 1 mol of solid calcium carbide reacts completely with 2 mol of liquid water to form 1 mol of solid calcium hydroxide and 1 mol of gaseous acetylene, and the initial and final temperatures are both 25°C and the initial and final pressures are both 1 atm, then

$H_{\text{products}} - H_{\text{reactants}} = -125.4 \text{ kJ}$. If the reaction is run under conditions such that the energy balance reduces to $Q = \Delta H$, then 125.4 kJ of heat must be transferred from the reactor in the course of the reaction.

If a reaction takes place at a temperature T_o and pressure P_o and the extent of reaction is ξ , the associated enthalpy change is

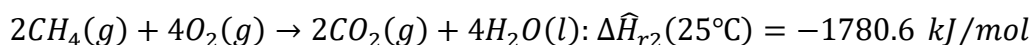
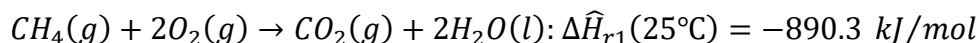
$$\Delta H = \xi \Delta \hat{H}_r(T_o, P_o)$$

For a continuous process, $n_{A,r} \text{ (mol)}$ would be replaced by $\dot{n}_{A,r} \text{ (mol/s)}$ in this expression, $\xi \text{ (mol)}$ would be replaced by $\dot{\xi} \text{ (mol/s)}$, and $\Delta H \text{ (kJ)}$ would be replaced by $\Delta \dot{H} \text{ (kJ/s)}$.

Following are several important terms and observations related to heats of reaction:

1. If $\Delta \hat{H}_r(T, P)$ is negative the reaction is exothermic at temperature T and pressure P , and if $\Delta \hat{H}_r(T, P)$ is positive the reaction is endothermic at T and P . These definitions of exothermic and endothermic are equivalent to the ones given earlier in terms of chemical bond strengths.
2. At low and moderate pressures, $\Delta \hat{H}_r(T, P)$ is nearly independent of pressure. We will presume this independence in the balance of in this lecture and write the heat of reaction as $\Delta \hat{H}_r(T)$.
3. The value of the heat of a reaction depends on how the stoichiometric equation is written.

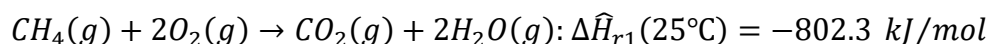
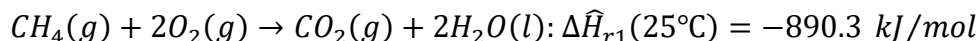
For example,



The first line states that the combined enthalpy of 1 gram-mole of CO_2 plus 2 gram-moles of liquid water is 890.3 kJ lower than the combined enthalpy of 1 gram-mole of methane plus 2 gram-moles of oxygen at 25°C . Doubling the quantity of reactants at a given condition doubles the total enthalpy of the reactants at that condition, and similarly for the products.

The difference between the product and reactant enthalpies in the second reaction (by definition, $\Delta \hat{H}_{r2}$ must therefore be double the enthalpy difference in the first reaction $\Delta \hat{H}_{r1}$.

4. *The value of a heat of reaction depends on the states of aggregation (gas, liquid, or solid) of the reactants and products.* For example,



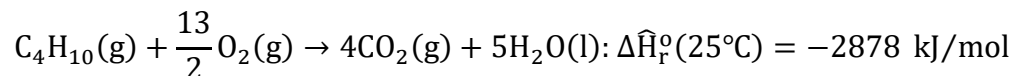
The only difference between the reactions is that the water formed is a liquid in the first one and a vapor in the second. Since enthalpy is a state function, the difference between the two heats of

reaction must be the enthalpy change associated with the vaporization of 2 mol of water at 25°C- that is, $2\Delta\hat{H}_v$ (25°C).

5. The standard heat of reaction, $\Delta\hat{H}_r^o$ is the heat of reaction when both the reactants and products are at a specified reference temperature and pressure, usually 25°C and 1 atm.

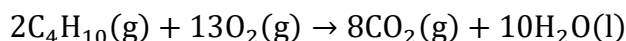
Example 7.1 Calculation of Heats of Reaction

The standard heat of the combustion of n-butane vapor is



Calculate the rate of enthalpy change, $\Delta\dot{H}$ (kJ/s), if 2400 mol/s of CO_2 is produced in this reaction and the reactants and products are all at 25°C.

