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High precision calorimetry to determine the enthalpy of combustion of methane

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Abstract

The enthalpy of combustion of methane is the most important property used in the determination of the calorific value of natural gas. Only two sets of values with high accuracy and precision and measured under appropriate conditions have been published since it was first determined in 1848. These studies were done by Rossini, at the National Bureau of Standards in the USA in 1931, and Pittam and Pilcher, at the University of Manchester in 1972.

This report details the design and operation of a high precision constant-pressure gas burning calorimeter, based on the design of those used in the previous studies, to measure the superior enthalpy of combustion of ultra-high purity methane at 25 °C.

The use of modern equipment and automatic data collection leads to a value, traceable to national standards, of 890.61 kJ mol^{-1} with a combined standard uncertainty of 0.21 kJ mol^{-1}. This is in full accord with the value of 890.63 kJ mol^{-1} calculated from the average of Rossini's and Pittam and Pilcher's work (with a random uncertainty based on 1 S.D. of 0.53 kJ mol^{-1}). Crown Copyright © 2002 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

The "reference calorimeter" at the Technical Directorate of the Office of Gas and Electricity Markets (OFGEM) was designed to be the primary standard for determining the heat of combustion of natural gas samples. The instrument is based on the one used by Pittam and Pilcher, at the University of Manchester in the late 1960s, to study the heat of combustion of methane and other hydrocarbons [1,2]. This instrument was, in turn, based on the one built by Rossini, at the National Bureau of Standards in the USA in the early 1930s, to study the heat of formation of water [3] and the heats of combustion of methane and carbon monoxide [4].

There have been three major changes from the designs of the previous workers: (1) we directly weigh the sample of gas burnt; (2) we control the experiment and collect data automatically by computer and (3) we take measurements at a faster rate.

The experiment produces a superior heat of combustion in kJ g^{-1}, at a constant pressure, for combustion at 25 °C. For a single component gas, such as methane, the result can be given in kJ mol^{-1}.

The experimental procedure has been analysed to calculate systematic and random uncertainties according to the method described in the latest ISO guide on uncertainty determinations [5]. The method is based

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on weighing the uncertainties of each individual term in the calculation. The weights are derived from the partial derivative of the equations used in the calculations with respect to each term. The heat of combustion for several sets of determinations have been compared with the uncertainty analysis and the values agree.

The reference calorimeter was constructed by Lythall. The author, working under the direction of Aucott and Sayer, took over the operation of the instrument in February 1993, making minor improvements and calculating the uncertainties. This paper describes the reference calorimeter; shows how it is different to previous calorimeters; gives the uncertainty on results; and gives the heat of combustion of methane.

2. Calorimeter theory

The objective of calorimetry is to measure the quantity of energy involved in a particular reaction. In the case of the reference calorimeter, the reaction is the complete combustion of a hydrocarbon fuel gas. This is achieved by allowing the energy liberated in the reaction to be given to a well-stirred liquid, in a calorimeter, and measuring its temperature rise. Multiplying this temperature rise by the energy equivalent of the calorimeter gives the amount of energy liberated in the reaction. The energy equivalent is the energy required to raise the temperature of the calorimeter by 1 °C at the same mean temperature as the combustion experiment. It is determined by electrical calibration experiments.

An ideal calorimeter would be thermally isolated from its environment so that the temperature change observed is solely due to the reaction. Isolation from the environment is not possible in practice, so a calorimeter is usually surrounded by a thermostatically controlled jacket and allowance made for the various sources and sinks of energy. In the reference calorimeter, there are three external influences and they are all sources of energy:

1. the water stirrer;
2. the self heating of the temperature measuring device and
3. energy flowing from the jacket to the calorimeter due to the temperature difference.

