# 3.9.2: Environment- Heating Values of Various Fuels

We noted previously that chemist's *"standard enthalpy (heat) of combustion"* may be a misleading measure of a fuel's heating value in real conditions. Standard enthalpies are precisely defined as the heat energy absorbed or released when a process occurs at 25 °C to give substances in their most stable state at that temperature. For example, for propane, water is produced as a liquid:

$C_3H_8(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O (l)$ $\Delta H_m = -2219.2$ kJ[1] (1)
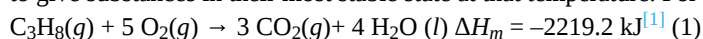
Most of the plume above smokestacks is condensed water droplets, which release heat of condensation to the atmosphere

But boilers are almost always operated with flue temperatures near the combustion temperature, and maintained at over 100 °C to prevent water from condensing to liquid. Since water is produced as a gas, the standard thermodynamic equation (1), does not apply. If it were formed, liquid water would dissolve acidic flue gases like HCl and SO_2 to make acidic solutions which corrode the system. These gases are normally removed by limestone "scrubbers",[2] leaving just the water vapor. The white plumes over smokestacks are water droplets forming by condensation of water vapor. They often disappear as the droplets evaporate.

The precision of our definition of *standard enthalpy* guarantees that our calculations of heat energy will be sound, but it requires that we *pay attention to* each energy cost and source. We'll see that inattention to such details has led to misinformation and confusion. Since Higher Heating Value (HHV) may be used by some air quality management authorities,[3] while Lower Heating Values are used by many engineers and European power facilities, it is important to know precisely what the terms mean and which is being used. The USDA[4] reports the following heating costs apparently, but not explicitly, stated to be LHVs:

USDA[4] reports the following heating costs

| Fuel	Gross heating value	Efficiency (%)	Net heating value[b]	Fuel required for 1 million Btu of usable heat	Average cost/unit	Total annual fuel cost[a]
Natural gas	1.03 million Btu/1000 ft^3	80	0.82 million Btu/1000 ft3	1,220 ft^3	$7/1000 ft3	$854
Propane	91,200 Btu/gal	79	72,000 Btu/gal	13.86 gal	$1.25/gal	$1,730
Fuel oil #2	138,800 Btu/gal	83	115,000 Btu/gal	8.68 gal	$1.40/gal	$1,220
Seasoned firewood	20 million Btu/cord	77	15.4 million Btu/cord	0.065 cord	$115/cord	$747
Electricity	3,413 Btu/kWh	98	3,340 Btu/kWh	299 kWh	$0.08/kWh	$2,390
Premium wood pellets	16.4 million Btu/ton	83	13.6 million Btu/ton	0.073 ton	$120/ton	$882

[a] Based on 100 million Btu of energy for the heating season, a typical value for an average sized house.

There are many variables that affect total heating costs (furnace efficiencies, local energy costs, etc.), but one variable that can potentially be understood is the heat available from fuel combustion. Without precise definitions, even this may be obscured. To

illustrate this point, let's examine what are known as the Higher Heating Value (HHV)[5] and Lower Heating Value (LHV)[6] are calculated for propane.

The HHV

The standard heat of combustion of propane is

$C_3H_8(g)$ + 5 $O_2(g)$ → 3 $CO_2(g)$+ 4 H_2O (l) ΔH_m = -2219.2 kJ[7] = **HHV** = ΔH_1 (1)
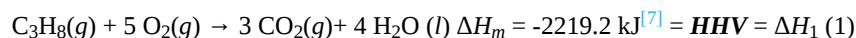
This is the process which yields the HHV, because the fuel is burned and the combustion products are cooled to 25 °C, removing all heat resulting from the condensation of water in the process.