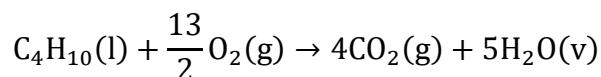
2. What is the standard heat of the reaction



Calculate $\Delta\dot{H}$ if 2400 mol/s of CO_2 is produced in this reaction and the reactants and products are all at 25°C.

3. The heats of vaporization of n-butane and water at 25°C are 19.2 kJ/mol and 44.0 kJ/mol respectively.

What is the standard heat of the reaction



Calculate $\Delta\dot{H}$ if 2400 mol/s of CO_2 is produced in this reaction and the reactants and products are all at 25°C.

Solution

- 1.

$$\xi = \frac{(\dot{n}_{\text{CO}_2})_r}{|v_{\text{CO}_2}|} = \frac{2400 \text{ mol/s}}{4} = 600 \text{ mol/s}$$

$$\Delta\dot{H} = \xi \Delta\hat{H}_r^o = \left(600 \frac{\text{mol}}{\text{s}}\right) \left(-2878 \frac{\text{kJ}}{\text{mol}}\right) = -1.73 \times 10^6 \text{ kJ/s}$$

2. Since doubling the stoichiometric coefficients of a reaction must double the heat of reaction

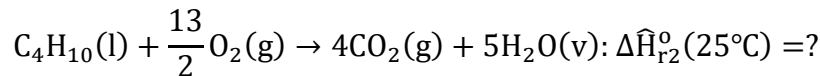
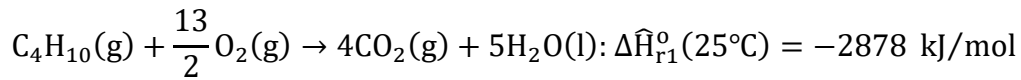
$$\Delta\hat{H}_{r2}^o = 2\Delta\hat{H}_{r1}^o = 2(-2878 \text{ kJ/mol}) = -5756 \text{ kJ/mol}$$

The enthalpy change associated with the production of 2400 mol/s of CO_2 at 25°C cannot depend on how the stoichiometric equation is written (the same quantities of reactants and products at the same temperatures must have the same enthalpies), and so $\Delta\dot{H}$ must be the value calculated in question 1 (a). Let us do the calculation and prove it, however.

$$\xi = \frac{(\dot{n}_{CO_2})_{out}}{|v_{CO_2}|} = \frac{2400 \text{ mol/s}}{8} = 300 \text{ mol/s}$$

$$\Delta\dot{H} = \xi \Delta\hat{H}_r^o = \left(300 \frac{\text{mol}}{\text{s}}\right) \left(-5756 \frac{\text{kJ}}{\text{mol}}\right) = -1.73 \times 10^6 \text{ kJ/s}$$

3. Compare the two reactions:



The total enthalpy of the products in the second reaction [4 mol $CO_2(g)$ + 5 mol $H_2O(g)$ at 25°C] is greater than that of the products in the first reaction [4 mol $CO_2(g)$ + 5 mol $H_2O(l)$ at 25°C] by five times the heat of vaporization of water. Similarly, the total enthalpy of the reactants in the second reaction is lower than that of the reactants in the first reaction by the heat of vaporization of butane.

Since $\Delta\hat{H}_r = H_{\text{products}} - H_{\text{reactants}}$, it follows that

$$\begin{aligned} \Delta\hat{H}_{r2}^o &= \Delta\hat{H}_{r1}^o + 5(\Delta\hat{H}_v)_{H_2O} + (\Delta\hat{H}_v)_{C_4H_{10}} = [-2878 + 5(44.0) + 19.2] \text{ kJ/mol} \\ &= -2639 \text{ kJ/mol} \end{aligned}$$

$$\Delta\dot{H} = \xi \Delta\hat{H}_{r2}^o = \left(600 \frac{\text{mol}}{\text{s}}\right) \left(-2639 \frac{\text{kJ}}{\text{mol}}\right) = -1.58 \times 10^6 \text{ kJ/s}$$

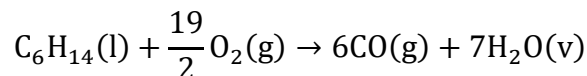
For a closed System

If a reaction takes place in a closed reactor at constant volume, the heat released or absorbed is determined by the change in internal energy between reactants and products. The **internal energy of reaction**, $\Delta\hat{U}_r(T)$, is the difference $U_{\text{products}} - U_{\text{reactants}}$ if stoichiometric quantities of reactants react completely at temperature T .