Fig. 1 shows a temperature versus time curve for a typical experiment (combustion or calibration). Data collection starts at a predetermined temperature. The temperature of the calorimeter is allowed to rise, due to the influences mentioned above, for 750 s. This is the fore period. At time t_b, the main period begins as either combustion is initiated or the calibration heater is switched on. During the main period, which continues for 1030 s, the temperature quickly rises by about 3 °C. At the end of the heat input, the main

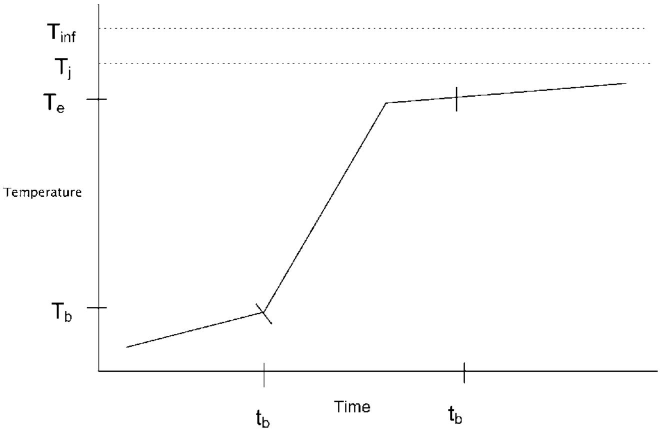

Fig. 1. Temperature versus time curve. T_{inf}: temperature at time = infinity; T_j: temperature of jacket; T_e: temperature at the end of heating period; T_b: temperature at the beginning of heating period; t_b: time at the beginning of heating period; t_e: time at the end of heating period.

period continues for an extra 1020 s, to time t_e, to allow the calorimeter to equilibrate. The aft period then begins, where the temperature rise is again solely due to the external influences, and continues for 1780 s.

The observed temperature rise during the main period is due to the energy liberated from the reaction and the energy from the three external influences. This temperature rise is corrected by use of the fore and aft period data to remove the temperature rise due to the external influences.

The rate of change of temperature of the calorimeter during the fore and aft periods is given by the following equation:

$$\frac{dT}{dt} = u + k(T_j - T), \tag{1}$$

where T is the temperature of the calorimeter, T_j the jacket temperature, u a constant power input due to the stirrer and the thermometer; and k is the cooling constant due to thermal leakage from the jacket derived from Newton's law of cooling.

If left for a long time, the calorimeter will reach a temperature T_{inf}, above the jacket temperature. At this point, $dT/dt = 0$ and from Eq. (1), $T_j = T_{inf} - (u/k)$. Substituting for T_j in Eq. (1) gives

$$\frac{dT}{dt} = k(T_{inf} - T). \tag{2}$$

Integrating Eq. (2) gives

$$T = T_{inf} - (T_{inf} - T_0)\exp(-kt), \tag{3}$$

where $T = T_0$ at $t = 0$ is not the same for the fore and aft period.

The temperature versus time data for the fore and aft periods is initially fitted to Eq. (2) using a linear regression. Taking T_f and T_a as the mid-point temperatures of the fore and aft periods and using g_f and g_a to denote the equivalent dT/dt, we can eliminate T_{inf} from Eq. (2) to give

$$k = \frac{g_f - g_a}{T_a - T_f}$$

and

$$T_{inf} = \frac{g_f T_a - g_a T_f}{g_f - g_a}.$$

Using these values of k and T_{inf}, the data is now fitted to Eq. (3), using a linear regression of temperature versus $\exp(-kt)$, for both the fore and aft periods. This gives accurate values for T_{inf} and T_0. The values of T_{inf} for both periods should be the same. Using these new values, the temperatures T_b and T_e at the beginning and end of the main heating period, at times t_b and t_e, can be interpolated using Eq. (3).

The corrected temperature rise is now found by subtracting T_{ex}, due to the external energy sources, from the temperature rise $T_e - T_b$. This correction is evaluated using an integrated form of Eq. (2):

$$T_{ex} = k\int_{t_b}^{t_e} (T_{inf} - T)\,dt$$

which becomes

$$T_{ex} = k(T_{inf} - T_m)(t_e - t_b),$$

where

$$T_m = \frac{1}{t_e - t_b}\int_{t_b}^{t_e} T\,dt.$$

where T_m is the mid-point temperature of the main period. It is found by numerical integration of the temperature versus time data using the trapezium rule. It is not necessarily equal to $(T_b + T_e)/2$.

