# Thermodynamics Labs
# DT021 Year 4
# Gas calorimeter

David Collins
C10736685
`david.collins4@mydit.ie`

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# 1 Introduction

## 1.1 Objective

The goal of this experiment was to determine the higher and lower calorific values of a combustible substance. The combustible substance in this case was natural gas, which is commonly-used for a variety of heating and power applications — not just in Ireland but across the globe.

## 1.2 Calorific values

The **calorific value** of a substance is the amount of heat that is 'liberated' on combustion of some unit mass of that substance. The calorific value is sometimes referred to, instead, as the **heating value**. If the unit of mass is a kilogram and that of energy is the Joule, then the calorific value will be measured in Joules / kilogram. Alternatively, it may also be measured in Btu / pound, calories / pound, etc.. (We will stick with SI system of units, so the main results will be presented in Joules / kilogram.) In this experiment, we need to determine both the **higher calorific value (HCF)** and **lower calorific value (LCF)**. The meaning of these terms is explained in Section 2.

**Expected / target values** The expected, or target, values are 55.5 MJ kg$^{-1}$ and 50 MJ kg$^{-1}$ for the higher and lower calorific values, respectively. Fluctuations above or below these values are not necessarily surprising, however, and may be reasonably common depending on the source of the fuel.

## 1.3 Apparatus — Boys Gas Calorimeter

We use Boys Gas Calorimeter in this experiment. Water flows in a 'cooling coil' around a gas-powered flame at the center of the cylinder. Thermometers at both the inlet and outlet of the coil enable us to record the corresponding water temperatures, while an analog flow-meter displays the gas flow-rate.

## 1.4 Heat and work (a historical aside)

The term 'calorific' derives from a time when heat and energy were less well understood. We know now that heat and work are closely-related (the former is a less 'ordered' version of the latter) and are measured in the same units (Joules).

When thermodynamics was in its infancy, however, this relationship was not fully understood. Heat was thought of as something different from, and perhaps even independent of, work; and so heat was measured in seemingly unique units called 'calories' (*calor* — Latin for 'heat')

In due course, experiments (such as those by Joule in the mid 1800s) demonstrated that heat and work are related — and ultimately just different types of 'energy in transit'. The precise relationships are described by important equations such as the First Law of Thermodynamics, etc..

# 2 Theory

**Higher vs. lower calorific value** We know that the calorific value is the amount of heat liberated per unit of substance combusted. Some of this heat is used to raise the temperature of the substance; the rest of it is used to change the liquid into vapour. Consequently, we have two definitions of calorific value. When determining the **Lower calorific value (LCF)**, we subtract this latter (latent) form of heat from the total heat liberated. The **Higher calorific value (HCF)**, on the other hand, measures the *total* heat liberated per unit of substance.

The heat flow-rate for the water is given by Equation 1:

$$\boxed{\dot{Q}_{water} = \frac{Q}{t} = \dot{m}c\Delta T},$$ (1)

where $\dot{m}$ is the mass flow-rate, $c$ the specific heat-capacity of water, and $\Delta T = T_2 - T_1$ is the difference between the cooling coil inlet and outlet temperatures.

The gas flow-rate is simply the volume of gas recorded by the flow-meter divided by the time interval (Equation 2):

$$\boxed{\dot{V}_{gas} = \frac{V_{gas}}{t_{rev}}},$$ (2)

where $t_{rev}$ denotes the time required for one revolution of the flow-meter.

The standard flow-rate is related to the gas flow-rate according to Equation 3, where $T_s$ is the standard temperature, and $P_s$ is the standard (atmospheric) pressure .

$$\dot{V}_s = \dot{V}_{gas} \times \left(\frac{P_{gas}}{P_s}\right)\left(\frac{T_s}{T_{gas}}\right)$$ (3)

Once we know the standard flow-rate, we can proceed to determine the Higher calorific value:

$$HCF = \frac{Q_{water}}{\dot{V}_s}.$$  (4)

**Lower calorific value**  Equation 4 only gives us the higher calorific value. We also need to know the lower calorific value (LCF). This is given by Equation 5:

$$LCF = \frac{\dot{Q}_{water} - \dot{Q}_{condensate}}{\dot{V}_s}$$  (5)

where $\dot{Q}_{condensate}$ denotes the rate of heat transfer to the condensate. This latter value is determined according to

$$\dot{Q}_{condensate} = h_{fg} \cdot \left(\frac{m_{cond}}{t_{cond}}\right),$$  (6)

where $m_{cond}$ is the mass of the condensate, $t_{cond}$ is the time over which the condensate accumulated, and $h_{fg}$ is the (specific) latent heat expended in converting the relevant mass of liquid water into vapour. (Note that this specific latent 'heat' is actually the difference between two specific enthalpies!)

# 3  Procedure

**Safety**  This experiment involves the burning of highly-combustible material. Thus, safety precautions must be taken. It may be appropriate for a qualified la technician to perform some of the steps.