Suppose a reaction occurs, and v_i is the stoichiometric coefficient of the i th gaseous reactant or product. If ideal gas behavior can be assumed and specific volumes of liquid and solid reactants and products are negligible compared with those of the gases, the internal energy of reaction is related to the heat of reaction by

$$\Delta \hat{U}_r(T) = \Delta \hat{H}_r(T) - RT \left(\sum_{\substack{\text{gaseous} \\ \text{products}}} |v_i| - \sum_{\substack{\text{gaseous} \\ \text{reactants}}} |v_i| \right)$$

For example



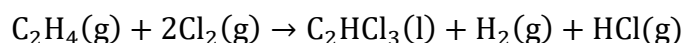
The internal energy of reaction is

$$\Delta \hat{U}_r(T) = \Delta \hat{H}_r(T) - RT \left(6 + 7 - \frac{19}{2} \right) = \Delta \hat{H}_r(T) - \frac{7}{2} RT$$

If there are no gaseous reactants or products then to a good approximation $\Delta \hat{U}_r = \Delta \hat{H}_r$.

Example 7.2 Evaluation of $\Delta \hat{U}_r$

The standard heat of reaction



is $\Delta \hat{H}_r^\circ = -420.8 \text{ kJ/mol}$. Calculate $\Delta \hat{U}_r^\circ$ for this reaction.

Solution

From stoichiometric equation

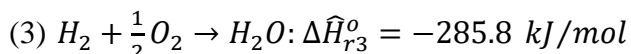
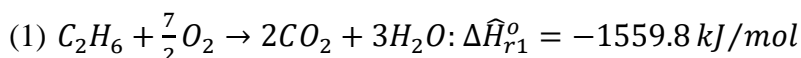
$$\begin{aligned} \sum v_i (\text{product gases}) &= 1 + 1 = 2 \\ \sum v_i (\text{reactant gases}) &= 1 + 2 = 3 \\ \Delta \hat{U}_r(T) &= \Delta \hat{H}_r(T) - RT \left(\sum_{\substack{\text{gaseous} \\ \text{products}}} |v_i| - \sum_{\substack{\text{gaseous} \\ \text{reactants}}} |v_i| \right) = \Delta \hat{H}_r - RT(2 - 3) \\ &= -420.8 \text{ kJ/mol} - \left(\frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} \right) \times (298 \text{ K}) \times (-1) \times \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) \\ &= -418.3 \text{ kJ/mol} \end{aligned}$$

7.2 MEASUREMENT AND CALCULATION OF HEATS OF REACTION: HESS' LAW

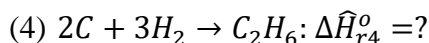
Hess's law states that if the stoichiometric equation for reaction 1 can be obtained by algebraic operations (multiplication by constants, addition, and subtraction) on stoichiometric equations for reactions 2, 3, ..., then the heat of reaction $\Delta \hat{H}_{r1}^\circ$ can be obtained by performing the same operations on the heats of reactions $\Delta \hat{H}_{r2}^\circ$, $\Delta \hat{H}_{r3}^\circ$...

Example 7.3 Hess' Law

The standard heats of the following combustion reactions have been determined experimentally:



Use Hess's law and the given heats of reaction to determine the standard heat of the reaction



Since from equations above (1-4) it can be seen that $(4) = 2 \times (2) + 3 \times (3) - (1)$