There are several energy sources or sinks in a gas burning calorimeter which need to be corrected for. These can be either quantified or eliminated. To quantify them, they need to be measured. To eliminate them, they must be constant from run to run. To eliminate the constant ones, a short run is performed where gas is burnt for about 80 s instead of 16 min. The energy input and mass of gas used in the short run are subtracted from the equivalent values for the long gas run, thus eliminating the effects. These energy sources and sinks are listed in Table 1.

Calibration of a calorimeter to determine the energy equivalent can be achieved in one of the following two ways: (1) by burning a gas of known heat of combustion (e.g. hydrogen), or (2) by electrical heating. Each method has advantages and disadvantages. The reference calorimeter is calibrated electrically as this is traceable to national standards. The rate of energy input during the calibration is set by the voltage and current flowing through the heater. The same rate of energy input is achieved during a gas burn by choosing an appropriate gas flow rate.

Table 1
Energy sources and sinks—quantification and elimination

Energy source or sink	Quantification or elimination
Unburnt gas at ignition	Eliminated by short run
Unburnt gas at extinction	Eliminated by short run
Spark energy to ignite gas	Eliminated by short run
Water vapour left in calorimeter after being flushed out overnight	Eliminated by short run
The heat of condensation of water leaving the calorimeter as vapour during gas burn	Energy is quantified
Increase in mass of calorimeter due to water condensing during gas burn	Energy is quantified
Oxygen, argon and fuel gas temperatures	Energy is quantified
Correction to 101.325 kPa	Energy is quantified

3. Construction and operation

3.1. Basic structure

The reference calorimeter is shown in Fig. 2. It consists of two nested cans with an air gap between them. The inner can is filled with distilled water and contains a glass reaction vessel with heat exchanger, a calibration heater, a constant speed stirrer and a platinum resistance thermometer (Tinsley). A recess is included for the insertion of a cold finger to bring the calorimeter to its starting temperature. The cold finger is removed and the recess plugged when the calorimeter is in use. Where components pass through the lid of the inner can they are sealed with O-rings and silicon rubber to prevent water loss.

The inner can sits on three plastic feet, on the base of the outer can, keeping a uniform distance between the two. The outer can is closed at the top by a hollow lid and is immersed to just above the bottom of the lid in a thermostatically controlled bath of water. This water is pumped through the hollow lid, thus keeping a constant temperature environment around the inner can.

The outer bath is temperature controlled at about 27.3 °C. There is constant background cooling from a coil supplied with a 10 °C water and antifreeze mixture. Power is supplied to the bath heater from an Automatic Systems Laboratories (ASL) Series 3000 Precision Temperature Controller connected to an ASL F17 Resistance Bridge and a platinum resistance thermometer. This system keeps the bath temperature stable to ±0.001 °C during a run.

3.2. Temperature measurement and data collection

The platinum resistance thermometer feeds one side of an ASL F18 Resistance Bridge with a Tinsley 25 Ω

