

# Chapter Five – Energy Balances: How to Account for Chemical Reaction

## 25.1 The Standard Heat (Enthalpy) of Formation

## 25.2 The Heat (Enthalpy) of Reaction

## 25.3 Merging the Heat of Formation with the Sensible Heat of a Compound in Making an Energy Balance

## 25.4 The Heat of Combustion

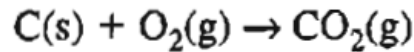
## 25.1 The Standard Heat (Enthalpy) of Formation

As you probably know from chemistry, the observed heat transfer that occurs in an isothermal system in which a reaction takes place represents the energy change associated with the rearrangement of the bonds holding together the atoms of the reacting molecules. For an **exothermic reaction**, the energy required to hold the products of the reaction together is less than that required to hold the reactants together, and heat leaves the system. The reverse is true of an **endothermic reaction**. In this chapter we are concerned primarily with the enthalpy term in the steady-state energy balance for an open system, and to a lesser extent with the energy balance for a closed system.

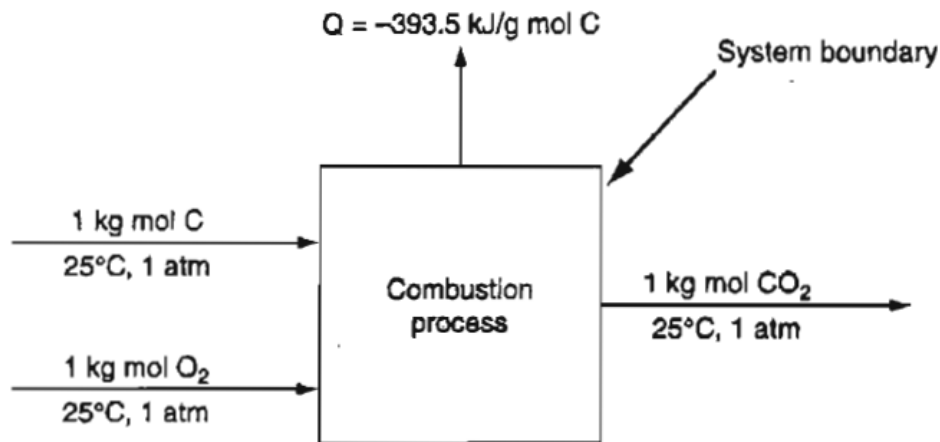
To include energy changes caused by a reaction in the energy balance, we make use of a quantity called the **standard heat (really enthalpy) of formation**, often called just the heat of formation,\*  $\Delta \hat{H}_f^\circ$ . The superscript  $^\circ$  denotes the **standard state** for reaction of 25°C and 1 atm, and the subscript  $f$  denotes “formation.”

The standard heat of formation is the name given to the special enthalpy change associated with the formation of 1 mole of a compound from its constituent elements in their standard state.

An example is the enthalpy change that occurs for the reaction of carbon and oxygen to form carbon dioxide at 25°C and 1 atm, as indicated in Figure 25.1



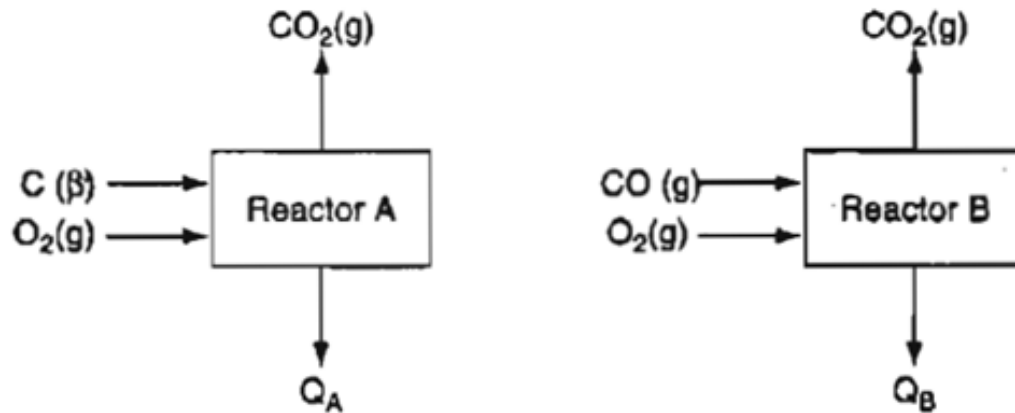
Note in the chemical reaction equation the explicit specification of the state of the compounds in parenthesis. For an energy balance applied to the process in Figure 25.1,  $\Delta H = Q = -393.5 \text{ kJ/g mol of CO}_2$ , and hence the standard heat of formation of  $\text{CO}_2$ , is  $-393.5 \text{ kJ/g mol}$ .



**Figure 25.1** The heat transferred from a steady-state combustion process for the reaction  $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$  with reactants and products at 25°C and 1 atm.

### EXAMPLE 25.1 Determination of a Heat of Formation from Heat Transfer Measurements

Suppose that you want to find the standard heat of formation of CO from experimental data. Can you prepare pure CO from the reaction of C and  $\text{O}_2$ , and measure the heat transfer? This would be far too difficult. It would be easier experimentally to find first the heat of reaction at standard conditions for the two reactions shown below for the flow process as shown in Figure E25.1.

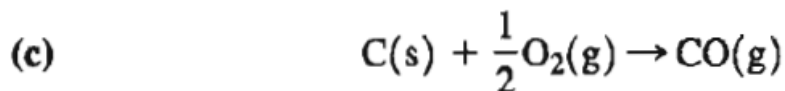


**Figure E25.1** Use of two convenient reactions to determine the heat of formation for an inconvenient reaction  $\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)}$ .