The LHV

But we want the enthalpy for the reaction:

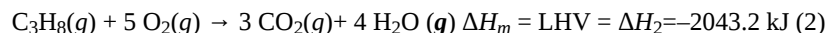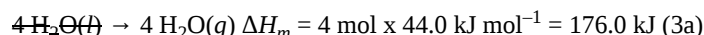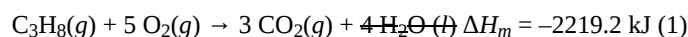$C_3H_8(g)$ + 5 $O_2(g)$ → 3 $CO_2(g)$+ 4 H_2O (**g**) ΔH_m = **LHV** = ΔH_2 (2)
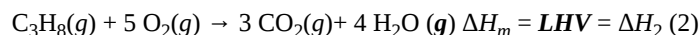
In this case, the water is not condensed, so some of the energy is not recovered, so the ΔH_m is the Lower Heating Value. We can imagine reaction (2) occurring in two steps. First, reaction (1), then

$H_2O(l)$ → $H_2O(g)$ ΔH_m = 44.0 kJ (3)
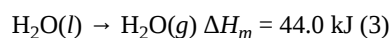
We notice that equation (1) produces 4 mol of H_2O (l), so we multiply equation (3) by 4, so that 4 moles of H_2O (l) are consumed in equation (3a):

4 $H_2O(l)$ → 4 $H_2O(g)$ ΔH_m = 4 x 44.0 kJ = 176.0 kJ (3a)
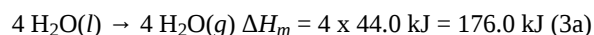
If we add equations (1) and (3a) as below, canceling the 4 mol H_2O (l) that are produced (appear on the right) with the 4 mol H_2O (l) which are consumed (appear on the left), we get equation (2).

$C_3H_8(g)$ + 5 $O_2(g)$ → 3 $CO_2(g)$ + 4 H₂O (l) ΔH_m = –2219.2 kJ (1)

4 H₂O(l) → 4 $H_2O(g)$ ΔH_m = 4 mol x 44.0 kJ mol^{-1} = 176.0 kJ (3a)

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$C_3H_8(g)$ + 5 $O_2(g)$ → 3 $CO_2(g)$+ 4 H_2O (**g**) ΔH_m = LHV = ΔH_2=–2043.2 kJ (2)

Experimentally it is found that the enthalpy change for reaction (2) is the *sum* of the enthalpy changes for reactions (1) and (3a):

ΔH_2 = –2219.2 kJ + (4 x 44.0 kJ) = –2043.2 kJ = ΔH_1 + 4 x ΔH_3

This value of ΔH_m should be the Lower Heating Value. Let's see if it matches the USDA value of 91,200 BTU/gal in the table above, given that a gallon of propane is about 4.23 lb[8]

$$\frac{2043.2.2 \text{ kJ}}{mol} \times \frac{1 \text{ mol}}{44.1 \text{ g}} \times \frac{1 \text{ BTU}}{1.055 \text{ kJ}} \times \frac{453.6 \text{ g}}{\text{lb}} \times \frac{4.23 \text{ lb}}{\text{gal}} = 84\,300 \text{ BTU/gal}$$

Our value is not close to the USDA LHV, but it matches the Oak Ridge National Laboratory (ORNL) value for the HHV of 84 250 BTU/gal[9].

The Higher Heating Value is the enthalpy change for reaction (1), which includes the heat released when 4 mol of gaseous water from the combustion cool to 25 °C, so its value is more negative than the LHV by four times the heat of condensation of water (–2043.2 + 4 x (–-44) = –2219.2 kJ):
$H_2O(g)$ → $H_2O(l)$ ΔH_m = –44 kJ (4)
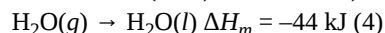
Repeating the calculation for the heat liberated in equation (1) in BTU/gal, we get 91 500 BTU/gal, which is the HHV reported by ORNL. The USDA table above apparently reports the HHV, perhaps unknowingly. The variety of values found on the web for both HHV and LHV attests to the fact that much confusion can result from not being careful with the meaning and application of a *standard enthalpy*.[10] Technically, the lower heating value of a fuel is defined as the amount of heat released in the combustion of the fuel to give products at 150°C.[11]

Hess' Law

In the general case it is always true that *whenever two or more chemical equations can be added algebraically to give a net reaction, their enthalpy changes may also be added to give the enthalpy change of the net reaction.*

This principle is known as **Hess' law**. If it were not true, it would be possible to think up a series of reactions in which energy would be created but which would end up with exactly the same substances we started with. This would contradict the law of conservation of energy. Hess' law enables us to obtain ΔH_m values for reactions which cannot be carried out experimentally, as the next example shows.