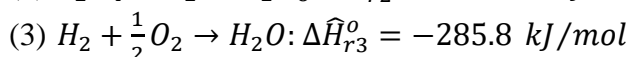
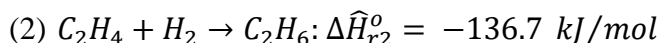
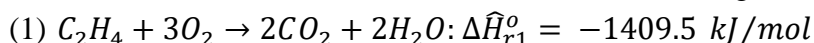
From Hess's law

$$\Delta\hat{H}_{r4}^o = 2\Delta\hat{H}_{r2}^o + 3\Delta\hat{H}_{r3}^o - \Delta\hat{H}_{r1}^o = 2(-393.5) + 3(-285.8) - (-1559.8) = -84.6 \text{ kJ/mol}$$

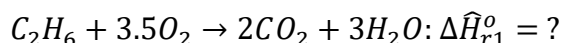
This heat of reaction could not have been measured directly, since you cannot react carbon and hydrogen in such a way that ethane is the only reaction product.

Example 7.4

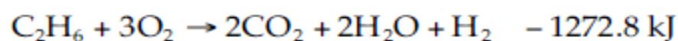
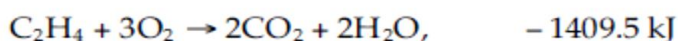
Calculate the heat of combustion for C_2H_6 from the following reactions:



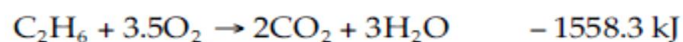
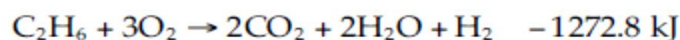
The reaction for combustion of ethane is as follows:



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



The resulting reaction is added with the third one:



Accordingly, the heat of combustion of C_2H_6 is -1558.3 kJ

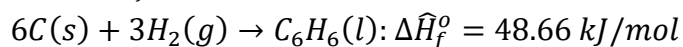
7.3 FORMATION REACTIONS AND HEATS OF FORMATION

A formation reaction of a compound is the reaction in which the compound is formed from its elemental constituents as they normally occur in nature (e.g., O_2 rather than O). The enthalpy change associated with the formation of 1 mole of the compound at a reference temperature and pressure (usually 25°C and 1 atm) is the standard heat of formation of the compound, $\Delta\hat{H}_f^\circ$.

Standard heats of formation for many compounds are listed in Table B.1 (Felder and Rosseau) and on pp. 2-187 through 2-198 of *Perry's Chemical Engineers' Handbook*. For example, $\Delta\hat{H}_f^\circ$ for crystalline ammonium nitrate is given in Table B.1 as -365.14 kJ/mol , signifying



Similarly, for liquid benzene $\Delta\hat{H}_f^\circ = 48.66 \text{ kJ/mol}$ or



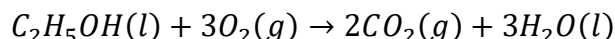
The standard heat of formation of an elemental species (e.g., O_2) is zero.

It may be shown using Hess's law that if v_i is the stoichiometric coefficient of the i^{th} species participating in a reaction (+ for products, - for reactants) and $\Delta\hat{H}_{fi}^\circ$ is the standard heat of formation of this species, then the standard heat of the reaction is

$$\Delta\hat{H}_r^\circ = \sum_i v_i \Delta\hat{H}_{fi}^\circ = \sum_{\text{products}} |v_i| \Delta\hat{H}_{fi}^\circ - \sum_{\text{reactants}} |v_i| \Delta\hat{H}_{fi}^\circ$$

Example 7.5

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



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

$$\Delta\hat{H}_r^\circ = 3\Delta\hat{H}_{f,H_2O(l)}^\circ + 2\Delta\hat{H}_{f,CO_2}^\circ - 0 - \Delta\hat{H}_{f,C_2H_5OH(l)}^\circ$$

Substitute the values of the standard heat of formation:

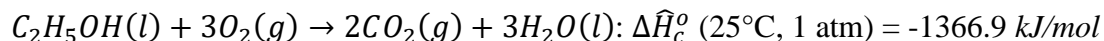
$$\Delta\hat{H}_r^\circ (\text{kJ/mol}) = 3(-285.84) + 2(-393.51) - 0 - (277.63) = -1366.9 \text{ kJ/mol}$$

7.4 HEATS OF COMBUSTION

The **standard heat of combustion** of a substance, $\Delta\hat{H}_c^\circ$, is the heat of the combustion of that substance with oxygen to yield specified products [e.g., $CO_2(g)$ and $H_2O(l)$], with both reactants and products at 25°C and 1 atm (the arbitrary but conventional reference state).