- (a)  $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad Q = -393.51 \text{ kJ/g mol C} = \Delta H_A$
- (b)  $\text{CO(g)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad Q = -282.99 \text{ kJ/g mol CO} = \Delta H_B$

Basis: 1 g mol of C and CO

According to Hess's Law, you subtract reaction (b) from reaction (a), subtract the corresponding  $\Delta H$ 's, and rearrange the compounds to form the desired chemical equation



for which the net heat of reaction per g mol CO is the heat of formation of CO

$$\Delta H_f^\circ = -393.51 - (-282.99) = -110.52 \text{ kJ/g mol C}$$

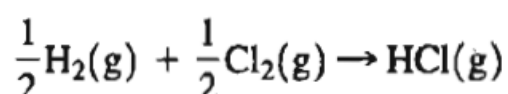
## EXAMPLE 25.2 Retrieval of Heats of Formation from Reference Data

What is the standard heat of formation of HCl(g)?

### Solution

Look in Appendix F. The column heading is  $\Delta \hat{H}_f^\circ$ , and in the column opposite HCl(g) read  $-92.311 \text{ kJ/g mol}$ .

In the reaction to form  $\text{HCl(g)}$  at  $25^\circ\text{C}$  and 1 atm



Both  $\text{H}_2(\text{g})$  and  $\text{Cl}_2(\text{g})$  are assigned  $\Delta\hat{H}_f^\circ$  values of 0, and consequently the value shown in Appendix F for  $\text{HCl(g)}$  of  $-92.311 \text{ kJ/g mol}$  is the standard heat of formation for this compound

$$\Delta H_f^\circ = 1(-92.311) - \left[ \frac{1}{2}(0) + \frac{1}{2}(0) \right] = -92.311 \text{ kJ/g mol HCl(g)}$$

The value tabulated in Appendix F might actually be determined by carrying out the reaction shown for  $\text{HCl(g)}$  and measuring the heat transfer from a calorimeter, or by some other more convenient method.

### Heats of Formation and Combustion

Appendix F

Compound	Formula	Mol. wt.	State	$\Delta\hat{H}_f^\circ$ (kJ/g mol)	$\Delta\hat{H}_c^\circ$ (kJ/g mol)
Ethane	$\text{C}_2\text{H}_6$	30.07	g	-84.667	-1559.9
Ethyl acetate	$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	88.10	l	-442.92	-2274.48
Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	46.068	l	-277.63	-1366.91
Hydrogen	$\text{H}_2$	2.016	g	0	-285.84
Hydrogen bromide	$\text{HBr}$	80.924	g	-36.23	
Hydrogen chloride	$\text{HCl}$	36.465	g	-92.311	
Sulfur	S	32.07	c	0	

## 25.2 The Heat (Enthalpy) of Reaction

As we mentioned previously, one method of including the effect of chemical reaction in the energy balance uses the heat of reaction. The **heat of reaction** (that should be but is only rarely called the **enthalpy of reaction**) is the enthalpy change that occurs when *stoichiometric quantities* of reactants at some  $T$  and  $p$  react to form products at the *same*  $T$  and  $p$ . The **standard heat of reaction** ( $\Delta\hat{H}_{\text{rxn}}^\circ$ ) is the name

given to the heat of reaction (enthalpy change) for one mole of a compound that reacts at 25°C and 1 atm\* (the standard state for reaction) when stoichiometric quantities of reactants in the standard state **react completely** to produce products in the standard state. Don't confuse the symbol for the standard heat of reaction,  $\Delta \hat{H}_{\text{rxn}}^{\circ}$ , for one mole with the more general heat of reaction symbol,  $\Delta H_{\text{rxn}}$ , which can apply to more or less than 1 mole. If the reaction is not at 25°C and 1 atm, the superscript  $^{\circ}$  is deleted. In your calculations, you usually base the heat of reaction on a chemical reaction equation.

You can obtain the heat of reaction from experiments of course, but it is easier to calculate the standard heat of reaction from the tabulated values of the heats of formation as follows. Consider a steady-state flow process with no work involved, such as shown in Figure 25.2 in which benzene ( $\text{C}_6\text{H}_6$ ) reacts with the stoichiometric amount of  $\text{H}_2$  to produce cyclohexane ( $\text{C}_6\text{H}_{12}$ ) in the standard state:

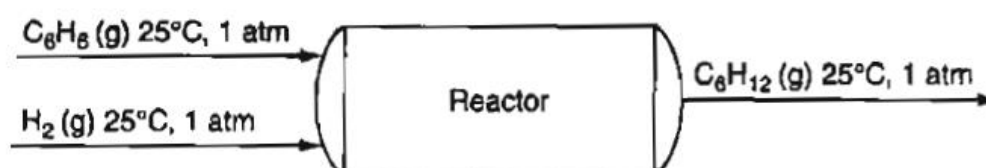
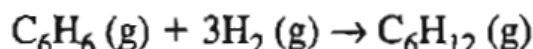


Figure 25.2 Reaction of benzene to form cyclohexane.



The energy balance for the process reduces to  $Q = \Delta H$  where  $\Delta H$  is by definition  $\Delta \hat{H}_{\text{rxn}}^{\circ}$  for the specified chemical reaction equation.

Because we adopt for the heat of reaction the same reference conditions (0 enthalpy for the elements at 25°C and 1 atm) as used in defining the heats of formation, the values of the enthalpies associated with each species involved in the reaction are just the values of the respective heats of formation. For the process shown in Figure 25.2, the data are

Compound	Specific Enthalpy = $\Delta \hat{H}_f^{\circ}$ (kJ/g mol)
$\text{C}_6\text{H}_6 (\text{g})$	82.927
$\text{H}_2 (\text{g})$	0
$\text{C}_6\text{H}_{12} (\text{g})$	-123.1

You calculate the standard heat of reaction thus:

$$\begin{aligned}\Delta \hat{H}_{\text{rxn}}^{\circ} &= \nu_{\text{C}_6\text{H}_{12}} \Delta \hat{H}_{f, \text{C}_6\text{H}_{12}}^{\circ} - \nu_{\text{C}_6\text{H}_6} \Delta \hat{H}_{f, \text{C}_6\text{H}_6}^{\circ} - \nu_{\text{H}_2} \Delta \hat{H}_{f, \text{H}_2}^{\circ} \\ &= (1)(-123.1) - (1)(82.927) - (3)(0) = -206.0 \text{ kJ}\end{aligned}$$

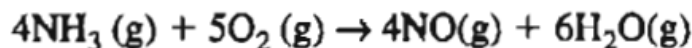
The  $\Delta \hat{H}_{\text{rxn}}^{\circ}$  is for the reaction as written, and actually has the units of energy per moles reacting for the specified chemical equation.