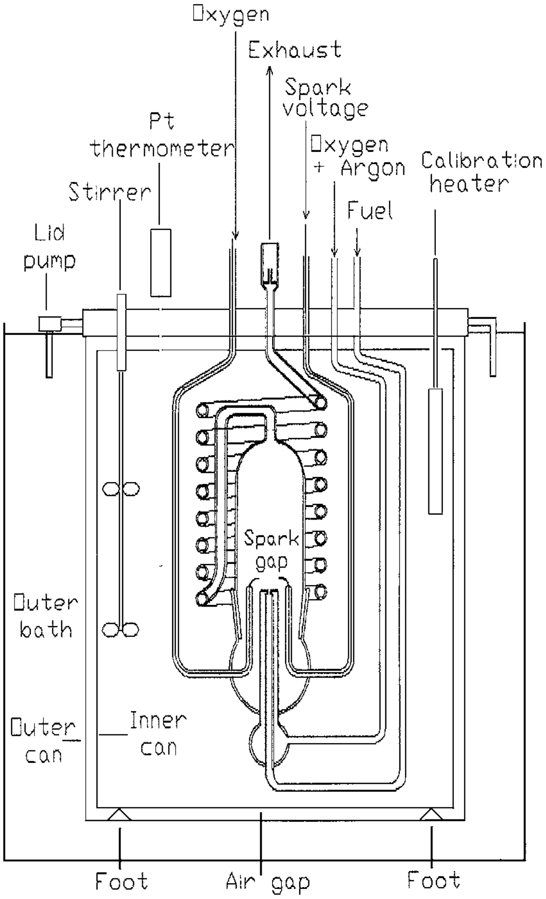

Fig. 2. Schematic of the reference calorimeter.

standard resistor (type 5685) balancing the other side. Resistance ratio readings are recorded every 3 s. The 25 Ω standard resistor is immersed in an oil filled bath controlled to 20 °C. The temperature of the resistor is measured and is stable to better than 0.1 °C. The temperature is used to calculate the value of the 25 Ω resistor from its calibration curve.

Calorimeter control and data collection are carried out by a Cube EuroBeeb running Real Time Basic. This is an event driven language whose event timings are accurate to better than 0.002 s. The EuroBeeb has IEEE488, RS232 and digital I/O interfaces. At the end of a run the data is passed to a PC for processing.

3.3. Gas runs

3.3.1. Overview

Combustion of the sample gas takes place inside the glass reaction vessel submerged in the water in the inner can. Ultra high purity oxygen is mixed with argon and then fed to the burner, through one arm of the vessel. Here it mixes with the fuel gas, supplied along a second arm. The argon acts as a moderator to lift the flame off the tip preventing decomposition of the sample, heat transfer up the arm and carbon build-up on the tip. A second feed from the oxygen supply goes to the base of the reaction vessel through a third arm to provide an oxygen rich atmosphere.

Two platinum electrodes act as a spark gap just above the tip of the burner. A series of 20 kV pulses to ignite the gas are supplied from a car ignition coil and fed to the electrodes along wires situated inside two of the arms of the reaction vessel.

3.3.2. Gas sample

A 250 ml cylinder is filled to a pressure of 14 bar with the sample gas. The cylinder weighs about 190 g and about 1 g of gas is burnt during a run. The weighings of the cylinder before and after a run are carried out on a Mettler AT201 balance which reads to 10^{-5} g. To allow for buoyancy changes, which can be quite sizeable, a dummy cylinder of identical external volume is weighed immediately before and after the sample cylinder. The difference in weight of the dummy cylinder before and after the run is due to buoyancy changes. This difference is applied as a correction to the change in weight of the sample cylinder to give the change in weight of the sample cylinder due to gas used.

The cylinder is connected to one arm of the reaction vessel via an ultra-fine flow needle valve. Near the end of the fore period, the computer opens two valves to start the oxygen and argon flowing. Sixty seconds later, on a signal from the computer, the operator manually opens the valve on the cylinder. A series of sparks to ignite the gas is initiated by the computer at the same time. Once ignition has occurred, the operator continuously adjusts the needle valve to maintain a constant flow rate. The flow rate is set to give the same rate of temperature rise as the calibration runs.

At the end of the gas burn, the operator turns off the sample gas and the computer switches on a flow of argon to purge the needle valve and fuel line to ensure that all the gas leaving the cylinder is burnt. Thirty seconds later, all gases are switched off and the equipment is allowed to continue to the end of the aft period. The cylinder is removed and reweighed.

