Heating value – definition

- Consider the complete combustion of a fuel in air
  (or in oxygen or in a mixture of oxygen and other gases).

- The initial temperatures of the fuel and the surrounding gas
  are assumed to be equal (normally 298 K is assumed).

- The *heating value* of the fuel is

  the amount of energy recovered per unit quantity of fuel

  when the combustion products are cooled
 to the initial temperature.

  (cf. Borman & Ragland pp. 28–30)

Heating value / heat of reaction

- Heat of reaction: viewpoint in the system

  => energy release in a reaction is associated with a − sign

  Heating value: viewpoint in the surroundings

  => energy release in a reaction is associated with a + sign

- Chemical formulas for combustion reactions are of the type

$$\text{Fuel} + \text{Oxygen} \rightarrow \text{Combustion products}$$
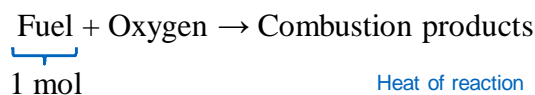
  1 mol   Heat of reaction

=> Molar heating value $Q_m = -\Delta H_{m,R}$

A! ”Unit quantity of fuel”

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- Possible choices for ”Unit quantity of fuel”:

  1 mol   => Q_m [kJ/mol]   Molar heating value

  1 kg   => q = Q_m/M_{Fuel} [kJ/kg]   Heating value

  1 m³   => Q = Q_m/V_M [kJ/m³]   Heating value

  For this last one, there seems to be no specific name and
  symbol which is a potential source of confusion.
  For calculation of V_m, the NTP conditions must be specified.

A! Condensation of water vapor

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- ”Cooled down to initial temperature”:

  Normally, the mole fraction of H_2O in flue gas is around 10 %
  (depending on fuel composition, quantity of combustion air
  and relative humidity of combustion air).

  => The partial pressure of H_2O is around 10 kPa
  (assuming that the system operates at atmospheric pressure).

  The saturation pressure of H_2O at 298 K is 3.2 kPa

  => A significant fraction of the H_2O in combustion products
  is expected to condense into liquid water, but not all of it.

LHV and HHV

- Lower heating value (LHV, net calorific value, q_L):

    All H_2O in flue gas is expected to remain in gas phase when the flue gas is cooled down to 298 K.

- Higher heating value (HHV, gross calorific value, q_H):

    All H_2O in flue gas is expected to condense into liquid when the flue gas is cooled down to 298 K.

- Both concepts are *theoretical*.

- See Borman & Ragland Ex. 2.1 on p. 30.

Real life applications – 1

- In practical combustion applications, the most common policy is to discharge the flue gas at such a high temperature that no condensation occurs.
- This is because of a number of reasons:
    - We might have no use for heat recovered at a very low temperature.
    - Sometimes we must avoid the condensation water vapor because the simultaneous presence of corrosive compounds and liquid water in the flue gas might lead to very severe corrosion.
- When no condensation occurs, the energy balance calculations can be carried out equally well using the lower heating value or the higher heating value.
- It has become a tradition to use LHV in Europe and HHV in the United States.

A! Real life applications – 2

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- In some applications, the flue gases are deliberately cooled down to such a low temperature that some H_2O is condensed into liquid => more energy can be recovered.
- There are several reasons for that:
  - Heating systems are getting better at utilizing low temperature heat, thanks to the development of solar energy systems and heat pumps.
  - Condensation may also be advantageous from the point of view of removing harmful compounds from the flue gas.
- To analyze such systems, it is much better to use HHV in calculations than to use LHV.

A! Measurement of heating values

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- Heating values are measured experimentally with a bomb calorimeter.
- In this device, the fuels are burned in pure oxygen at high pressure => high H_2O partial pressure => all H_2O will be condensed into liquid => the value of HHV is obtained.
- The value of LHV can then be calculated if the fuel composition is known.
- Normally, the heating values presented in literature are heating values at constant pressure. However, the bomb calorimeter measures the heating values at constant volume. The difference between these two is normally insignificant, but can be calculated if necessary.