In general for complete reaction

$$\Delta \hat{H}_{\text{rxn}}^{\circ}(25^{\circ}\text{C}) = \left( \sum_i^{\text{Products}} \nu_i \Delta \hat{H}_{f,i}^{\circ} - \sum_i^{\text{Reactants}} \nu_i \Delta \hat{H}_{f,i}^{\circ} \right) \quad (25.1)$$

### EXAMPLE 25.3 Calculation of the Standard Heat of Reaction from the Standard Heats of Formation

Calculate  $\hat{H}_{\text{rxn}}^{\circ}$  for the following reaction of 4 g mol of  $\text{NH}_3$ :



#### Solution

Basis: 4 g mol of  $\text{NH}_3$

<i>Tabulated data</i>	<u><math>\text{NH}_3(\text{g})</math></u>	<u><math>\text{O}_2(\text{g})</math></u>	<u><math>\text{NO}(\text{g})</math></u>	<u><math>\text{H}_2\text{O}(\text{g})</math></u>
$\Delta \hat{H}_{\text{rxn}}^{\circ}$ per mole at $25^{\circ}\text{C}$ and 1 atm (kJ/g mol)	-46.191	0	+90.374	-241.826

We shall use Equation (25.1) to calculate  $\Delta \hat{H}_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}(25^{\circ}\text{C})$  for 4 g mol of  $\text{NH}_3$  assuming complete reaction:

$$\begin{aligned}\Delta H_{\text{rxn}}(25^{\circ}\text{C}) &= [4(90.374) + 6(-241.826)] - [5(0) + 4(-46.191)] \\ &= -904.696 \text{ kJ/4 g mol NH}_3.\end{aligned}$$

Per g mol of reaction  $\Delta \hat{H}_{\text{rxn}}^{\circ} = -226.174 \text{ kJ/g mol NH}_3$ .

Equation (25.1), and use the extent of reaction if you know it or can calculate it. For each species associated with the reaction for a batch system

$$n_i^{\text{final}} = n_i^{\text{initial}} + v_i \xi$$

or the equivalent for a flow system

$$n_i^{\text{out}} = n_i^{\text{in}} + v_i \xi$$

Thus

$$\Delta H_{\text{rxn}}(25^\circ\text{C}) = \sum_i^{\text{Products}} (n_i^{\text{in}} + v_i \xi) \Delta \hat{H}_{f,i}^\circ - \sum_i^{\text{Reactants}} (n_i^{\text{in}}) \Delta \hat{H}_{f,i}^\circ$$

You can change the summations to sum over all the species associated with the reaction if you let  $n_i = 0$  for any species not present as a product or reactant

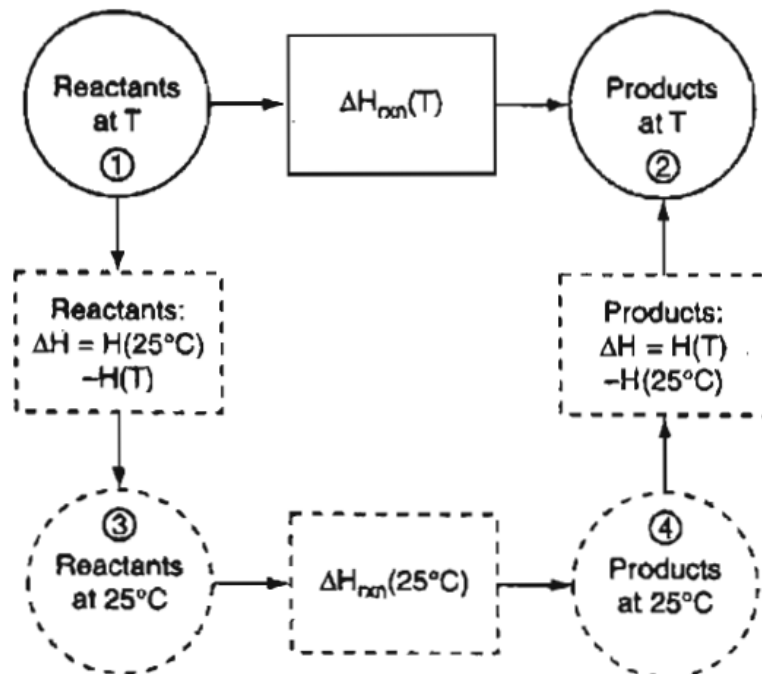
$$\begin{aligned} \Delta H_{\text{rxn}}(25^\circ\text{C}) &= \sum_i n_i^{\text{in}} \Delta \hat{H}_{f,i}^\circ + \sum_i v_i \xi \Delta \hat{H}_{f,i}^\circ - \sum_i n_i^{\text{in}} \Delta \hat{H}_{f,i}^\circ \\ &= \xi \sum_{\text{all species}} v_i \Delta \hat{H}_{f,i}^\circ = \xi \Delta H_{\text{rxn}}^\circ \end{aligned} \quad (25.2)$$

For example, for the reaction in Figure 25.2, assume the fraction conversion is 0.80. Then, based on the limiting reactant  $\text{C}_6\text{H}_{12}$ ,

$$\xi = \frac{-(0.80)(1)}{-1} = 0.80$$

$$\Delta H_{\text{rxn}}(25^\circ\text{C}) = (0.80)[(1)(-123.1) + (-3)(0) + (-1)(82.927)] = -164.8 \text{ kJ}$$