3.3.3. Reaction products

The hot combustion gases flow out of the reaction vessel, through the heat exchanger, and give their energy to the water, leaving the calorimeter at the prevailing calorimeter temperature. The gases then pass into a chain of three water absorption tubes and an electronic carbon monoxide monitor.

The carbon monoxide monitor is used to check for incomplete combustion. Test runs are conducted to find the correct flow rates, for the argon, and primary and secondary oxygen, to reduce the CO level as much as possible, while still being able to ignite the gas.

The water absorption tubes contain magnesium perchlorate. These are weighed on the Mettler balance against a dummy tube to correct for buoyancy changes. When magnesium perchlorate absorbs water, it expands in volume by $0.6\,\mathrm{cm}^3\,\mathrm{g}^{-1}$ of water absorbed. This expansion displaces an equivalent volume of oxygen from within the tubes so appearing as a weight loss. This loss is calculated and applied as a correction to the weight of water. Newly filled tubes are conditioned for 12 h prior to use by flowing dry oxygen through them.

3.3.4. Water leaving the calorimeter

Most of the water produced during combustion condenses and remains as a liquid in the reaction vessel. However, about 10% of the water is carried out of the vessel during the combustion period as a vapour. This water represents about 470 J as its heat of condensation is not given up (2441.78 J g^{-1}). At the end of the run, the output arm from the reaction vessel is flushed with oxygen for 20 min to transfer all traces of water in this arm to the water absorption tubes. This also ensures that the absorption tubes are filled with oxygen as they were when first weighed. The tubes are then removed, weighed and a correction applied to the energy balance.

3.3.5. Water remaining in the calorimeter

The water absorption tubes are reconnected to the outlet of the reaction vessel and oxygen is used to flush out the remaining water overnight. This water represents an increase in energy equivalent of the calorimeter. It is corrected for by adding half the heat capacity (4.18 J g^{-1} K^{-1}) of the weight of water times the temperature rise. It represents about 12 J.

3.3.6. Gas corrections

The temperatures of the oxygen, argon and fuel gas are usually different to the mid point of the reaction. This represents a source or sink of energy to the experiment that needs to be corrected for. The duration of the gas flows is timed by use of the pulse counter and the off-air frequency standard described in Section 3.4. This time along with the measured flow rates of the gases gives the total volume of gas fed into the calorimeter during the run. The gases are assumed to be at room temperature, so the total source or sink of energy is calculated using the molar heat capacities of the various gases (methane: 35.64 J mol^{-1} K^{-1}; oxygen: 29.37 J mol^{-1} K^{-1}; argon: 20.79 J mol^{-1} K^{-1}). The closer the room temperature is to the mid-point of the reaction the smaller is the correction. For this reason, the room is kept at 25 °C. This correction can be up to ±20 J depending on the temperatures.

3.3.7. Correction to 101.325 kPa

The reaction takes place at the prevailing atmospheric pressure plus the excess pressure in the reaction vessel. These pressures are measured during the run and the Van't Hoff equation is used to correct the result to 101.325 kPa:

$$q = nRT \ln\left(\frac{P}{101.325}\right),$$

where q is the energy to be added to the experiment, P the total pressure in the reaction vessel, R the gas constant, T the absolute temperature and n is the number of moles decrease in gaseous volume. The energy correction can be up to ±80 J.

3.3.8. Other energy corrections

There is a small correction due to the water vapour left in the reaction vessel after the second flushing. The volume of vapour represents 7 J of energy not given up by condensing. This correction varies slightly with temperature and pressure but mostly cancels itself out between long and short runs.

Two other corrections that need to be applied are for: (1) energy from the spark; (2) effects due to incomplete combustion at ignition and extinction. These two factors could be quantified by performing runs where no gas is burnt and measuring the temperature rise. On the reference calorimeter, these factors are corrected for by conducting a short gas run where gas is burnt for about 80 s. The mass of gas which is lost at ignition and extinction and the energy input due to the spark should be the same for long and short runs. So, if the energy liberated and the mass of gas burnt in the short run (E_s and m_s) are subtracted from the energy and mass for the long run (E_l and m_l), the resultant values should then be due to just the gas burnt, i.e. heat of combustion $= (E_l - E_s)/(m_l - m_s)$. Only long and short runs within a few days of each other are used together for calculating the heat of combustion. This prevents any variations in sparking conditions from affecting the results.

