

The last result expresses the energy balance over a period of time  $\delta t$ . For the calculation of the enthalpy change we adopt the following path:

1. Inlet stream is separated to its pure components and each component is brought to its standard state at  $T_0 = 25^\circ\text{C}$ .
2. Reaction progresses to extent  $\xi$  at  $T_0$  to produce all species at their standard state at the same temperature.
3. The species after the reaction are mixed and brought to the pressure and temperature of the outlet.

This procedure can be applied to any reacting system to obtain the enthalpy change. A general expression cannot be written for all cases because the details of the process (phase of streams, enthalpy of mixing) can vary between cases. A simple result will be given here under the following simplifying assumptions: (i) neglect all mixing effects on enthalpy during mixing and separation of components, and (ii) assume that no phase transitions take place during the heating/cooling steps between  $T_0$  and the temperature of the inlet and outlet streams. With these assumptions the enthalpy change is

$$\Delta(\dot{n}H) = \xi \Delta H_{\text{rxn}}^\circ(T_0) + \sum_{\text{inlet}} \int_{T_{\text{in}}}^{T_0} \dot{n}_{i0} C_{P_i} dT + \sum_{\text{outlet}} \int_{T_0}^{T_{\text{out}}} n_i C_{P_i} dT. \quad (14.13)$$

Here,  $\Delta H_{\text{rxn}}^\circ(T_0)$  is the standard heat of reaction at  $T_0$ ,  $n_i$  are the moles of species  $i$  in the outlet stream,  $n_{i0}$  are the moles of species  $i$  in the inlet, and  $C_{P_i}$  is its heat capacity. Notice that the moles in the inlet, the moles in the outlet, and the extent of reaction are interrelated by stoichiometry:

$$n_i = n_{i0} + \nu_i \xi.$$

The general procedure for the calculation is to first obtain the mole balance through stoichiometry, and then to calculate the energy balance via eqs. (14.12) and (14.13). If the simplifying assumptions are not valid, the enthalpy must be calculated by applying steps 1 to 3 of the calculation path to the inlet and outlet streams.

#### Example 14.4: Heat of Combustion

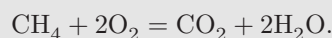
Methane is mixed with air at 20% excess over the stoichiometric requirement and undergoes combustion in a burner operating at 2 bar. The inlet gases are at  $4^\circ\text{C}$  and the effluent stream is at  $1000^\circ\text{C}$ . Determine the amount of heat assuming complete oxidation of methane to

$40^\circ\text{C}$

carbon dioxide and water. For simplicity, assume the heat capacities of the species to be constant and equal to the values given below (in J/mol):

$$C_{P,\text{CH}_4} = 55.42, \quad C_{P,\text{O}_2} = 32.53, \quad C_{P,\text{N}_2} = 30.37, \quad C_{P,\text{CO}_2} = 48.65, \quad C_{P,\text{H}_2\text{O}} = 36.94.$$

**Solution** The combustion reaction of methane is



For stoichiometric combustion we need 2 mol of oxygen. The actual amount of oxygen is 20% above the stoichiometric requirement, or,  $2 + (0.1)(2) = 2.2$  mol. Assuming air to be 21% oxygen and 79% nitrogen, the inlet stream contains nitrogen in the amount (79/21) times the amount of oxygen:

$$\frac{79}{21}(2.2) = 9.02857.$$

Even though nitrogen does not participate in the reaction, it is a component of the mixture and must be included in the mole and energy balance. We now construct the stoichiometric table:

	CH <sub>4</sub>	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	
$\nu_i$	-1	-2	0	1	2	
$n_{i0}$	1	2.4	9.02857	0	0	mol
$n_i$	$1 - \xi$	$2.4 - 2\xi$	9.02857	$\xi$	$2\xi$	mol
$H_{298}^\circ$	-75520	0	0	-393509	-241818	J/mol
$C_{Pi}$	55.42	32.53	30.37	48.65	36.94	J/mol K

For complete combustion of methane,  $\xi = 1$ .

The assumptions behind eq. (14.13) are acceptable in this problem: mixing effects can be neglected as products and reactants are close to the ideal-gas state at 2 bar and at the temperatures of this problem; in addition, no phase changes take place in bringing the inlet species from inlet conditions (40 °C, 2 bar) to standard conditions at 25 °C, 1 bar, or the outlet species from standard conditions to 1000 °C, 2 bar. Therefore, eq. (14.13) may be used. With  $T_{\text{in}} = 40^\circ\text{C} = 313.15\text{ K}$ ,  $T_{\text{out}} = 1000^\circ\text{C} = 1273.15\text{ K}$ ,  $T_0 = 25^\circ\text{C} = 298.15\text{ K}$ , we have:

$$\Delta H_{\text{rxn}}^\circ(T_0) = (-1)(-75,520) + (-2.4)(0) + (1)(-393,509) + (2)(-241,818) = -801,625\text{ J},$$

$$\sum_{\text{inlet}} \int_{T_{\text{in}}}^{T_0} n_{i0} C_{Pi} dT = \left( (1)(55.42) + (2.4)(32.53) + (9.02857)(30.37) \right) (298.15 - 313.15) = -6,115.35\text{ J},$$

$$\sum_{\text{outlet}} \int_{T_0}^{T_{\text{out}}} n_i C_{Pi} dT = \left( (0.4)(32.53) + (9.02857)(30.37) + (1)(48.65) + (2)(36.94) \right) \times (1,273.15 - 298.15) = 399,496\text{ J}.$$