Look at Figure 25.3. We want to calculate the  $\Delta H_{\text{rxn}}(T)$  (enthalpy change [heat of reaction] from state 1 to 2 at  $T$ ). The value is the same as summing the value of all the enthalpy changes 1 to 3, 3 to 4, and 4 to 2. The enthalpy change  $H(T) - H(25^\circ\text{C})$  for the reactants and products is the combination of the sensible and latent heat (enthalpy) changes that might be taken from a table, or be calculated for one species as follows:



**Figure 25.3** Information used in calculating the enthalpies comprising  $\Delta H_{\text{rxn}}(T)$ .

$$H_i(T) - H_i(25^\circ\text{C}) = n_i \int_{25^\circ\text{C}}^T C_{p,i} dT + n_i \Delta \hat{H}_{i, \text{phase change}} \quad (25.3)$$

In summary, ignoring any slight pressure and mixing effects, the heat of reaction at a temperature other than the reference temperature is

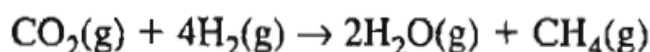
$$\Delta H_{\text{rxn}}(T) = \sum_i^{\text{Reactants}} n_i [\hat{H}_i(25^\circ\text{C}) - \hat{H}_i(T)] + \Delta H_{\text{rxn}}(25^\circ\text{C}) \quad (25.4)$$

$$+ \sum_i^{\text{Products}} n_i [\hat{H}_i(T) - \hat{H}_i(25^\circ\text{C})]$$

$$= [H(T) - H(25^\circ\text{C})]_{\text{Products}} - [H(T) - H(25^\circ\text{C})]_{\text{Reactants}} + \Delta H_{\text{rxn}}(25^\circ\text{C}) \quad (25.4a)$$

### EXAMPLE 25.4 Calculation of the Heat of Reaction at a Temperature Different from the Standard Conditions

Public concern about the increase in the carbon dioxide in the atmosphere has led to numerous proposals to sequester or eliminate the carbon dioxide. An inventor believes he has developed a new catalyst that can make the gas phase reaction



proceed with 100% conversion of  $\text{CO}_2$ . The source of the hydrogen would be from the electrolysis of water using electricity generated from solar cells. Assume stoichiometric amounts of the reactants enter the reactor. Determine the heat of reaction if the gases enter and leave at 1 atm and  $500^\circ\text{C}$ .

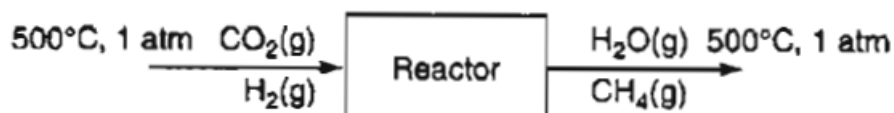


Figure E25.4

### Solution

Basis: 1 g mol  $\text{CO}_2$  (g) at  $500^\circ\text{C}$  and 1 atm

Compounds	g mol	$\Delta \hat{H}_f^\circ$ (kJ/g mol)	$\Delta \hat{H}_{25^\circ\text{C}}^{500^\circ\text{C}}$ (kJ/g mol)
$\text{CO}_2(\text{g})$	1	-393.250	21.425
$\text{H}_2(\text{g})$	4	0	13.834
$\text{H}_2\text{O}(\text{g})$	2	-241.835	17.010
$\text{CH}_4(\text{g})$	1	-74.848	23.126

$$\Delta H_{\text{rxn}}(25^\circ\text{C}) = [(1)(-74.848) + 2(-241.835)] - [(1)(-393.250) + 4(0)] = -165.27 \text{ kJ}$$

$$\sum_{\text{Reactants}} [H_i(500^\circ\text{C}) - H_i(25^\circ\text{C})] = (1)(21.425) + (4)(13.834) = 76.761$$

$$\sum_{\text{Products}} [H_i(500^\circ\text{C}) - H_i(25^\circ\text{C})] = (2)(17.010) + (1)(23.126) = 57.146$$

$$\Delta H_{\text{rxn}}(500^\circ\text{C}) = 57.146 - 76.761 + (-165.27) = -184.9 \text{ kJ}$$

### EXAMPLE 25.5 Calculation of the Heat Transfer Using the Heat of Reaction in a Process in which the Reactants Enter and the Products Leave at Different Temperatures

A test of the process described in Example 25.4 showed on the basis of 1 g mol of  $\text{CO}_2$  entering from another process at 800 K, and reacting with 4 g mol  $\text{H}_2$  entering at 298 K, that only 70% conversion of the  $\text{CO}_2$  occurred. The products exited from the reactor at 1000 K. Calculate the heat transfer to or from the reactor for the test.

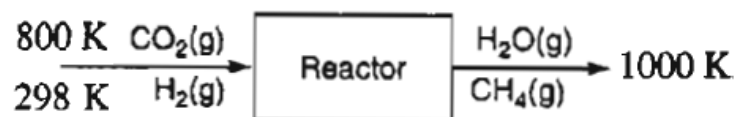


Figure E25.5

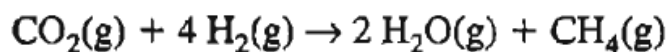
#### Solution

The system is steady state and open with reaction. Assume 1 atm.

Basis: 1 g mol of  $\text{CO}_2(\text{g})$

The reference temperature is  $25^\circ\text{C}$ .

The first step is to calculate the heat of reaction at the reference temperature. The reaction is



$$\Delta \hat{H}_{\text{rxn}}^\circ = [(1)(-74.84) + (2)(-241.835)] - [(1)(-393.51) + (4)(0)] = -165.27 \text{ kJ}$$

For 70% conversion of the  $\text{CO}_2$

$$\Delta H_{\text{rxn}}(25^\circ\text{C}) = (0.70)(-165.27) = -115.69 \text{ kJ}$$

The next step is to calculate the enthalpy changes from 298K to the respective temperatures of the compounds entering and leaving the reactor. The material balance results are listed in column 2 of the table below.

