CHAPTER 5
ENERGY BALANCES: HOW TO ACCOUNT FOR CHEMICAL REACTION

1 The Standard Heat (Enthalpy) of Formation
2 The Heat (Enthalpy) of Reaction
3 Merging the Heat of Formation with the Sensible Heat of a Compound in Making an Energy Balance
4 The Heat of Combustion

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,* $\Delta \hat{H}_f^o$. The superscript ^{o} 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

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

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, $\Delta H = Q = -393.5$ kJ/g mol of CO_2, and hence the standard heat of formation of CO_2, is -393.5 kJ/g mol.
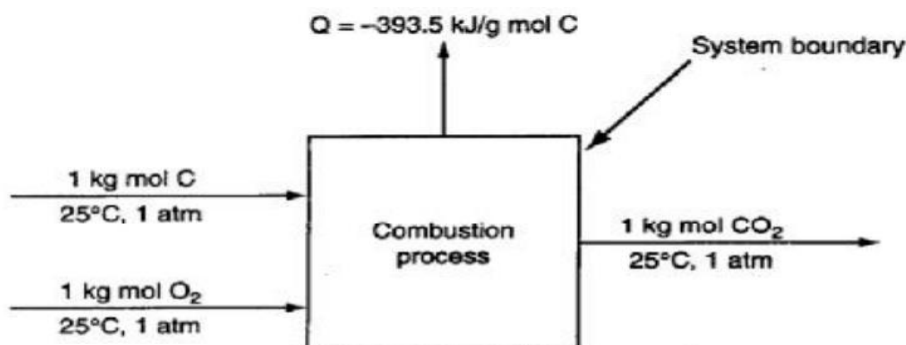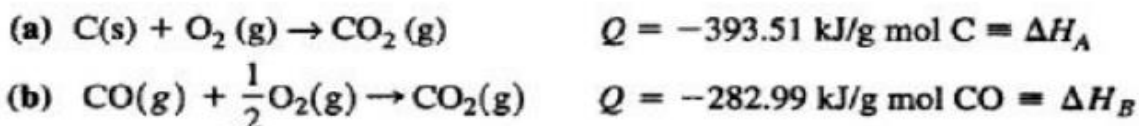

Figure 25.1 The heat transferred from a steady-state combustion process for the reaction $C(s) + O_2(g) \rightarrow CO_2$ (g) with reactants and products at 25°C and 1 atm.

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 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.
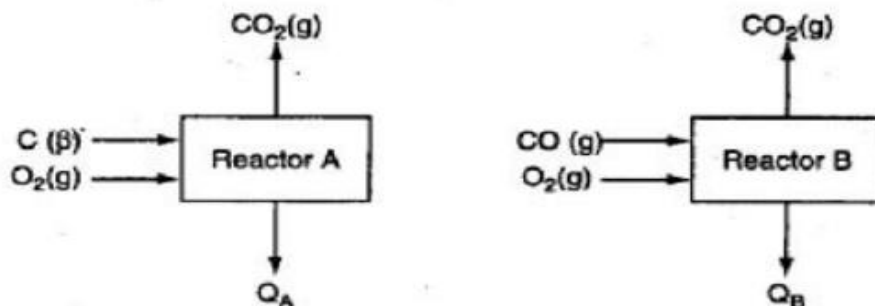

Figure E25.1 Use of two convenient reactions to determine the heat of formation for an inconvenient reaction $C(s) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$.

(a) $C(s) + O_2(g) \rightarrow CO_2(g)$ $Q = -393.51$ kJ/g mol C $= \Delta H_A$

(b) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $Q = -282.99$ 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 ΔH's, and rearrange the compounds to form the desired chemical equation

(c) $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$
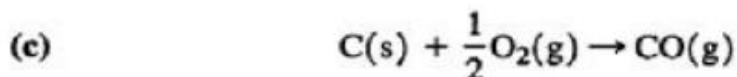
for which the net heat of reaction per g mol CO is the heat of formation of CO

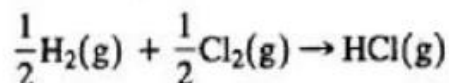$$\Delta H_f^\circ = -393.51 - (-282.99) = -110.52 \text{ kJ/g mol C}$$

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 kJ/g mol.

