

CHEMICAL ENERGY

Determining the energy released by a given fuel in a particular combustion situation is a critical aspect of combustion engineering. This section introduces the tools needed by the combustion engineer to make this determination. This includes the concepts of heat of reaction at constant pressure and constant volume, higher and lower heating value, heat of formation, and absolute enthalpy.

Heat of Reaction

Heat of reaction is the chemical energy released when a fuel reacts with air to form products. The starting point for determining the heat of reaction is to specify the chemical species and their states in the reactants and products. This is done by writing a balanced reaction with the phase of each species noted. The heat of vaporization of liquid fuels and the heat of pyrolysis of solid fuels are typically small compared to the chemical energy released by combustion. However, the effect of water condensation can be important. For example, there is a substantial increase in furnace efficiency when water is condensed in the heat exchanger of a home gas-fired furnace.

For very lean hydrocarbon-air mixtures where the temperature is low, the products may be assumed to be complete (usually CO₂, H₂O, O₂, and N₂). However, with high product temperatures and for rich mixtures, it is generally necessary to include other species and assume chemical equilibrium to determine the species mole fractions. If the products are not in equilibrium, then a chemical kinetic analysis or direct measurement is required to determine the end state. For example, the amount of solid carbon produced by very rich mixture combustion is typically not predicted correctly by equilibrium. The gaseous composition of rich mixture products is also somewhat uncertain, even if equilibrium prevails, because the identity of the unburned hydrocarbon species is not easily determined. A solution to this problem is to complete the oxidation in a separate reactor and measure the additional energy release.

To understand the heat of reaction, consider the reaction of a fuel and air mixture of mass m (the total mass of the system). For constant volume combustion with heat transfer there is no work and the first law of thermodynamics (Equation 3.4) is

$$Q_v = m \left[(u_2 - u_1)_s + (u_2 - u_1)_{chem} \right]$$

where the subscripts *s* and *chem* refer to sensible and chemical energy. Note that in Equation 3.46, the values of *u* at State 1 and State 2 are obtained by summing over all *I* species, *i* = 1, 2, . . . , *I*. Thus

$$[u_1]_s = [u_{T_1}]_s = \sum_{i=1}^I y_i [u_{i,T_1}]_s = \sum_{i=1}^I y_i \int_{T_0}^{T_1} (c_{v,i})_{\text{react}} dT = \int_{T_0}^{T_1} (c_v)_{\text{react}} dT$$

where T_0 is the reference temperature. The quantity $(c_v)_{\text{react}}$ is the specific heat of the reactant mixture. Similarly

$$[u_2]_s = \int_{T_0}^{T_2} (c_v)_{\text{prod}} dT$$

where T_0 is the reference temperature, and the quantity $(c_v)_{\text{prod}}$ is the specific heat of the product mixture.

If the heat transfer is just large enough to bring the product's temperature back to the reactant temperature, and if this temperature is taken as the reference temperature, T_0 , for the sensible energy, then $(u_2 - u_1)_s = 0$ by definition, and Q_v is the chemical energy released by the reaction. For constant volume combustion if the water in the products is not condensed, then the lower heating value can be expressed as

$$\text{LHV} = \frac{-Q_v}{m} \left(\frac{1+f}{f} \right) \quad (3.47)$$

If the water in the products is condensed, then the higher heating value,

$$\text{HHV} = \frac{-Q_v}{m} \left(\frac{1+f}{f} \right) \quad (3.48)$$

is obtained for constant volume combustion.

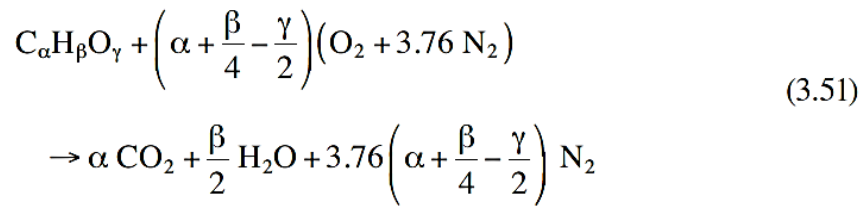
If the reaction takes place at constant pressure and the total heat transfer is Q_p , then the energy equation (Equation 3.12) becomes

$$m [(h_2 - h_1)_s + (h_2 - h_1)_c] = Q_p \quad (3.49)$$

Again, if $T_1 = T_2 = T_0$, then Q_p is the chemical energy released. For the constant pressure case if the number of moles of gaseous products, N_{prod} , is larger than the number of moles of gaseous reactants, N_{react} , then some of the chemical energy is expended as work as the expanding gases push aside the ambient pressure. Thus for reactants and products which are ideal gases,

$$Q_p - Q_v = \Delta(pV) = (N_{\text{prod}} - N_{\text{react}}) \hat{R}T_0 = \Delta N \hat{R}T \quad (3.50)$$