	Comp.	g mol	T(K)	Sensible heat $\Delta \hat{H}_{298}^T$ (kJ/g mol)	Total enthalpy $\Delta H_{298}^T$ (kJ)
<i>In</i>					
	CO <sub>2</sub> (g)	1	800	22.798	22.798
	H <sub>2</sub> (g)	4	298	0	0
				Total	22.798
<i>Out</i>					
	H <sub>2</sub> (g)	1.2	1000	20.620	24.744
	CH <sub>4</sub> (g)	0.7	1000	38.325	26.828
	CO <sub>2</sub> (g)	0.3	1000	33.396	10.019
	H <sub>2</sub> O(l)	1.4	1000	25.986	36.380
				Total	97.971

The energy balance reduces to  $Q = \Delta H$ .

$$Q = \Delta H = 97.971 - 22.798 + (-115.69) = -40.517 \text{ kJ/g mol CO}_2$$

### EXAMPLE 25.6 Calculation of the Enthalpy Change in an Anerobic Culture

An anerobic (in the absence of air) culture of *Lacto bacillus casei* used mannitol as the energy source for the production of ethanol, acetate, formate, and lactate compounds. The values of the enthalpy changes for each compound in the solution were calculated from estimates of the oxidation of each metabolite:

	$\Delta H$ (kJ/g mol)	g mol produced/g mol mannitol
Ethanol	-1330.51	1.29
Acetate	-887.01	0.22
Formate	-221.75	1.6
Lactate	-1330.51	0.4
Mannitol	-2882.78	1.0 (consumed)

The biomass growth was 40.5 g cells/g mol mannitol. Calculate the net enthalpy change for the several products (metabolites) per (a) g mol mannitol consumed and (b) g cells produced.

**Solution**

Basis: 1 g mol of mannitol reacting

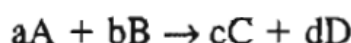
$$\Delta H = [1.29(-1330.51) + 0.22(-887.01) + 1.6(-221.75) + 0.4(-1330.51)] - 1.0(-2882.78) = -84.28 \text{ kJ/g mol mannitol}$$

$$\text{Per gram of cells: } \Delta H = \frac{-84.28 \text{ kJ}}{1 \text{ g mol mannitol}} \left| \frac{1 \text{ g mol mannitol}}{40.5 \text{ g cells}} \right| = 2.08 \text{ kJ/g cells}$$

## 25.3 Merging the Heat of Formation with the Sensible Heat of a Compound in Making an Energy Balance

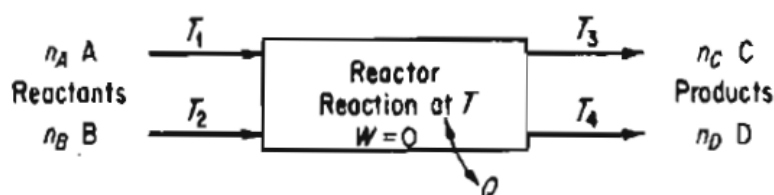
In this section we explain how the heats of formation can be merged directly with the sensible heats and the phase changes, and thus bypass the direct calculation of the heat of reaction. The procedure is attractive from the viewpoint of using process simulators. The basic idea is to include  $\Delta \hat{H}_f^0$  for each component in the enthalpy change for that component.

To illustrate the concept, consider the process illustrated in Figure 25.4, for which the reaction is



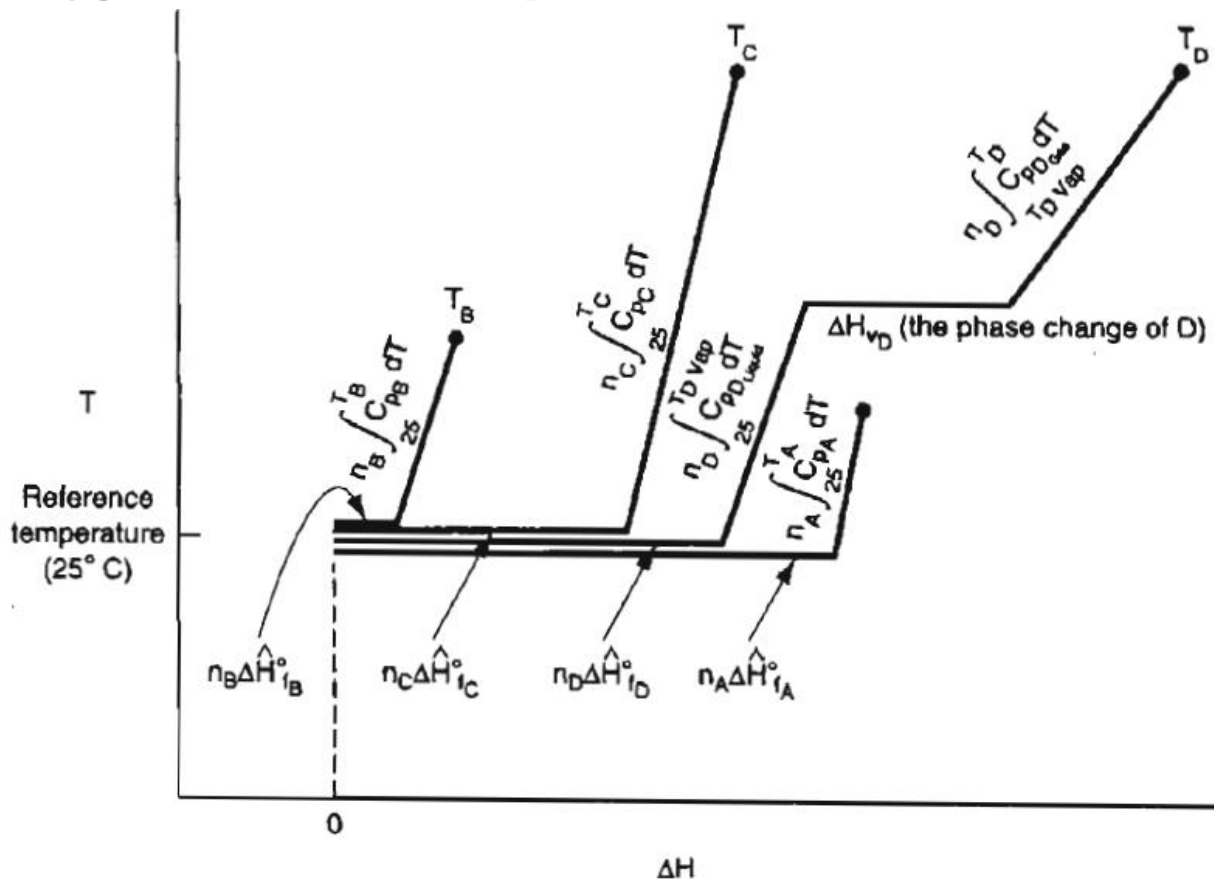
Assume that *nonstoichiometric amounts of reactants and products, respectively, enter and leave the reactor at different temperatures*. You cannot always assume that reactions occur with stoichiometric quantities of reactants, that the reactions go to completion, and that the temperatures of any of the inlet and outlet streams are the same. You should always **first choose a reference state** for the enthalpies at which the heats of formation are known, namely 25°C and 1 atm. (If no reaction takes place, the reference state can be the state of an inlet or outlet stream.)