In the reaction to form HCl(g) at 25°C and 1 atm

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g)$$

Both $H_2(g)$ and $Cl_2(g)$ are assigned $\Delta \hat{H}_f^\circ$ values of 0, and consequently the value shown in Appendix F for HCl(g) of -92.311 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 HCl(g) and measuring the heat transfer from a calorimeter, or by some other more convenient method.

1054   Heats of Formation and Combustion   Appendix F

TABLE F.1   *(cont.)*

Compound	Formula	Mol. wt.	State	$\Delta \hat{H}_f^\circ$ (kJ/g mol)	$\Delta \hat{H}_c^\circ$ (kJ/g mol)
Ethane	C_2H_6	30.07	g	−84.667	−1559.9
Ethyl acetate	$CH_3CO_2C_2H_5$	88.10	l	−442.92	−2274.48
Ethyl alcohol	C_2H_5OH	46.068	l	−277.63	−1366.91
Hydrogen	H_2	2.016	g	0	−285.84
Hydrogen bromide	HBr	80.924	g	−36.23	
Hydrogen chloride	HCl	36.465	g	−92.311	

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** ($\Delta \hat{H}_{rxn}^\circ$) is the name given to the heat of reaction (enthalpy change) for one mole of a compound that re-acts at 25°C and 1 atm* (the standard state for reaction) when stoichiometric quanti-ties 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, $\Delta \hat{H}_{rxn}^\circ$, for one mole with the more general heat of reaction symbol, ΔH_{rxn}, which can apply to more or less than 1 mole. If the reaction is not at 25°C and 1 atm, the superscript ° 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 (C_6H_6) reacts with the stoichiomet-ric amount of H_2 to produce cyclohexane (C_6H_{12}) in the standard state:
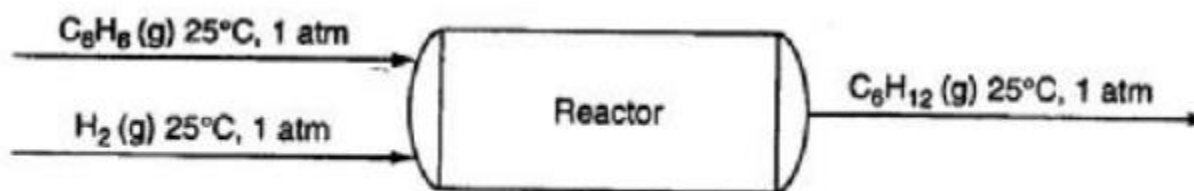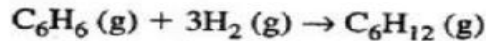
C₈H₆ (g) 25°C, 1 atm

H₂ (g) 25°C, 1 atm

Reactor

C₆H₁₂ (g) 25°C, 1 atm

Figure 25.2   Reaction of benzene to form cyclohexane.

$$C_6H_6 \text{ (g)} + 3H_2 \text{ (g)} \rightarrow C_6H_{12} \text{ (g)}$$

The energy balance for the process reduces to $Q = \Delta H$ where ΔH is by definition $\Delta \hat{H}^o_{rxn}$ 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 Enthalphy = $\Delta \hat{H}^o_f$(kJ/g mol)
C_6H_6 (g)	82.927
H_2 (g)	0
C_6H_{12} (g)	−123.1

You calculate the standard heat of reaction thus:

$$\Delta \hat{H}^o_{rxn} = \nu_{C_6H_{12}} \Delta \hat{H}^o_{f,C_6H_{12}} - \nu_{C_6H_6} \Delta \hat{H}^o_{f,C_6H_6} - \nu_{H_2} \Delta \hat{H}^o_{f,H_2}$$

$$= (1)(-123.1) - (1)(82.927) - (3)(0) = -206.0 \text{ kJ}$$

The $\Delta \hat{H}^o_{rxn}$ 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

$$\Delta \hat{H}^o_{rxn}(25°C) = \left(\overset{Products}{\underset{i}{\sum}} \nu_i \Delta \hat{H}^o_{f,i} - \overset{Reactants}{\underset{i}{\sum}} \nu_i \Delta \hat{H}^o_{f,i} \right) \qquad (25.1)$$

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

Calculate $\hat{H}^o_{rxn}$ for the following reaction of 4 g mol of NH_3:

$$4NH_3 \text{ (g)} + 5O_2 \text{ (g)} \rightarrow 4NO\text{(g)} + 6H_2O\text{(g)}$$
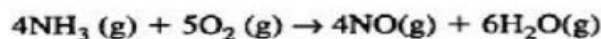
Solution

