4.7-5 Energy Balance When the Products and Reactants Are Not at 25°C

Your objectives in studying this section are to be able to:

1. Calculate heats of reaction at other than the standard temperature.
2. Calculate how much material must be introduced into a system to provide a prespecified quantity of heat transfer for the system.
3. Apply the general energy balance to processes involving reactions.
4. Determine the temperature of an incoming stream of material given the exit stream temperature (when a reaction occurs).

You no doubt realize that the standard state of 25°C for the heats of formation is only by accident the temperature at which the products enter and the reactants leave a process. In most instances the temperatures of the materials entering and leaving will be higher or lower than 25°C. However, since enthalpies (and hence heats of reaction) are point functions, you can use Eq. (4.24a) together with Eq. (4.33), (4.34), or (4.35), to answer questions about the process being analyzed. Typical questions might be:

(a) What is the heat of reaction at a temperature other than 25°C, but still at 1 atm?
(b) What is the temperature of an incoming or exit stream?
(c) What is the temperature of the reaction?
(d) How much material must be introduced to provide a specified amount of heat transfer for the system?

Consider the process illustrated in Fig. 4.16, for which the reaction is

$$\text{aA} + \text{bB} \longrightarrow \text{cC} + \text{dD}$$

Nonstoichiometric amounts of reactants and products, respectively, enter and leave the system.

In employing Eq. (4.24a) you should always **first choose a reference state** at which the heats of formation are known. This usually turns out to be 25°C and 1 atm. (If no reaction takes place, the reference state can be an inlet or outlet stream temperature.) Then the next step is to calculate the enthalpy changes for each stream

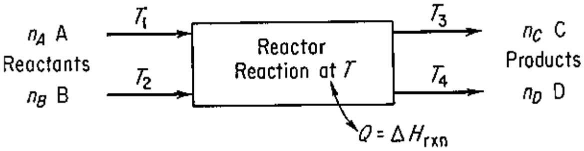

Figure 4.16 Process with reaction.

entering and leaving *relative to this reference state*. Usually, it proves convenient in calculating the enthalpy change to compute the sensible heat changes, the phase changes, and the heat of reaction separately, but this arrangement is not essential. **Any phase changes taking place among the reactants or products not accounted for in the heats of formation must be taken into account in applying the general energy balance.**

Because enthalpy is a state function, you can choose any path you want to execute the calculations for the overall enthalpy change in a process as long as you start and finish at the specified initial and final states, respectively. Figure 4.17 illustrates the idea. For example, suppose that the reference state is chosen to be 25°C and 1 atm, the state for which the $\Delta \hat{H}_f^\circ$'s are known. Figure 4.17 indicates that the path for the calculation for the reactants is from T_A (for A) and T_B (for B) to 25°C; next, the heats of formation are used to get ΔH_{rxn} at 25°C and 1 atm employing A, B, C, and D; and finally, the path for the products goes from 25°C to T_C and T_D. In Fig. 4.17, $T_C = T_D$. Pressure effects can be included along with temperature effects on the enthalpy, but we will omit consideration of the effect of pressure except for problems in which the enthalpy data are retrieved from tables (such as the steam tables) or data bases.

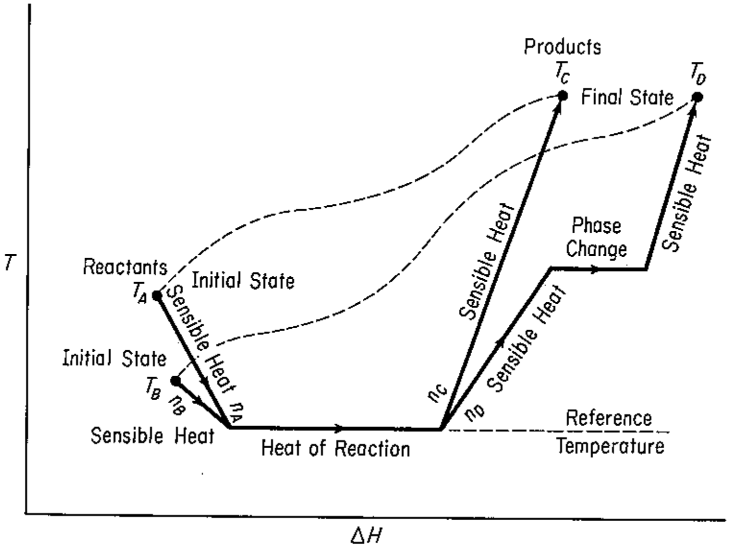

Figure 4.17 Calculation of enthalpy changes for a process in which a reaction takes place. The solid lines indicate an arbitrary selection of path whereas the dashed lines figuratively indicate the actual path taken by the materials—the actual path may not be known in practice.