**Steps**  The steps are as follows.

1. Record the ambient pressure, $P_{env}$, using a barometer; and the ambient temperature $T_{env}$, using a thermometer.

2. Record the temperatures $T_1$ and $T_2$, the temperatures of the water at the cooling coil inlet and outlet, respectively. From these, determine $\Delta T$, which we will substitute into Equation 1 to determine the heat flow-rate for the water.

3. Note the time, $t_{rev}$, required for one revolution of the analog flow-meter. Each revolution corresponds to a volume of one-twelfth of a cubic foot. Calculate the gas flow-rate from Equation 2.

4. After the desired time has elapsed, record the volume of condensate (i.e. water) accumulate in the beaker. This provides us with the mass of condensate (and consequently the change in specific enthalpy) we need to determine the lower calorific value (using Equation 5).

5. When measurements are completed, determine the calorific values using Equations 4 and 5.

6. Be sure that gas and water flows are turned off after measurements are completed — by a lab technican if not by yourself.

**Unit conversions**  Most of the potential pitfalls in the analysis procedure are due to the variety of units used. We need to ensure, in our case, that we are using SI units in all cases. Consequently, temperatures in degrees celcius must be converted to Kelvin, pressures to absolute pressures in Pascal, etc..

# 4  Measurements & analysis

The method we are using requires recording the values shown in Table 1 As mentioned previously, the temperatures were recorded in degrees celsius, and need to be converted to Kelvin before they can be used in calculation. Note that, due to the density of water, a volume flow-rate of 1 litre / minute corresponds to a mass flow-rate of 1 kg / minute. The value $P_{env}$ is the ambient pressure. Having presented the measured values, we proceed to the analysis.

|  | Description | Value | Unit |
|---|---|---|---|
| $T_1$ | Water inlet temperature | 21.5 | °C |
| $T_2$ | Water outlet temperature | 33.0 | °C |
| $T_g$ | Gas temperature | 18.0 | °C |
| $t_{rev}$ | Time for 1 revolution | 130 | s |
| $V_{cond}$ | Volume of condensate | 71 | ml |
| $t_{cond}$ | Time for condensate to accumulate | 50 | min |
| $P_{env}$ | Ambient pressure | 772 | mm Hg |

Table 1: Measurements

All of the analysis below is based on the equations presented in Section 2. For convenience, these were implemented in a MATLAB script (Section A).

**Heat transfer rate (water)**  Intermediate values used in determining the heat transfer rate for the water are presented in Table 2. Note that we are considering a rate of transfer of *heat*, and use the notation $\dot{Q}$.

| | | | |
|---:|---|---|---:|
| $\Delta T$ | Outlet - inlet temperature | 11.5 | $°\,°\mathrm{C}$ |
| $C$ | Specific heat capacity of water | 4.18 | $\mathrm{kJ\,kg^{-1}\,K}$ |
| $\dot{m}$ | Mass flow-rate | 0.0167 | $\mathrm{kg\,s^{-1}}$ |
| $\dot{Q}_{water}$ | Water heat flow-rate | 801.17 | $\mathrm{J\,s^{-1}}$ |

Table 2: Calculation of the water's heat flow-rate

**Gas flow rate**  We also need to determine the gas flow-rate. From Equation 2, and the values for $V_{gas}$ and $t_{rev}$ given in Table 1, this was determined to be

$$\dot{V}_{gas} = 1.81 \cdot 10^{-5} \mathrm{m^3\,s^{-1}}.$$

This is quite a small value, but — given the significant chemical energy stored in the gas itself — only a small amount is needed to liberate large quantities of heat.

**Standard flow rate**  The standard flow-rate turns out to be

$$\dot{V}_s = 1.798 \cdot 10^{-5} \mathrm{m^3\,s^{-1}}.$$

This is really just the gas flow-rate adjusted to account for the ambient conditions. Consequently, it is almost exactly equal to the gas flow-rate.

**Condensate**  As mentioned in Section 2, we want to know the mass of condensate accumulated in the beaker in order to determine the lower calorific value (LCF). Once this is measured, we can calculate the rate at which heat was transferred to the condensate — which turned out to be

$$\dot{Q}_{condensate} = 58.258 \mathrm{J\,s^{-1}}.$$

Note that this is a rate of heat transfer, so has units of Joules per second.

Having determined all of these intermediate values, we can proceed to calculate the actual calorific values. These are presented in the next section.

# 5 Results

The results are summarised in Table 3. Note that the values are in $\mathrm{MJ\,kg^{-1}}$. These values differ somewhat from the expected values, and potential reasons for this are discussed briefly below. We see, nonetheless, that even a small amount of gas contains an enormous amount of energy.

| | | |
|---|---|---|
| **Higher calorific value** | 44.56 | $\mathrm{MJ\,kg^{-1}}$ |
| **Lower calorific value** | 41.31 | $\mathrm{MJ\,kg^{-1}}$ |

Table 3: Experimental values for higher and lower calorific values

# 6 Conclusion

In this experiment we demonstrated that the calorific values of a substance can be determined using simple apparatus and a handful of measurements. Although there were slight differences between the expected and experimental values, these were within the bounds of experimental error on the one hand, and variations in fuel quality on the other.