Consider the generalized combustion reaction



Assuming that the fuel is in the gas phase and the water remains water vapor, then

$$\Delta N = \frac{\beta}{4} + \frac{\gamma}{2} - 1$$

For methane (CH₄) $\beta = 4$ and $\gamma = 0$. Therefore, the number of moles of reactants equals the number of moles of reactants ($\Delta N = 0$) for methane. Because both Q_p and Q_v are typically negative, $\Delta N > 0$ implies $|Q_v| > |Q_p|$ as anticipated. For most cases of interest the difference, $Q_p - Q_v$, is only a few kilocalories and is thus often neglected.

The heat of reaction may be calculated for reactions taking place at temperatures other than T_0 and for cases where the initial and final temperature are not equal by use of the heat of reaction data taken at T_0 . Consider the reaction at constant pressure with reactant temperature T_1 and product temperature T_2 . Assume, for example, $T_2 > T_1 > T_0$. To use the $Q_p(T_0)$ value, first imagine the reactants are cooled from T_1 to T_0 , then the reaction takes place at T_0 , and finally the products are heated from T_0 to T_2 .

$$Q_p = m \int_{T_1}^{T_0} c_{p,\text{react}} dT + Q_{p,T_0} + m \int_{T_0}^{T_2} c_{p,\text{prod}} dT$$

or

$$Q_p - Q_{p,T_0} = m(h_{s2} - h_{s1}) \quad (3.52)$$

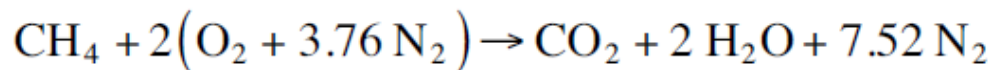
Remember that Q_{p,T_0} is negative for an exothermic reaction.

Example 1:

The higher heating value of gaseous methane and air at 25°C is 55.5 MJ/kg. Find the heat of reaction at constant pressure of a stoichiometric mixture of methane and air if the reactants and products are at 500 K.

Solution

The reaction is



Determining the molecular weight of the reactant mixture,

Reactants	N_i (moles)	x_i	M_i (kg/kgmol)	$M_i x_i$ (kg/kgmol)
CH ₄	1	0.095	16	1.5
O ₂	2	0.190	32	6.1
N ₂	7.52	0.715	28	20.0
	10.52	1.000		27.6

$$N_{\text{react}} = 1 + 2(4.76) = 10.52$$

$$M_{\text{react}} = \sum_i x_i M_i = 27.6 \text{ kg/kgmol}$$

Analysis of the reactants using sensible enthalpies from Appendix C yields

Reactants	x_i	\hat{h}_i (MJ/kgmol)	$\hat{h}_i x_i$ (kg/kgmol)
CH ₄	0.095	8.20	0.779
O ₂	0.190	6.09	1.157
N ₂	0.715	5.91	4.226
	1.000		6.162

$$\hat{h}_{s,\text{react}} = \sum_i x_i h_{si} = 6.16 \text{ MJ/kgmol}$$

$$h_{s,\text{react}} = \frac{6.16 \text{ MJ}}{\text{kgmol}} \cdot \frac{\text{kgmol}}{27.6 \text{ kg}} = \frac{223 \text{ kJ}}{\text{kg}}$$