Basis: 4 g mol of NH_3

Tabulated data	NH_3(g)	O_2(g)	NO(g)	H_2O(g)
ΔH^o_{rxn} per mole at 25°C and 1 atm (kJ/g mol)	−46.191	0	+90.374	−241.826

We shall use Equation (25.1) to calculate $\Delta H^o_{rxn} = \Delta H_{rxn}$ (25°C) for 4 g mol of NH_3 assuming complete reaction:

$$\Delta H_{rxn} \text{ (25°C)} = [4(90.374) + 6(-241.826)] - [5(0) + 4(-46.191)]$$

$$= -904.696 \text{ kJ/4 g mol } NH_3.$$

Per g mol of reaction $\Delta \hat{H}^o_{rxn} = -226.174 \text{ kJ/g mol } NH_3$.

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

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

or the equivalent for a flow system

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

Thus

$$\Delta H_{rxn}(25°C) = \overset{Products}{\underset{i}{\sum}} (n_i^{in} + v_i\xi)\Delta\hat{H}_{f,i}^o - \overset{Reactants}{\underset{i}{\sum}} (n_i^{in})\Delta\hat{H}_{f,i}^o$$

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

$$\Delta H_{rxn}(25°C) = \Sigma n_i^{in}\Delta\hat{H}_{f,i}^o + \Sigma v_i\xi\Delta\hat{H}_{f,i}^o - \Sigma n_i^{in}\Delta\hat{H}_{f,i}$$

$$= \xi \underset{all\ species}{\sum} v_i\Delta\hat{H}_{f,i}^o = \xi\Delta H_{rxn}^o \qquad (25.2)$$

For example, for the reaction in Figure 25.2, assume the fraction conversion is 0.80. Then, based on the limiting reactant C_6H_{12},

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

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

Look at Figure 25.3. We want to calculate the $\Delta H_{rxn}(T)$ (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 $H(T)-H(25°C)$ 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:
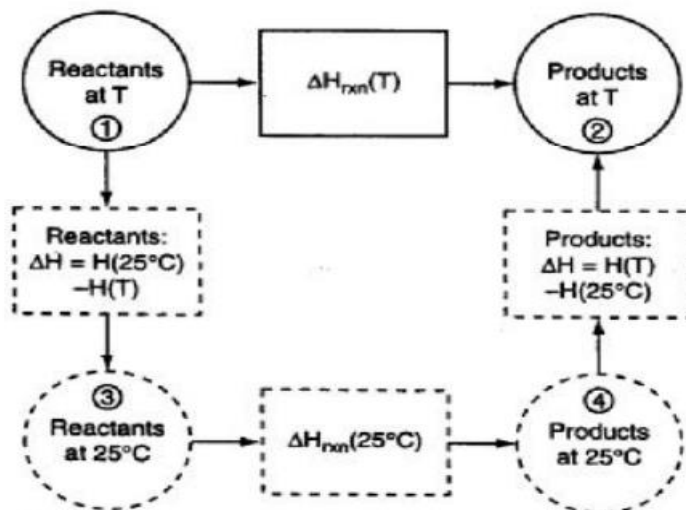

Figure 25.3   Information used in calculating the enthalpies comprising $\Delta H_{rxn}(T)$.

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

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

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

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

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

EXAMPLE 25.4   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

$$CO_2(g) + 4H_2(g) \rightarrow 2H_2O(g) + CH_4(g)$$
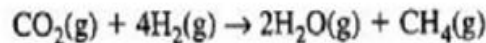
proceed with 100% conversion of CO_2. The source of the hydrogen would be from the electrolysis of water using electricity generated from solar cells. Assume stoichiometric amounts of the reactants enter the reactor. Determine the heat of reaction if the gases enter and leave at 1 atm and 500°C.
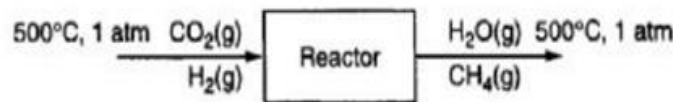