Table B.1 (Felder and Rosseau) lists standard heats of combustion for a number of substances. The given values are based on the following assumptions: (a) all carbon in the fuel forms $CO_2(g)$, (b) all hydrogen forms $H_2O(l)$, (c) all sulfur forms $SO_2(g)$, and (d) all nitrogen forms $NO_2(g)$. The

standard heat of combustion of liquid ethanol, for example, is given in Table B.1 as $\Delta\hat{H}_c^o = 1366.9 \text{ kJ/mol}$, which signifies



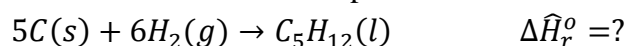
Additional heats of combustion are given on pp. 2-195 through 2-199 of *Perry's Chemical Engineers' Handbook*.

Standard heats of reactions that involve only combustible substances and combustion products can be calculated from tabulated standard heats of combustion, in another application of Hess's law. A hypothetical reaction path may be constructed in which (a) all combustible reactants are burned with O_2 at 25°C and (b) CO_2 and H_2O combine to form the reaction products plus O_2 . Step (b) involves the reverse of the combustion reactions of the reaction products. Since both steps involve only combustion reactions, the total enthalpy change—which equals the desired heat of reaction—can be determined entirely from heats of combustion as

$$\Delta\hat{H}_r^o = - \sum_i v_i (\Delta\hat{H}_c^o)_i = \sum_{\text{reactants}} |v_i| (\Delta\hat{H}_c^o)_i - \sum_{\text{products}} |v_i| (\Delta\hat{H}_c^o)_i$$

If any reactants or products are combustion products (i.e., CO_2 , H_2O , SO_2), their heats of combustion are equal to zero.

Consider the formation of pentane:

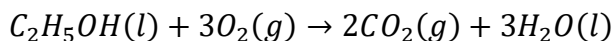


Carbon, hydrogen, and pentane can all be burned, and their standard heats of combustion can be determined experimentally. Therefore,

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

Example 7.6

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



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

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

$$\Delta\hat{H}_r^o = \Delta\hat{H}_{c,\text{C}_2\text{H}_5\text{OH}(l)}^o + 3\Delta\hat{H}_{c,\text{O}_2(g)}^o - 3\Delta\hat{H}_{c,\text{H}_2\text{O}(l)}^o - 2\Delta\hat{H}_{c,\text{CO}_2(g)}^o$$

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:

$$\Delta\hat{H}_r^o = -1366.91 + 0 - 0 - 0 = -1366.9 \text{ kJ/mol}$$

7.5 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.

7.5.1 Heat of Reaction Method

The heat of reaction method is ideal when there is a single reaction for which $\Delta\hat{H}_r^o$ 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 25°C and 1 atm in the states for which the heat of reaction is known (Figure 7.1).

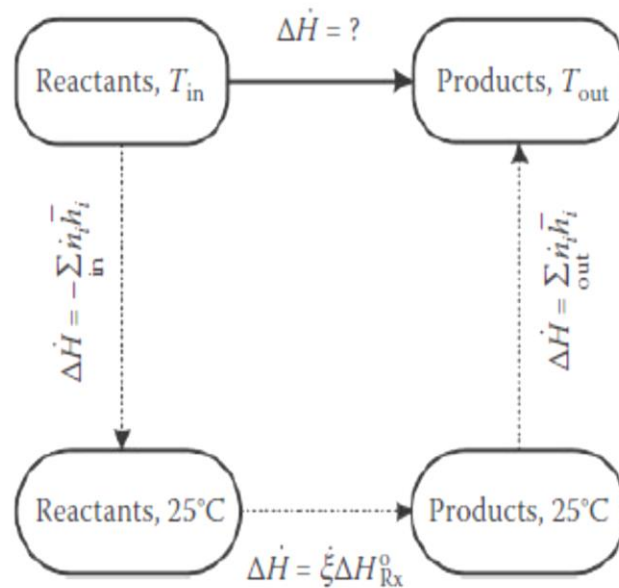


Figure 7.1: Rate of change in enthalpy for a reactive process.