We have discussed in earlier sections of this chapter methods that you can use to determine the sensible heat ΔH values for the individual streams:

(a) Obtain the enthalpy values from a set of published tables (e.g., the steam tables or tables such as in Appendix D).

(b) Analytically, graphically, or numerically, find

$$\Delta H = \int_{T_1}^{T_2} C_p \, dT$$

for each component individually, using the respective heat capacity equations.

(c) Retrieve values from a data base.

Let us first demonstrate how to calculate the **heat of reaction at a temperature other than 25°C.** By this we mean that stoichiometric quantities of the reactants enter and the products leave at the same temperature—a temperature different from the standard state of 25°C in stoichiometric quantities. Figure 4.18 illustrates the information flow for the calculations corresponding to those associated with Eq. (4.33) assuming a steady-state process ($\Delta E = 0$), no kinetic or potential energy changes, and $W = 0$. The general energy balance [Eq. (4.24)] reduces to

$$Q = \Delta H = [\Delta H_f^\circ + \Delta(H - H^\circ)]_{\text{products}} - [\Delta H_f^\circ + \Delta(H - H^\circ)]_{\text{reactant}}$$

or

$$Q = \overbrace{(\Delta H_{\text{P}} - \Delta H_{\text{R}})}^{\text{sensible}} + (\Delta H_{\text{rxn}_{T_{\text{ref}}}}) \tag{4.40}$$

in terms of the notation in Fig. 4.18. By definition, Q, as calculated by Eq. (4.40), is equal to the "heat of reaction at the temperature T," so that

$$\Delta H_{\text{rxn}_T} = \Delta H_{\text{rxn}_{T_{\text{ref}}}} + \Delta H_{\text{P}} - \Delta H_{\text{R}} \tag{4.41}$$

To indicate a simplified way to calculate $\Delta H_{\text{P}} - \Delta H_{\text{R}}$, particularly using a computer code, suppose that the heat capacity equations are expressed as

$$C_p = \alpha + \beta T + \gamma T^2 \tag{4.42}$$

Then, to obtain $\Delta H_{\text{P}} - \Delta H_{\text{R}}$, we add up the sensible heat enthalpy changes for the

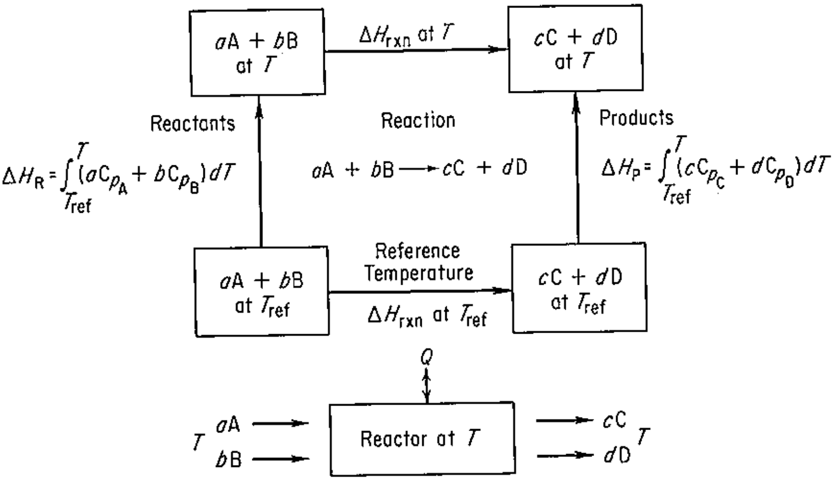

Figure 4.18 Heat of reaction at a temperature other than standard conditions.

products and subtract those for the reactants. Rather than integrate separately, let us consolidate like terms as follows. Each heat capacity equation is multiplied by the proper number of moles:

$$aC_{p_A} = a(\alpha_A + \beta_A T + \gamma_A T^2) \tag{4.43a}$$

$$bC_{p_B} = b(\alpha_B + \beta_B T + \gamma_B T^2) \tag{4.43b}$$

$$cC_{p_C} = c(\alpha_C + \beta_c T + \gamma_c T^2) \tag{4.43c}$$

$$dC_{p_D} = d(\alpha_D + \beta_D T + \gamma_D T^2) \tag{4.43d}$$

Then we define a new term ΔC_p which is equal to

$$\overset{\text{original expression}}{cC_{p_C} + dC_{p_D} - (aC_{p_A} + bC_{p_B})} = \overset{\substack{\text{equivalent}\\ \text{new term}}}{\Delta C_p}$$

and

$$\begin{aligned} [(c\alpha_C + d\alpha_D) - (a\alpha_A + b\alpha_B)] &= \Delta\alpha \\ T[(c\beta_C + d\beta_D) - (a\beta_A + b\beta_B)] &= T\,\Delta\beta \\ T^2[(c\gamma_C + d\gamma_D) - (a\gamma_A + b\gamma_B)] &= T^2\,\Delta\gamma \end{aligned} \tag{4.44}$$