The fuel-air mass ratio is

Reactants	x_i	M_i	M_i/M	y_i
CH ₄	0.095	16	0.580	0.055
O ₂	0.190	32	1.159	0.220
N ₂	0.715	28	1.014	0.725
	1.000			1.000

$$f = \frac{y_f}{y_{\text{air}}} = \frac{0.055}{0.220 + 0.725} = 0.0582$$

In the same way analysis of the products yields

Products	x_j	$\hat{h}_{s,j}$ (MJ/kgmol)	M_j
CO ₂	0.095	8.31	44
H ₂ O	0.190	6.92	18
N ₂	0.715	5.91	28

$$N_{\text{prod}} = 10.52$$

$$\hat{h}_{s,\text{prod}} = 6.33 \text{ MJ/kgmol}$$

$$M_{\text{prod}} = 2.76 \text{ kg/kgmol}$$

$$h_{s,\text{prod}} = 229 \text{ kJ/kg}$$

Because the water vapor does not condense at 500 K, the lower heating value is used;

Because the water vapor does not condense at 500 K, the lower heating value is used;

$$\begin{aligned} \text{LHV} &= \frac{55,000 \text{ kJ}}{\text{kg}_{\text{H}_2\text{O}}} - \frac{2394 \text{ kJ}}{\text{kg}_{\text{H}_2\text{O}}} \cdot \frac{2 \text{ kmol}_{\text{H}_2\text{O}}}{\text{kmol}_{\text{CH}_4}} \cdot \frac{18 \text{ kg}_{\text{H}_2\text{O}}}{\text{kgmol}_{\text{H}_2\text{O}}} \cdot \frac{\text{kgmol}_{\text{CH}_4}}{16 \text{ kg}_{\text{CH}_4}} \\ &= \frac{50,113 \text{ KJ}}{\text{kg}_{\text{CH}_4}} \end{aligned}$$

Remembering that

$$\frac{m_f}{m_{\text{react}}} = \frac{m_f}{m_{\text{air}} + m_f} = \frac{f}{1 + f}$$

we can write

$$\begin{aligned}\frac{Q_{p,T_0}}{m} &= \frac{f}{1+f}(\text{LHV}) = \frac{0.0582}{1+0.0582}(50,113)\text{kJ/kg}_{\text{react}} \\ &= -2747 \text{kJ/kg}_{\text{react}}\end{aligned}$$

From Equation 3.52 the heat of reaction per unit mass of reactants at 500 K is

$$Q_p = -2747 + (229 - 223) = -2741 \text{kJ/kg}_{\text{react}}$$

The negative sign indicates that the heat flows out of the system.

The heat of reaction of fuels combusting in air (or oxygen) with the starting and ending points at 25°C and 1 atm gives the fuel heating value. These heating values are then tabulated for common fuels. Following this same practice for all possible reactions would, however, lead to an enormous amount of tabulated data. The

solution to this problem comes by noting that we may simply add selected reactions and their heats of reaction to obtain any given reaction and its heat of reaction. The most basic set of reactions are thus for the formation of compounds from their elements. Once the data for this basic set is tabulated, any reaction can be constructed from it.

Example 2:

The higher heating value of gaseous methane and air at 25 C IS 55.5MJ/kg .find the heat of reaction at

constant pressure of a stoichiometric mixture of methane and air if the reactant and products are at 500k.

since the water vapour dose not Np=10.52 ,hsp=6.33 MJ/kgmole , Mp=27.6 kg/kgmole ,hsp=229 KJ/kg condense ,the lower heating value is used

=-2747 KJ/kg fuel reactants

The reaction is :- $CH_4 + 2(O_2 + 3.76 N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2$

Analysis of reactants and products using sensible enthalpies from appendix yield

Reactants	X_i	$h_{i,s}(MJ/kgmole)$	Mj	$Y_i(kg)$
CH ₄	0.095	8.2	16	0.055
O ₂	0.19	6.09	32	0.22
N ₂	0.715	5.91	28	0.725

$$N_r = 1 + 2(4.76) = 10.52$$

$$M_r = \sum X_i M_i = 27.6 \text{ kg/kgmole}$$

$$h_{s,r} = \sum X_i h_{i,s} = 6.16 \text{ MJ/kgmole}$$

$$h_{s,r} = 6.16 / 27.8 \text{ KJ/kg}$$

the fuel to air mass ratio is $f = 0.055 / (0.22 + 0.725) = 0.0582$

Products	X_i	$H_{i,s}$	Mj
CO ₂	0.095	8.31	44
H ₂ O	0.19	6.92	18
N ₂	0.715	5.91	28

$$Q_p = -2747 + (229 - 223) = -2741 \text{ KJ/kg reactants}$$

The negative sign indicates that the heat flow out of the system.