500°C, 1 atm $CO_2(g)$ → Reactor → $H_2O(g)$ 500°C, 1 atm
$H_2(g)$ $CH_4(g)$

Figure E25.4

Solution

Basis: 1 g mol CO_2 (g) at 500°C and 1 atm

Compounds	g mol	$\Delta \hat{H}_f^\circ$(kJ/g mol)	$\Delta \hat{H}_{25^\circ C}^{500^\circ C}$(kJ/g mol)
$CO_2(g)$	1	-393.250	21.425
$H_2(g)$	4	0	13.834
$H_2O(g)$	2	-241.835	17.010
$CH_4(g)$	1	-74.848	23.126

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

Reactants

$\displaystyle\sum_i [H_i(500^\circ C) - H_i(25^\circ C)] = (1)(21.425) + (4)(13.834) = 76.761$

Products

$\displaystyle\sum_i [H_i(500^\circ C) - H_i(25^\circ C)] = (2)(17.010) + (1)(23.126) = 57.146$

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

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 CO_2 entering from another process at 800 K, and reacting with 4 gmol H_2 entering at 298 K, that only 70% conversion of the CO_2 occurred. The products exited from the reactor at 1000 K. Calculate the heat transfer to or from the reactor for the test.
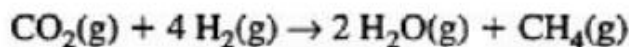
Solution

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

Basis: 1 g mol of $CO_2(g)$

The reference temperature is 25°C.

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

$$CO_2(g) + 4 H_2(g) \rightarrow 2 H_2O(g) + CH_4(g)$$

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

For 70% conversion of the CO_2

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

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 $\Delta \hat{H}^T_{298}$(kJ/g mol)	Total enthalpy ΔH^T_{298}(kJ)
In					
	$CO_2(g)$	1	800	22.798	22.798
	$H_2(g)$	4	298	0	0
				Total	22.798
Out					
	$H_2(g)$	1.2	1000	20.620	24.744
	$CH_4(g)$	0.7	1000	38.325	26.828
	$CO_2(g)$	0.3	1000	33.396	10.019
	$H_2O(l)$	1.4	1000	25.986	36.380
				Total	97.971

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

$$Q = \Delta H = 97.971 - 22.798 + (-115.69) = -40.517 \text{ kJ/g mo } CO_2$$

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 matabolite:

	ΔH (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 enthapy 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

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

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

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 $\Delta \hat{H}_f^\circ$ 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

$$aA + bB \rightarrow cC + dD$$

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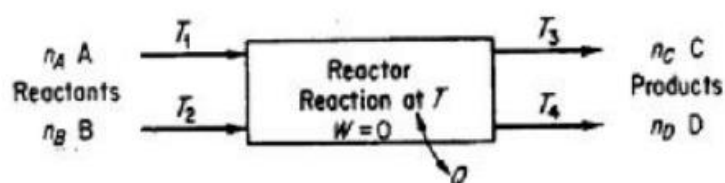
Figure 25.4   Steady-state flow process with reaction. The labels "Reactants" and "Products" can include compounds that may or may not react.

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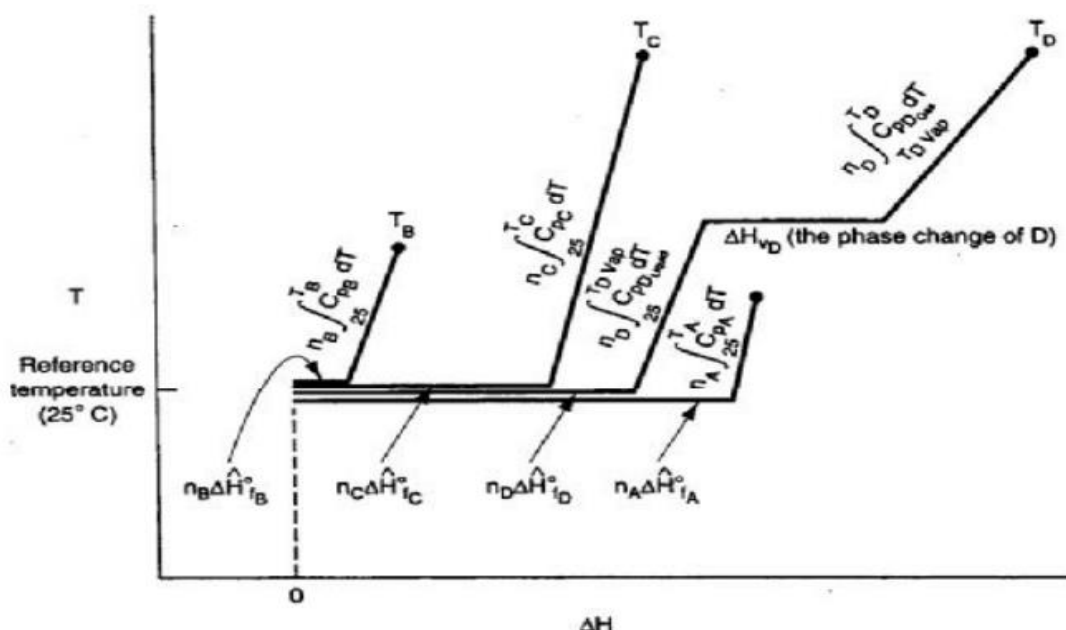(c) any phase changes of the compound.