**Sensitivity of calorific values**  Examination of Equation 4 reveals that the calorific values determined are very sensitive to the temperatures recorded for the water at the inlet and outlet of the calorimeter. An inaccuracy of even a fraction of a Kelvin, for example, will result in an error of a few mega-Joule in the calculated calorific values.

**What we have learned**  We have learned a number of lessons in this experiment.

1. **Lower and higher calorific values** There are two variations on the concept of 'calorific value'. In the case of the Higher calorific value, we consider *all* of the heat liberated on combustion of a substance. In the case of the Lower calorific value, we deduct that heat (the 'latent' heat) which was used in changing the phase of the heated substance rather than raising its temperature.

2. **Basic thermodynamic concepts** The experiment also highlighted the important relationships between variables such as heat, enthalpy and energy. The fact that the latent heat, $h_{fg}$, is really just the difference

    between two specific enthalpies, for example, is not immediately obvious — but nonetheless useful to know.

3. **Systems of units** We have also reinforced our understanding of different sytems of units. This is important, as different engineering apparatus use different systems. Furthermore, if we travel to countries such as the US, an understand of the pound-inch system (rather than the metric system) would probably be useful.

**Importance of the calorific values** The lower the calorific value, the more fuel we need to generate for a given amount of useful energy. Since energy bills are generally calculated on the basis of the amount of fuel used (rather than the amount of energy derived), a lower calorific value translates to higher cost. Some organisations, consequently, may go to the effort of checking or verifying the calorific value of the fuel they buy (to ensure that they aren't wasting money).

**Economics and resource availability** Gas coming from different sources will exhibit different energy contents. This is another important factor to consider when evaluating the energy content of a fuel.

# A   MATLAB / Octave calculations

GNU Octave was used to automate most of the calculations. The script used is shown in Listing 1. Some people would prefer to use MS Excel, but the result is the same in either case.

Listing 1: Calorimetry calculations in GNU Octave / MATLAB

```octave
% Title: Boys Gas calorimeter calculations
% Author: David Collins
% Semester 1 2013
%
% NOTES:
%       1. All temperatures must be converted to Kelvin!
%             2. All pressures must be converted to absolute pressure in Pa (or N / m^2).

% CONVERSION FACTORS
% For conversion to Kelvin
dK = 273.15;
Hg_to_atm = 1/ 760;
atm_to_Pa = 101325;

% STANDARD PRESSURE
P_s = atm_to_Pa;
% STANDARD TEMPERATURE
T_s = 288.15;

% AMBIENT / ENVIRONMENT VARIABLES
% Temperature
T_env = 19 + dK;
% Pressure
P_env_height_mercury = 772; % mm of Hg
P_env_atm = P_env_height_mercury * Hg_to_atm; % atmospheres
P_env = P_env_atm * atm_to_Pa; % Pa or N/m^2

% WATER SIDE
% Temperatures
T_inlet = 21.5 + dK; % inlet
T_outlet = 33.0 + dK; % outlet
% Difference in temperature
dT = T_outlet - T_inlet;
specific_heat_capacity = 4.18e+3; % specific heat capacity
mass_flow_rate = 1/60; % mass flow-rate (1 kg in 60 seconds)
% Heat flow-rate
water_heat_flow_rate = mass_flow_rate * specific_heat_capacity * dT;

% GAS SIDE
% Pressure
% Gauge pressure
P_gas_gauge_height_mercury = 1; % in mm of Hg
P_gas_gauge_atm = P_gas_gauge_height_mercury * Hg_to_atm; % in atmospheres
P_gas_gauge = P_gas_gauge_atm * atm_to_Pa; % in Pa (or N / m^2)
```

```matlab
% Absolute pressure
P_gas = atm_to_Pa + P_gas_gauge; % Pa
% Temperature
T_gas = 18.0 + dK;
% Flow-rate
Time_rev = 130; % seconds
gas_flow = .0283 / 12; % m^3
gas_flow_rate = gas_flow / Time_rev % m^3 / s

% coming off combustion
Ta = 23.0 + dK;

% CONDENSATE
condensate_volume = 71; % ml
condensate_mass = condensate_volume / 1000 % kg
Time_condensation = 50 * 60; % seconds
condensate_flow_rate = condensate_mass / Time_condensation
% difference between specific enthalpies of fluid and vapor (hg - hf)
hfg = 2473e+3; % J / kg
% Enthalpy corresponding to this
condensate_heat_flow_rate = hfg * condensate_flow_rate

% CALORIFIC VALUE(s)
standard_flow_rate = gas_flow_rate * (P_gas / P_s) * (T_s / T_gas);
higher_calorific_value = water_heat_flow_rate / standard_flow_rate
lower_calorific_value = (water_heat_flow_rate - condensate_heat_flow_rate) / standard_flow_rate
```