The enthalpies of each stream entering and leaving **calculated relative to the selected reference state** will include three components for *every compound in the stream whether it is involved in the reaction or not*:

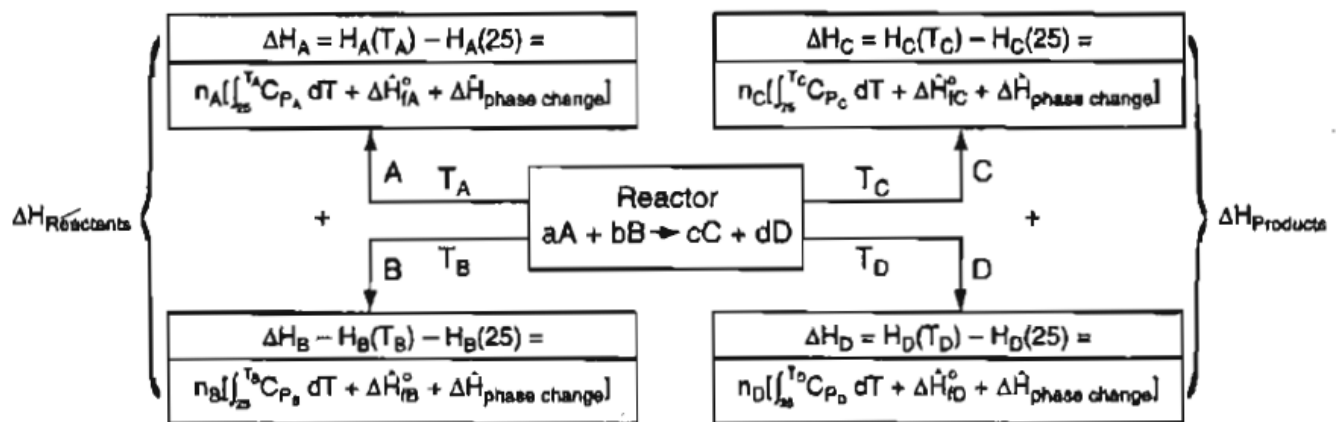


**Figure 25.4** Steady-state flow process with reaction. The labels "Reactants" and "Products" can include compounds that may or may not react.

- (a) the standard heat of formation of the compound
- (b) the “sensible heat” of the compound (relative to the reference temperature)
- (c) any phase changes of the compound.



**Figure 25.5** Illustration of how the enthalpy of each species entering and leaving the process shown in Figure 25.5 is calculated relative to the reference state of 25°C and 1 atm.



**Figure 25.6** Information flow diagram showing how to calculate the enthalpies of the compounds entering and leaving a reactor.

To make the presentation simple, assume a steady-state flow process ( $\Delta U = 0$ ) with no work ( $W = 0$ ), and  $KE = PE = 0$  so that the general energy balance reduces to

$$Q = \Delta H = \Delta H^{\text{out}} - \Delta H^{\text{in}} \quad (25.7)$$

Equation (25.7) includes all of the compounds entering and leaving whether they react or not. Rather than write a long equation, look at Figure 25.6, which shows how you calculate the values for the  $\Delta H^{\text{out}}$  and  $\Delta H^{\text{in}}$ .

### EXAMPLE 25.8 Example 25.4 Redone with the Heats of Formation Merged with the Sensible Heats

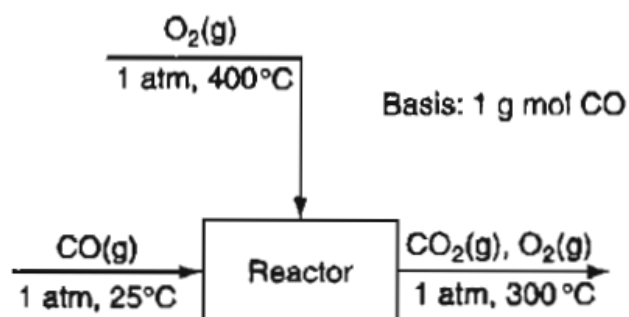
The problem and all of the data are in Example 25.4. The table below formulates the details of the solution.