For a single reaction at a reference state of 25°C and 1 atm while reactant and product are at different inlet and exit temperatures

$$\Delta\dot{H} = \xi\Delta\hat{H}_r^o + \sum_{out} \dot{n}_i \hat{H}_i - \sum_{in} \dot{n}_i \hat{H}_i$$

For multiple reactions where the reference state is 25°C and 1 atm and the inlet and exit streams are at temperatures other than the reference states,

$$\Delta\dot{H} = \sum_{reactions} \xi_j \Delta\hat{H}_{r,j}^o + \sum \dot{n}_{out} \hat{H}_{out} - \sum \dot{n}_{in} \hat{H}_{in}$$

7.5.2 Heat of Formation or Element Balance Method

In the heat of formation method, the heats of reaction terms ($\Delta \hat{H}_r^o$) are not required as they are implicitly included when heats of formation of the reactants are subtracted from the products. For single and multiple reactions

$$\Delta \dot{H} = \sum \dot{n}_{out} \hat{H}_{out} - \sum \dot{n}_{in} \hat{H}_{in}$$

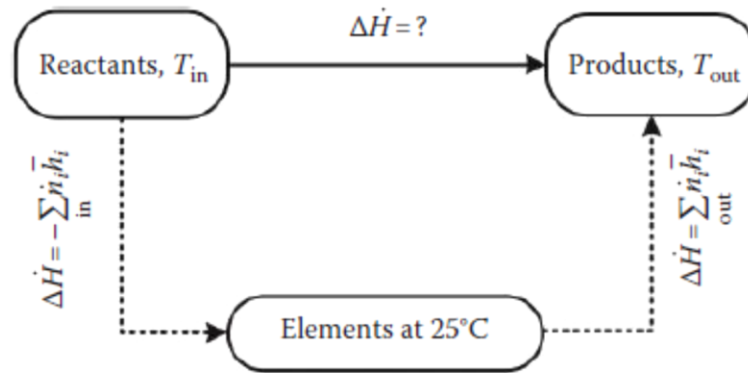


Figure 7.2 Heat of formation or element balance method.

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

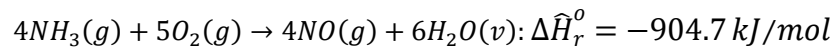
$$\hat{H}_{i,in} = \int_{25}^{T_{in}} C_{p,i} dT + \Delta \hat{H}_{f,i}^o$$

Specific molar enthalpy of component i in the exit streams is

$$\hat{H}_{i,out} = \int_{25}^{T_{out}} C_{p,i} dT + \Delta \hat{H}_{f,i}^o$$

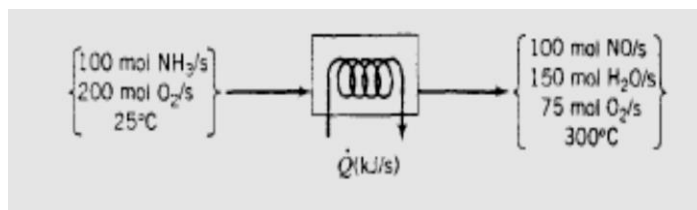
Example 7.7 Energy Balance About an Ammonia Oxidizer

The standard heat of reaction for the oxidation of ammonia is given below:



One hundred mol NH_3/s and 200 mol O_2/s at 25°C are fed into a reactor in which the ammonia is completely consumed. The product gas emerges at 300°C . Calculate the rate at which heat must be transferred to or from the reactor, assuming operation at approximately 1 atm.

Solution



Since only one reaction takes place and $\Delta \hat{H}_r^o$ is known, we will use the heat of reaction method for the energy balance, choosing as references the reactant and product species in the states for which the heat of reaction is given. The enthalpy table appears as follows:

References: $NH_3(g)$, $O_2(g)$, $NO(g)$, $H_2O(v)$ at 25°C and 1 atm

Substance	\dot{n}_{in} (mol/s)	\hat{H}_{in} (kJ/mol)	\dot{n}_{out} (mol/s)	\hat{H}_{out} (kJ/mol)
NH_3	100	0	-	-
O_2	200	0	75	\hat{H}_1
NO	-	-	100	\hat{H}_2
H_2O	-	-	150	\hat{H}_3