Simplified, ΔC_P can be expressed as

$$\Delta C_p = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 \tag{4.45}$$

Furthermore,

$$\begin{aligned} \Delta H_P - \Delta H_0 &= \int_{T_0}^{T} \Delta C_p \, dT = \int_{T_0}^{T} (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2)\, dT \\ &= \Delta\alpha(T - T_0) + \frac{\Delta\beta}{2}(T^2 - T_0^2) + \frac{\Delta\gamma}{3}(T^3 - T_0^3) \end{aligned} \tag{4.46}$$

where we let $T_0 = T_{\text{ref}}$ for simplicity.

If the integration is carried out without definite limits,

$$\Delta H_P - \Delta H_R = \int (\Delta C_P)\, dT = \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 + C \tag{4.47}$$

where C is the integration constant.

Finally, ΔH_{rxn} at the new temperature T is

$$\Delta H_{\text{rxn}_T} = \Delta H_{\text{rxn}_{T_0}} + \Delta\alpha(T - T_0) + \frac{\Delta\beta}{2}(T^2 - T_0^2) + \frac{\Delta\gamma}{3}(T^3 - T_0^3) \tag{4.48a}$$

or

$$\Delta H_{\text{rxn}_T} = \Delta H_{\text{rxn}_{T_0}} + \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 + C \tag{4.48b}$$

as the case may be. Using Eq. (4.48a) and knowing ΔH_{rxn} at the reference temperature T_0, you can easily calculate ΔH_{rxn} at any other temperature.

Equation (4.48b) can be consolidated into

$$\Delta H_{\text{rxn}_T} = \Delta H_0 + \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 \qquad (4.49)$$

where

$$\Delta H_0 = \Delta H_{\text{rxn}_{T_0}} + C$$

Now, if ΔH_{rxn} is known at any temperature T, you can calculate ΔH_0 as follows:

$$\Delta H_0 = \Delta H_{\text{rxn}_T} - \Delta\alpha(T) - \frac{\Delta\beta}{2}(T^2) - \frac{\Delta\gamma}{3}T^3 \qquad (4.50)$$

Once you calculate the value of ΔH_0, you can use it to calculate ΔH_{rxn} at any other temperature.

Probably the easiest way to compute the necessary enthalpy changes is to use enthalpy data obtained directly from published tables or published formulas. Do not forget to take into account phase changes, if they take place, in the enthalpy calculations. If there is a phase change in one or more of the streams entering or leaving the process, you can conceptually think of the enthalpy changes that take place as shown in Fig. 4.17 if the phase difference is not included in $\Delta\hat{H}_f^\circ$. For example, if the product of combustion is water vapor, use $\Delta\hat{H}_f^\circ$ for water vapor, not for liquid water. Then the phase change from liquid water at 25°C to water vapor at 25°C automatically is taken into account. Otherwise, ΔH of the phase change must be accounted for separately by incorporating it into Eq. (4.46).

EXAMPLE 4.38 Calculation of Heat of Reaction at a Temperature Different from Standard Conditions

An inventor thinks he has developed a new catalyst that can make the gas-phase reaction

$$CO_2 + 4H_2 \longrightarrow 2H_2O + CH_4$$

proceed with 100% conversion. Estimate the heat that must be provided or removed if the gases enter and leave at 500°C.

Solution

Figure 4.18 applies. In effect we need to calculate heat of reaction at 500°C from Eq. (4.41) or Q in Eq. (4.40). For illustrative purposes we use the technique based on Eqs. (4.49) and (4.50). At standard conditions

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

Tabulated data	*$CO_2(g)$*	*$H_2(g)$*	*$H_2O(g)$*	*$CH_4(g)$*
$-\Delta\hat{H}_f^\circ$(J/g mol)	393,513	0	241,826	74,848

$$\Delta\hat{H}_{\text{rxn}_{298\,\text{K}}} = [-74{,}848 - 2(241{,}826)] - [4(0) - 393{,}513]$$
$$= -164{,}987 \text{ J/g mol } CO_2$$