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.
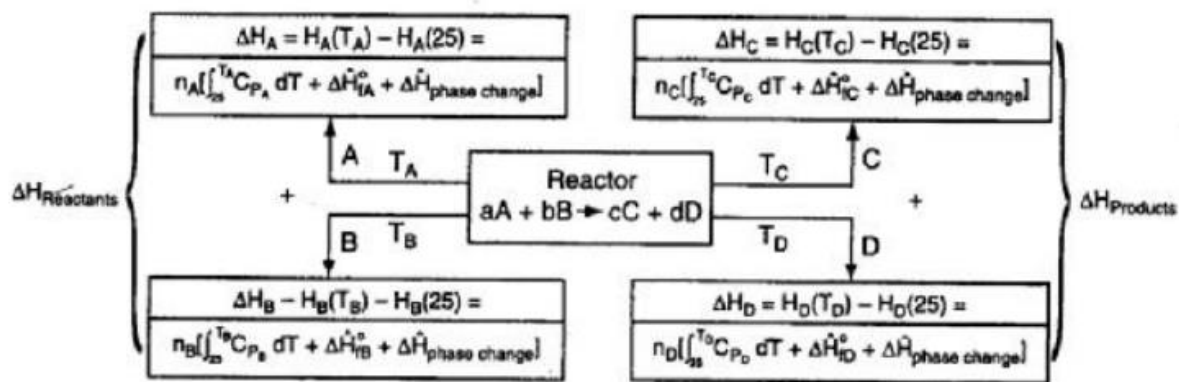

Figure 25.6 Information flow diagram showing how to calculate the enthalpies of the compounds entering and leaving a reactor.

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

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

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 ΔH^{out} and ΔH^{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	$T(°C)$	$\Delta \hat{H}_f°(kJ/g\ mol)$	$\Delta \hat{H}_{25°C}^{500°C}(kJ/g\ mol)$	$\Delta H(kJ)$
In					
$CO_2(g)$	1	500	−393.250	21.425	−371.825
$H_2(g)$	4	500	0	13.834	55.336
				Total	−316.489
Out					
$H_2O(g)$	2	500	−241.835	17.010	−449.650
$CH_4(g)$	1	500	−74.848	23.126	−51.772
				Total	−501.442

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

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 ΔH for the reaction shown in Figure E25.9.
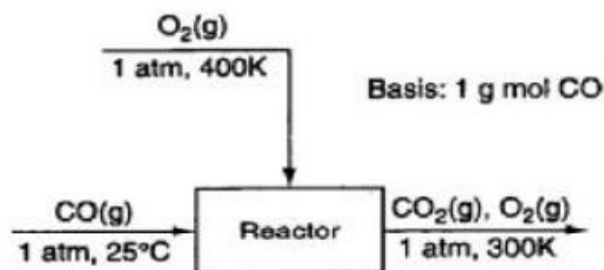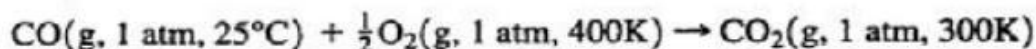

Figure E25.9

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

$$CO(g, 1\ atm, 25°C) + \tfrac{1}{2}O_2(g, 1\ atm, 400K) \rightarrow CO_2(g, 1\ atm, 300K)$$

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	$T(°C)$	Heat of formation $\Delta \hat{H}_f^o$ (kJ/g mol)	Sensible heat $\Delta \hat{H}_{25°C}^T$ (kJ/g mol)	Total ΔH (kJ)
In					
CO	1.0	25	−110.520	0	−110.520
O_2	1.5	400	0	(12.351−0.732) = 11.619	17,429
Out					
CO_2	1.0	300	−393.510	(12.556−0.912) = 11.644	−381.866
O_2	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°C, not 25°C, so that the enthalpy at 25°C is subtracted in the sensible heat column for each compound.