Calculate Unknown Enthalpies

$O_2(g, 300^\circ\text{C})$: From Table B.8, $\hat{H}_1 = 8.470 \text{ kJ/mol}$ (Insert value in enthalpy table)

$NO(g, 300^\circ\text{C})$: $\hat{H}_2 = \int_{25^\circ\text{C}}^{300^\circ\text{C}} (C_p)_{NO} dT \xrightarrow{\text{Table B.2}} \hat{H}_2 = 8.453 \text{ kJ/mol}$ (Insert in table)

$H_2O(v, 300^\circ\text{C})$: From Table B.8, $\hat{H}_3 = 9.570 \text{ kJ/mol}$ (Insert in table)

Calculate $\dot{\xi}$ and $\Delta\dot{H}$

Since 100 mol NH_3/s is consumed in the process ($A = \text{NH}_3$, $\dot{n}_{A,r} = 100 \text{ mol NH}_3 \text{ consumed/s}$), Equation 9.1-3 becomes

$$\dot{\xi} = \frac{\dot{n}_{\text{NH}_3,r}}{|\nu_{\text{NH}_3}|} = \frac{100 \text{ mol/s}}{4} = 25 \text{ mol/s}$$

Equation 9.5-1a

$$\begin{aligned}\Delta\dot{H} &= \dot{\xi}\Delta\hat{H}_r^\circ + \underbrace{\sum \dot{n}_{\text{out}}\hat{H}_{\text{out}} - \sum \dot{n}_{\text{in}}\hat{H}_{\text{in}}}_{\text{from table}} \\ &= (25 \text{ mol/s})(-904.7 \text{ kJ/mol}) + [(75)(8.470) + (100)(8.453) \\ &\quad + (150)(9.570) - (100)(0) - (200)(0)] \text{ kJ/s} = -19,700 \text{ kJ/s}\end{aligned}$$

Energy Balance

For this open system,

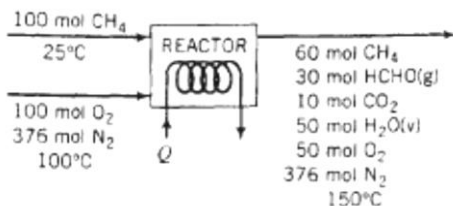
$$\begin{aligned}\dot{Q} - \dot{W}_s &= \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p \\ \left\{ \begin{array}{l} \dot{W}_s = 0 \quad (\text{no moving parts}) \\ \Delta\dot{E}_p = 0 \quad (\text{horizontal unit}) \\ \Delta\dot{E}_k \approx 0 \quad (\text{neglect kinetic energy changes}) \end{array} \right. \\ \dot{Q} \approx \Delta\dot{H} &= -19,700 \text{ kJ/s} = \boxed{-19,700 \text{ kW}}\end{aligned}$$

Thus, 19,700 kW of heat must be transferred from the reactor to maintain the product temperature at 300°C. If less heat were transferred, more of the heat of reaction would go into the reaction mixture and the outlet temperature would increase.

Example 7.8 Energy Balance on a Methane Oxidation Reactor

Methane is oxidized with air to produce formaldehyde in a continuous reactor. A competing reaction is the combustion of methane to form CO_2 .

A flowchart of the process for an assumed basis of 100 mol of methane fed to the reactor is shown below:

**Basis: 100 mol CH_4 Fed**

Since the component amounts of all streams are known, we may proceed directly to the energy balance. We choose as references the elemental species that form the reactants and products at 25°C and 1 atm (the state for which heats of formation are known) and the nonreactive species N_2 (g) also at 25°C and 1 atm (the reference state for Table B.8). The inlet-outlet enthalpy table is shown below.