$T_0$   
T superscript o

298.15

The overall balance is

$$Q = (-801,625) + (-6,115) + (399,496) = -408,244. \text{ J.}$$

**Comments** The combustion of hydrocarbons is highly exothermic and an important source of energy. In this case, the amount of heat that is released is less than that of the enthalpy of reaction. This is because a substantial amount of enthalpy is carried out by the hot effluent stream.

We have treated all species as ideal gases. Pressure does not enter the calculation because it has no effect on enthalpy in the ideal-gas state.

To simplify the calculations we used a constant  $C_P$  for all species. The calculation is only moderately more involved if temperature-dependent values are used.

#### Example 14.5: Adiabatic Flame Temperature

Adiabatic flame temperature is the temperature of the effluent gases that is obtained if no heat is exchanged between the flame and its surroundings. In this case the heat of reaction is consumed to increase the temperature of the effluent gases.

Calculate the adiabatic flame temperature of methane in 20% excess air at 2 bar.

**Solution** For adiabatic conditions the energy balance is

$$Q = 0 = \xi \Delta H_{\text{rxn}}^{\circ}(T_0) + \sum_{\text{inlet}} \int_{T_0}^{T_{\text{in}}} n_{0i} C_{Pi} dT + \sum_{\text{outlet}} \int_{T_{\text{out}}}^{T_0} n_i C_{Pi} dT.$$

reverse limits

In this equation the only unknown is the effluent temperature,  $T_{\text{out}}$ . If the heat capacities are taken to be constant, the above equation becomes,

$$\xi \Delta H_{\text{rxn}}^{\circ}(T_0) + \sum_{\text{inlet}} n_{0i} C_{Pi} (T_0 - T_{\text{in}}) + \sum_{\text{outlet}} n_{0i} C_{Pi} (T_{\text{outlet}} - T_0) = 0,$$

ni0

which is solved for  $T_{\text{out}}$  to give

$$T_{\text{out}} = T_0 + \frac{-\xi \Delta H_{\text{rxn}}^{\circ}(T_0) - \sum_{\text{inlet}} n_{0i} C_{Pi} (T_0 - T_{\text{in}})}{\sum_{\text{outlet}} n_{0i} C_{Pi}}.$$

ni (remove 0 from subscript)

Using

$$\xi = 1,$$

$$\Delta H_{\text{rxn}}^{\circ}(T_0) = -801,625 \text{ J,}$$

$$\sum_{\text{inlet}} n_{0i} C_{Pi} (T_0 - T_{\text{in}}) = -6115.35 \text{ J},$$

$$\sum_{\text{outlet}} \textcircled{n_{0i}} C_{Pi} = 409.74 \text{ J/K},$$

ni (delete 0 from subscript)

we obtain

$$T_{\text{out}} = 2269.5 \text{ K} = 1996 \text{ }^{\circ}\text{C}.$$

**Comments** The adiabatic flame temperature depends on the fuel (in this case methane) but also on the composition of the reacting mixture. The highest temperature is achieved when combustion is done in pure oxygen under stoichiometric conditions (why?). This calculation is left as an exercise.

## 14.4 Activity

Calculations of chemical equilibrium, which will be the topic of the next section, are facilitated through the introduction of the *activity*, a property closely related to fugacity and chemical potential. The activity of a component  $i$  in mixture is defined as the ratio of its fugacity over the fugacity of the same component at its *standard state*:

$$a_i = \frac{f_i}{f_i^{\circ}}. \quad (14.14)$$

Activity is dimensionless fugacity, normalized by the fugacity at the standard state. An immediate consequence of the definition of activity is its relationship to the chemical potential. First, recall that the standard state, which was introduced in Section 14.2, is at the same temperature as the state of interest. We now return to eq. (10.18), which relates fugacities and chemical potentials between two states at the same temperature:

$$\ln \frac{f_i^B}{f_i^A} = \frac{\mu_i^B - \mu_i^A}{RT}. \quad [10.18]$$

We apply this equation with  $\textcircled{A}$  referring to the state of interest and  $\textcircled{B}$  the standard state. The result is

$$\mu_i - \mu_i^{\circ} = RT \ln \frac{f_i}{f_i^{\circ}}. \quad (14.15)$$

Solving for the chemical potential we obtain the desired relationship:

$$\mu_i = \mu_i^{\circ} + RT \ln a_i. \quad (14.16)$$