Comp.	g mol	$T(^{\circ}\text{C})$	$\Delta \hat{H}_f^{\circ}(\text{kJ/g mol})$	$\Delta \hat{H}_{25^{\circ}\text{C}}^{500^{\circ}\text{C}}(\text{kJ/g mol})$	$\Delta H(\text{kJ})$
<i>In</i>					
$\text{CO}_2(\text{g})$	1	500	-393.250	21.425	-371.825
$\text{H}_2(\text{g})$	4	500	0	13.834	55.336
				Total	-316.489
<i>Out</i>					
$\text{H}_2\text{O}(\text{g})$	2	500	-241.835	17.010	-449.650
$\text{CH}_4(\text{g})$	1	500	-74.848	23.126	-51.772
				Total	-501.442

Now,  $Q = \Delta H = \Delta H^{\text{out}} - \Delta H^{\text{in}} = -501.442 - (-316.489) = -184.9 \text{ kJ}$

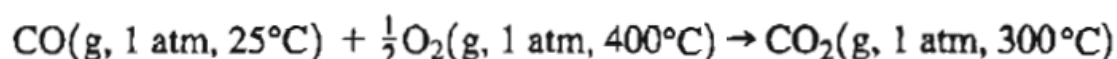
### EXAMPLE 25.9 Calculation of the Heat Transfer When the Reactants and Products Enter and Leave at Different Temperatures

As an example of the application of Figure 25.6, let us calculate  $\Delta H$  for the reaction shown in Figure E25.9.



**Figure E25.9**

Assume nonstoichiometric quantities of compounds enter and leave with the moles and temperatures shown in columns 2 and 3 of the table below, respectively. The reaction equation is



### Solution

Data you need to make the calculation (taken from Appendices D and E rather than integrating the heat capacity equations) are:

Compound	g mol	$T(^{\circ}\text{C})$	Heat of formation $\Delta \hat{H}_f^{\circ}$ (kJ/g mol)	Sensible heat $\Delta \hat{H}_{25^{\circ}\text{C}}^T$ (kJ/g mol)	Total $\Delta H$ (kJ)
<i>In</i>					
CO	1.0	25	-110.520	0	-110.520
O <sub>2</sub>	1.5	400	0	(12.351 - 0.732) = 11.619	17,429
<i>Out</i>					
CO <sub>2</sub>	1.0	300	-393.510	(12.556 - 0.912) = 11.644	-381.866
O <sub>2</sub>	1.0	300	0	(9.121 - 0.732) = 8.389	8.389

Note that in the tables in Appendix D, the reference temperature for  $\hat{H} = 0$  is  $0^{\circ}\text{C}$ , not  $25^{\circ}\text{C}$ , so that the enthalpy at  $25^{\circ}\text{C}$  is subtracted in the sensible heat column for each compound.

Based on the above data

$$\Delta H = (-381.866 + 8.389) - (-110.520 + 17.429) = -280.386 \text{ kJ/g mol CO}$$

## 25.4 The Heat of Combustion

An older method of calculating enthalpy changes when chemical reactions occur is via **standard heats (enthalpies) of combustion**,  $\Delta \hat{H}_c^\circ$ , which have a different set of reference conditions than do the standard heats of formation. The conventions used with the standard heats of combustion are:

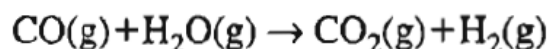
- The compound is oxidized with oxygen or some other substance to the products  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$ ,  $\text{HCl}(\text{aq})$ , and so on.
- The reference conditions are still  $25^\circ\text{C}$  and 1 atm.
- Zero values of  $\Delta \hat{H}_c^\circ$  are assigned to certain of the oxidation products as, for example,  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$ ,  $\text{HCl}(\text{aq})$ , and to  $\text{O}_2(\text{g})$  itself.
- If other oxidizing substances are present, such as S or  $\text{N}_2$  or if  $\text{Cl}_2$  is present, it is necessary to make sure that states of the products are carefully specified and are identical to (or can be transformed into) conditions that determine the standard state.
- Stoichiometric quantities are assumed to react completely.

You can calculate a standard heat of reaction using the heats of combustion by an equation analogous to Equation (25.1).

$$\Delta H_{\text{rxn}}^\circ(25^\circ\text{C}) = -\Delta \hat{H}_c^\circ \text{ of reaction} = -\left( \sum_{\text{Products}} n_i \Delta \hat{H}_{c,i}^\circ - \sum_{\text{Reactants}} n_i \Delta \hat{H}_{c,i}^\circ \right) \quad (25.7)$$

**Note:** The minus sign in front of the summation expression occurs because the choice of reference states is zero for the righthand products of the standard reaction. Refer to Appendix F for values of  $\Delta \hat{H}_c^\circ$ .

As an example of the calculation of  $\Delta H_{\text{rxn}}^\circ(25^\circ\text{C})$  from heat of combustion data, we will calculate  $\Delta H_{\text{rxn}}^\circ(25^\circ\text{C})$  for the reaction (the data are taken from Appendix F in kJ/g mol).



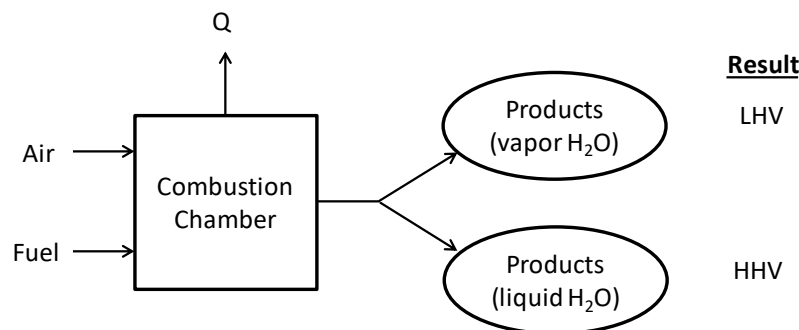
$$\begin{aligned} \Delta H_{\text{rxn}}^\circ(25^\circ\text{C}) &= -\{[(1)(0) + (1)(-285.84)] - [(1)(-282.99) + (1)(-44.00)]\} \\ &= -41.15 \text{ kJ} \end{aligned}$$

Note that the heat of combustion of  $\text{H}_2\text{O}(l)$  is zero, but is  $-44.00 \text{ kJ/g mol}$  for  $\text{H}_2\text{O}(g)$ —you have to subtract the heat of vaporization of water at  $25^\circ\text{C}$  and  $1 \text{ atm}$  from the value for  $\text{H}_2\text{O}(l)$ . (Look at Figure 25.9 as to the source of the  $\Delta \hat{H}_{\text{vap}} = 44.00 \text{ kJ/g mol}$ .)