References: C(s), O₂(g), H₂(g), N₂(g) at 25°C and 1 atm

Substance	n_{in} (mol)	\hat{H}_{in} (kJ/mol)	n_{out} (mol)	\hat{H}_{out} (kJ/mol)
CH ₄	100	\hat{H}_1	60	\hat{H}_4
O ₂	100	\hat{H}_2	50	\hat{H}_5
N ₂	376	\hat{H}_3	376	\hat{H}_6
HCHO	—	—	30	\hat{H}_7
CO ₂	—	—	10	\hat{H}_8
H ₂ O	—	—	50	\hat{H}_9

Calculate Unknown Enthalpies

In the following calculations, values of $\Delta\hat{H}_f^\circ$ come from Table B.1, formulas for $C_p(T)$ come from Table B.2, and values of $H(T)$ for O₂ and N₂ are specific enthalpies relative to the gaseous species at 25°C taken from Table B.8. Effects of any pressure changes on enthalpies are neglected and the details of the calculations are not shown.

$$\begin{aligned}
 \text{CH}_4(25^\circ\text{C}): \quad \hat{H}_1 &= (\Delta\hat{H}_f^\circ)_{\text{CH}_4} = -74.85 \text{ kJ/mol} \\
 \text{O}_2(100^\circ\text{C}): \quad \hat{H}_2 &= \hat{H}_{\text{O}_2}(100^\circ\text{C}) = 2.235 \text{ kJ/mol} \\
 \text{N}_2(100^\circ\text{C}): \quad \hat{H}_3 &= \hat{H}_{\text{N}_2}(100^\circ\text{C}) = 2.187 \text{ kJ/mol} \\
 \text{CH}_4(150^\circ\text{C}): \quad \hat{H}_4 &= (\Delta\hat{H}_f^\circ)_{\text{CH}_4} + \int_{25^\circ\text{C}}^{150^\circ\text{C}} (C_p)_{\text{CH}_4} dT \\
 &= (-74.85 + 4.90) \text{ kJ/mol} = -69.95 \text{ kJ/mol} \\
 \text{O}_2(150^\circ\text{C}): \quad \hat{H}_5 &= \hat{H}_{\text{O}_2}(150^\circ\text{C}) = 3.758 \text{ kJ/mol} \\
 \text{N}_2(150^\circ\text{C}): \quad \hat{H}_6 &= \hat{H}_{\text{N}_2}(150^\circ\text{C}) = 3.655 \text{ kJ/mol} \\
 \text{HCHO}(150^\circ\text{C}): \quad \hat{H}_7 &= (\Delta\hat{H}_f^\circ)_{\text{HCHO}} + \int_{25^\circ\text{C}}^{150^\circ\text{C}} (C_p)_{\text{HCHO}} dT \\
 &= (-115.90 + 4.75) \text{ kJ/mol} = -111.15 \text{ kJ/mol} \\
 \text{CO}_2(150^\circ\text{C}): \quad \hat{H}_8 &= (\Delta\hat{H}_f^\circ)_{\text{CO}_2} + \hat{H}_{\text{CO}_2}(150^\circ\text{C}) \\
 &= (-393.5 + 4.75) \text{ kJ/mol} = -388.6 \text{ kJ/mol} \\
 \text{H}_2\text{O}(v, 150^\circ\text{C}): \quad \hat{H}_9 &= (\Delta\hat{H}_f^\circ)_{\text{H}_2\text{O}(v)} + \hat{H}_{\text{H}_2\text{O}(v)}(150^\circ\text{C}) \\
 &= (-241.83 + 4.27) \text{ kJ/mol} = -237.56 \text{ kJ/mol}
 \end{aligned}$$

As each of these values is calculated, it should be substituted in the inlet-outlet enthalpy table. The table finally appears as follows:

References: C(s), O₂(g), H₂(g), N₂(g) at 25°C and 1 atm

Substance	n_{in} (mol)	\hat{H}_{in} (kJ/mol)	n_{out} (mol)	\hat{H}_{out} (kJ/mol)
CH ₄	100	-74.85	60	-69.95
O ₂	100	2.235	50	3.758
N ₂	376	2.187	376	3.655
HCHO	—	—	30	-111.15
CO ₂	—	—	10	-388.6
H ₂ O	—	—	50	-237.56

Evaluate ΔH

$$\Delta H = \sum n_{out} \hat{H}_{out} - \sum n_{in} \hat{H}_{in} = -15,300 \text{ kJ}$$

Energy Balance

Remember that we are dealing with a continuous process and hence an open system. [The reason we use n (mol) and not \dot{n} (mol/s) is that we took 100 mol CH₄ as a basis of calculation.] With ΔE_k , ΔE_p and W_s neglected, the open system energy balance yields

$$Q = \Delta H = -15,300 \text{ kJ}$$