Example 1

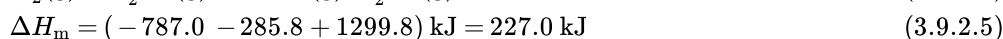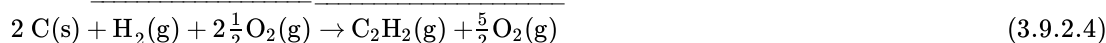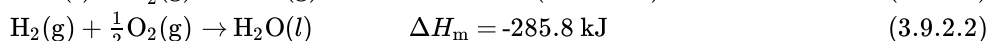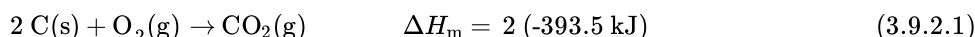Acetylene (C_2H_2) cannot be prepared directly from its elements according to the equation

$2C(s) + H_2(g) \rightarrow C_2H_2(g)$ (1) Calculate ΔH_m for this reaction from the following thermochemical equations, all of which can be determined experimentally: $C(s) + O_2(g) \rightarrow CO_2(g)$ ΔH_m = –393.5 kJ (2a) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ ΔH_m = –285.8 kJ (2b) $C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$ ΔH_m = –1299.8 kJ (2c)

Solution

We use the following strategy to manipulate the three experimental equations so that when added they yield Eq. (1):

a) Since Eq. (1) has 2 mol C on the left, we multiply Eq. (2a) by 2.

b) Since Eq. (1) has *1* mol H_2 on the left, we leave Eq. (2b) unchanged.

c) Since Eq. (1) has *1* mol C_2H_2 on the *right*, whereas there is *1* mol C_2H_2 on the *left* of Eq. (2c) we write Eq. (2c) in reverse.

We then have

$$2\,C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_m = \ 2\,(\text{-393.5 kJ}) \qquad\qquad (3.9.2.1)$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H_m = \text{-285.8 kJ} \qquad\qquad (3.9.2.2)$$

$$\underline{2\,CO_2(g) + H_2O(l) \rightarrow \ C_2H_2(g) + \tfrac{5}{2}O_2(g)} \ \ \underline{\Delta H_m = -(-1299.8\ \text{kJ})} \qquad (3.9.2.3)$$

$$2\,C(s) + H_2(g) + 2\tfrac{1}{2}O_2(g) \rightarrow C_2H_2(g) + \tfrac{5}{2}O_2(g) \qquad\qquad\qquad (3.9.2.4)$$

$$\Delta H_m = (-787.0 \ -285.8 + 1299.8)\ \text{kJ} = 227.0\ \text{kJ} \qquad\qquad (3.9.2.5)$$

Thus the desired result is $2C(s) + H_2(g) \rightarrow C_2H_2(g)$ ΔH_m = 227.0 kJ

References

1. ↑ Gas phase thermochemistry data [webbook.nist.gov]
2. ↑ en.Wikipedia.org/wiki/Flue-gas_desulfurization
3. ↑ en.Wikipedia.org/wiki/Talk:Heat_of_combustion
4. ↑ Gas phase thermochemistry data [www.fpl.fs.fed.us]
5. ↑ en.Wikipedia.org/wiki/Lower_heating_value
6. ↑ en.Wikipedia.org/wiki/Lower_heating_value
7. ↑ Gas phase thermochemistry data [webbook.nist.gov]
8. ↑ The density of liquid propane at room temperature is variously reported as 0.498 g/mL (4.1 lb/gal) at 25 $^{\circ}$C also here or 4.23 lb/gal to 5.1 lb/gal at 60 $^{\circ}$F. Part of the problem is that the density is pressure dependent, and the tank (vapor) pressure of propane changes significantly with temperature. It is about 883 kPa (~8 Atm) at 27 $^{\circ}$C
9. ↑ Transportation Energy Data Book [cta.ornl.gov]
10. Neither the LHV or HHV correct for the difference between the enthalpy of the reaction at 25 $^{\circ}$C and the enthalpy change at the actual compustion temperature, which depends on the heat capacities of the reactants and products
11. Transportation Energy Data Book [cta.ornl.gov]