For a fuel such as coal or oil, the *negative* of the standard heat of combustion is known as the **heating value** of the fuel. Both a **lower (net) heating value (LHV)** and a **higher (gross) heating value (HHV)** exist, depending upon whether the water in the combustion products is in the form of a vapor (for the LHV) or a liquid (for the HHV). For  $\text{H}_2\text{O}$

$$\text{HHV} = \text{LHV} + (n_{\text{H}_2\text{O},(g)} \text{ in product} \times \Delta \hat{H}_{\text{vap}} \text{ of } \text{H}_2\text{O} \text{ at } 25^\circ\text{C} \text{ and } 1 \text{ atm})$$

Look at Figure 25.7.



**Figure 25.7** The classification of LHV or HHV for a fuel depends on the state of the water exiting from the system.

Calculation of the heat of reaction for fuels and compounds with complicated analysis requires you to use empirical formulas to estimate  $\Delta \hat{H}_{\text{rxn}}^\circ$ . You can estimate the heating value of a coal within about 3% from the Dulong formula\*:

Higher heating value (HHV) in Btu per pound

$$= 14,544 C + 62,028 \left( H - \frac{O}{8} \right) + 4050 S$$

where  $C$  is the weight fraction carbon,  $H$  is the weight fraction hydrogen, and  $S$  is the weight fraction sulfur. The values of  $C$ ,  $H$ ,  $S$ , and  $O$  can be taken from the fuel or the flue-gas analysis. A general relation between the gross heating and net heating values is

$$\text{net Btu/lb coal} = \text{gross Btu/lb coal} - 91.23 \times (\% \text{ total H by weight})$$

The HHV of fuel oils in Btu per pound can be approximated by

$$\text{HHV} = 17,887 + 57.5^\circ\text{API} - 102.2 (\%S).$$

### EXAMPLE 25.10 Heating Value of Coal

Coal gasification consists of the chemical transformation of solid coal into a combustible gas. For many years before the widespread adoption of natural gas, gas generated from coal served as a fuel (and also as an illuminant). The heating values of coals differ, but the higher the heating value, the higher the value of the gas produced. The analysis of the following coal has a reported heating value of 29,770 kJ/kg as received. Assume that this is the gross heating value at 1 atm and 25°C obtained in an open system. \*\* Use the Dulong formula to check the validity of the reported value.

Component	Percent
C	71.0
H <sub>2</sub>	5.6
N <sub>2</sub>	1.6
Net S	2.7
Ash	6.1
O <sub>2</sub>	13.0
Total	100.0

#### Solution

$$\begin{aligned} \text{HHV} &= 14,544(0.71) + 62,028 \left[ (0.056) - \frac{0.130}{8} \right] + 4050(0.027) \\ &= 12,901 \text{ Btu/lb} \end{aligned}$$

Note 0.056 lb of H<sub>2</sub> is also 0.056 lb of H, and 0.130 lb of O<sub>2</sub> is 0.130 lb of O.

$$\frac{12,901 \text{ Btu}}{\text{lb}} \left| \frac{1 \text{ lb}}{0.454 \text{ kg}} \right| \frac{1.055 \text{ kJ}}{1 \text{ Btu}} = 29,980 \text{ kJ/kg}$$

The two values are quite close.

**EXAMPLE 25.11 Selecting a Fuel to Reduce SO<sub>2</sub> Emissions**

SO<sub>2</sub> emissions from power plants are the primary source of acid rain, that is, SO<sub>2</sub> in the atmosphere is absorbed by rain, thus increasing the acidity of lakes and rivers. Consider the two fuels listed in the table below. Determine which fuel would be preferred to provide 10<sup>6</sup> Btu of thermal energy from combustion while minimizing the SO<sub>2</sub> emissions. SO<sub>2</sub> removal from the flue gas can be implemented to reduce the SO<sub>2</sub> discharge, but at additional cost, bringing into play another important factor in choosing a fuel.

	No. 6 Fuel Oil	No. 2 Fuel Oil
Density (lb/ft <sup>3</sup> )	60.2	58.7
Lower heating value (Btu/gal)	155,000	120,000
Carbon (wt %)	87.2	87.3
Hydrogen (wt %)	10.5	12.6
Sulfur (wt %)	0.72	0.62
Ash (wt %)	0.04	<0.01

**Solution**

Basis: 10<sup>6</sup> Btu from combustion

For No. 6 Heating Oil:

$$\frac{10^6 \text{ Btu}}{155,000 \text{ Btu}} \left| \frac{1 \text{ gal}}{1 \text{ gal}} \right| \left| \frac{60.2 \text{ lb fuel}}{1 \text{ gal}} \right| \left| \frac{0.0072 \text{ lb S}}{1 \text{ lb fuel}} \right| = 2.80 \text{ lb S}$$

For No. 2 Heating Oil:

$$\frac{10^6 \text{ Btu}}{120,000 \text{ Btu}} \left| \frac{1 \text{ gal}}{1 \text{ gal}} \right| \left| \frac{58.7 \text{ lb fuel}}{1 \text{ gal}} \right| \left| \frac{0.0062 \text{ lb S}}{1 \text{ lb fuel}} \right| = 3.03 \text{ lb S}$$

The No. 6 Heating Oil should be selected because its combustion will generate less SO<sub>2</sub> emissions, even though it has a higher weight percent S.



**Notice This** **Home Work:** *Basic Principles and Calculation in Chemical Engineering*, 7<sup>th</sup> edition, **Problems of chapter 25, page 793 – 801.**