First we shall calculate ΔC_p; units are $\dfrac{\text{J}}{(\text{g mol})(\text{K})}$

$$C_{p\text{CO}_2} = 26.75 + 42.26 \times 10^{-3}T - 14.25 \times 10^{-6}T^2 \qquad T \text{ in K}$$

$$C_{p\text{H}_2} = 26.88 + 4.35 \times 10^{-3}T - 0.33 \times 10^{-6}T^2 \qquad T \text{ in K}$$

$$C_{p\text{H}_2\text{O}} = 29.16 + 14.49 \times 10^{-3}T - 2.02 \times 10^{-6}T^2 \qquad T \text{ in K}$$

$$C_{p\text{CH}_4} = 13.41 + 77.03 \times 10^{-3}T - 18.74 \times 10^{-6}T^2 \qquad T \text{ in K}$$

$$\begin{aligned}\Delta\alpha &= [1(13.41) + 2(29.16)] - [1(26.75) + 4(26.88)] \\ &= -62.54\end{aligned}$$

$$\begin{aligned}\Delta\beta &= [1(77.03) + 2(14.49)](10^{-3}) - [1(42.26) + 4(4.35)](10^{-3}) \\ &= 46.35 \times 10^{-3}\end{aligned}$$

$$\begin{aligned}\Delta\gamma &= [1(-18.74) + 2(-2.02)](10^{-6}) - [1(-14.25) + 4(-0.33)](10^{-6}) \\ &= -7.21 \times 10^{-6}\end{aligned}$$

$$\Delta C_p = -62.54 + 46.35 \times 10^{-3}T - 7.21 \times 10^{-6}T^2$$

Next we find ΔH_0, using as a reference temperature 298 K.

$$\begin{aligned}\Delta H_0 &= \Delta H_{\text{rxn}_{298}} - \Delta\alpha\, T - \frac{\Delta\beta}{2}T^2 - \frac{\Delta\gamma}{3}T^3 \\ &= -164{,}987 - \left[(-62.54)(298) + \frac{46.35 \times 10^{-3}}{2}(298)^2 \right. \\ &\quad \left. + \frac{-7.21 \times 10^{-6}}{3}(298)^3\right] \\ &= -164{,}987 + 18{,}637 - 2058 + 64 = -148{,}345 \text{ J/g mol CO}_2\text{(g)}\end{aligned}$$

Then, with ΔH_0 known, the ΔH_{rxn} at 773 K can be determined.

$$\begin{aligned}\Delta H_{\text{rxn}_{773\,\text{K}}} &= \Delta H_0 + \Delta\alpha\, T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 \\ &= -148{,}345 + \left[-62.54(773) + \frac{46.35 \times 10^{-3}}{2}(773)^2 \right. \\ &\quad \left. + \frac{-7.21 \times 10^{-6}}{3}(773)^3\right] \\ &= -183{,}950 \text{ J} = Q\end{aligned}$$

Hence 183,950 J/g mol CO_2 must be removed.

EXAMPLE 4.39 Calculation of Heat of Reaction at a Temperature Different from Standard Conditions

Repeat the calculation of the preceding example using enthalpy values from Table 4.4 and Appendix D. Use linear interpolation in the tables.

Solution

The heat of reaction at 25°C and 1 atm from the preceding example is

$$\Delta\hat{H}_{\text{rxn}_{298\,\text{K}}} = -164{,}987\frac{\text{J}}{\text{g mol}}$$

From Tables D.2 and 4.4b, $\Delta\hat{H}$ (J/g mol) values are [reference is 0°C (273 K)]:

Temp. (°C)	CO_2	H_2	H_2O	CH_4
25	912	718	837	879
500	22,345	14,615	17,795	24,014

From Eq. (4.41),

$$\begin{aligned}\Delta H_{\text{rxn}_{500°\text{C}}} &= \Delta H_{\text{rxn}_{25°\text{C}}} + \Delta H_{\text{products}} - \Delta H_{\text{reactants}}\\ &= -164{,}987 + [(1)(24{,}014 - 879) + (2)(17{,}795 - 837)]\\ &\quad -[(1)(22{,}345 - 912) + (4)(14{,}615) - 718)]\\ &= -184{,}957\frac{\text{kJ}}{\text{kg mol CO}_2}\end{aligned}$$

Note that the enthalpies of the products and of the reactants are both based on the reference temperature of 25°C. The answer is not quite the same as in Example 4.38 because the heat capacity data used there were not quite the same as those used in calculating the ΔH values in the tables, and because of the use of linear interpolation in the tables.

In most processes with reaction, the temperature of the entering materials and exit materials is not the same. Such cases can be represented by an information diagram such as Fig. 4.19. Equation (4.40) still applies. Phase changes must still be included, if applicable, as explained previously.

EXAMPLE 4.40 Application of the Energy Balance to a Process in which the Temperatures of the Entering and Exit Streams Differ

Carbon monoxide at 50°F is completely burned at 2 atm pressure with 50% excess air that is at 1000°F. The products of combustion leave the combustion chamber at 800°F. Calculate the heat evolved from the combustion chamber expressed as British thermal units per pound of CO entering.

Solution

Steps 1, 2, and 3 Refer to Fig. E4.40a. A material balance is needed before an energy balance can be made.

Step 4

Basis: 1 lb mol of CO (easier to use than 1 lb of CO)