Based on the above data

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

4 The Heat of Combustion

An older method of calculating enthalpy changes when chemical reactions occur is via **standard heats (enthalpies) of combustion**, $\Delta \hat{H}_c^o$, 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:

a. The compound is oxidized with oxygen or some other substance to the products $CO_2(g)$, $H_2O(l)$, $HCl(aq)$, and so on.

b. The reference conditions are still 25°C and 1 atm.

c. Zero values of $\Delta \hat{H}_c^o$ are assigned to certain of the oxidation products as, for example, $CO_2(g)$, $H_2O(l)$, $HCl(aq)$, and to $O_2(g)$ itself.

d. If other oxidizing substances are present, such as S or N_2 or if 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.*

e. 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).

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

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 $\Delta \hat{H}_c^o$.

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

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$
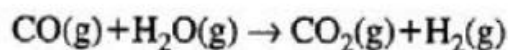
$$\Delta H_{rxn}^{o}(25°C) = -\{[(1)(0) + (1)(-285.84)] - [(1)(-282.99) + (1)(-44.00)]$$

$$= -41.15 \text{ kJ}$$

Note that the heat of combustion of $H_2O(l)$ is zero, but is -44.00 kJ/g mol for
$H_2O(g)$—you have to subtract the heat of vaporization of water at 25°C and 1 atm
from the value for $H_2O(l)$. (Look at Figure 25.9 as to the source of the
$\Delta \hat{H}_{vap} = 44.00$ 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 H_2O
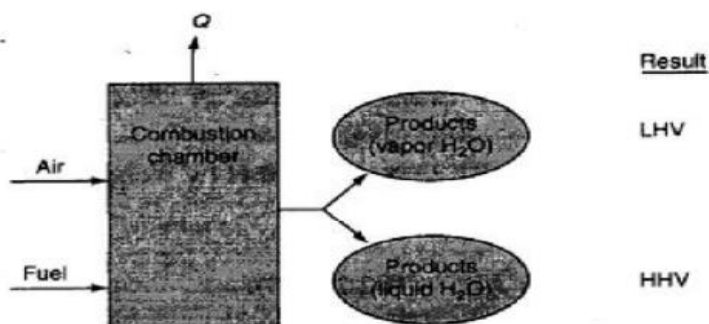
Figure 25.7 The classification of
LHV or HHV for a fuel depends on the
state of the water exiting from the
system.

$$HHV = LHV + (n_{H_2O,(g)} \text{ in product} \times \Delta \hat{H}_{vap} \text{ at } 25°C \text{ and } 1 \text{ atm}).$$

Look at Figure 25.7.

Calculation of the heat of reaction for fuels and compounds with complicated analysis requires you to use empirical formulas to estimate ΔH°_{rxn}. 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

net Btu/lb coal = gross Btu/lb coal − 91.23 × (% 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_2	5.6
N_2	1.6
Net S	2.7
Ash	6.1
O_2	13.0
Total	100.0

Solution

$$HHV = 14{,}544(0.71) + 62{,}028\left[(0.056) - \frac{0.130}{8}\right] + 4050(0.027)$$

$$= 12{,}901 \text{ Btu/lb}$$

Note 0.056 lb of H_2 is also 0.056 lb of H, and 0.130 lb of O_2 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 SO₂ Emissions

SO₂ emissions from power plants are the primary source of acid rain, that is, SO₂ 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 10^6 Btu of thermal energy from combustion while minimizing the SO₂ emissions. SO₂ removal from the flue gas can be implemented to reduce the SO₂ 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/ft³)	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: 10^6 Btu from combustion

For No. 6 Heating Oil:

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

For No. 2 Heating Oil:

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

The No. 6 Heating Oil should be selected because its combustion will generate less SO₂ emissions, even though it has a higher weight percent S.

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