3.4. Electrical calibration

A 50 Ω heater was constructed by winding resistance wire around a small hollow cylinder. This is connected to a stabilised 50 V power supply via a Tinsley 1 Ω standard resistor (type 1659). A Solatron type 7065 Microprocessor Voltmeter switches every 3 s between measuring the voltage across the 50 Ω heater and the 1 Ω resistor. The voltage across the 1 Ω gives the current flowing in the circuit. To stabilise the temperature of the 1 Ω resistor, it has been removed from its case and is suspended in the oil in the same bath as the 25 Ω resistor. Its temperature is measured and is stable to better than 0.1 K. The value of the 1 Ω resistor is calculated from its temperature coefficient.

When heating is not required, a dummy 50 Ω heater is switched into circuit to stabilise the power supply and 1 Ω resistor.

The duration of the heating period is measured by a Malden 8816 pulse counter fed from a Quartzlock 2A Off-Air Frequency Standard (Dartington Frequency Standards). The Quartzlock gives a 10 MHz signal phase locked to the BBC Radio 4 transmissions on 198 kHz.

The product of time, voltage and current give the energy input into the calorimeter. Using the corrected temperature rise, they give an energy equivalent for the calorimeter in terms of J K^{-1}. Calibration runs are fully automatic once started and up to four runs can be performed in a day. Several runs are averaged to produce long and short energy equivalents for use in the long and short gas runs.

4. Differences with previous experimenters

There are several differences between the reference calorimeter and those used by Rossini and Pittam and Pilcher. These differences are given in Table 2.

5. Heat of combustion of methane

Two sets of determinations of the heat of combustion of methane have been carried out using the reference calorimeter (Lythall and Dale). These results along with those of Rossini and Pittam and Pilcher are given in Table 3. Rossini's results have been reworked by Armstrong and Jobe to bring them into line with modern values of energy, temperature and molar mass [6].

Table 3
Heat of combustion of methane (kJ mol^{-1})

Rossini	Pittam and Pilcher	Lythall	Dale
891.82	890.36	890.60	890.34
890.63	891.23	890.69	890.11
890.01	890.62	890.87	890.49
890.50	890.24	890.62	891.34
890.34	890.61	890.81	890.36
890.06	891.17	890.94	890.44
		890.71	890.47
		890.59	890.87
		890.64	890.31
			890.33
890.56	890.71	890.72	890.51

Rossini ignored his first result to give a mean of 890.31 kJ mol^{-1}. The 1983 edition of ISO6976 [7] gives a value of 890.36 kJ mol^{-1}. The 1995 edition [8] has the value of 890.63 kJ mol^{-1} calculated as the average of all of Rossini's results and Pittam and Pilcher's results.

The mean of the measurements taken using the reference calorimeter is 890.61 kJ mol^{-1}.

6. Uncertainty analysis

The method given in the ISO publication "Guide to the Expression of Uncertainty in Measurement" was used to evaluate the uncertainties present in the reference calorimeter. The method analyses the equations relating the input quantities, x_i, to the output quantity, f. The input quantities fall into three categories:

1. physical constants taken from reference books;
2. values from calibration certificates and
3. measurements taken during the experiment.

Table 2
Differences with previous experiments

	Rossini	Pittam and Pilcher	OFGEM
Mass of gas burnt	Determined from mass of water produced	Determined from mass of carbon dioxide produced	Is directly weighed. Correction for unburnt gas from short runs
Calibration	Electrically: voltage and current readings taken every minute	Combustion of hydrogen and oxygen	Electrically: voltage and current readings taken alternately every 3 s
Temperature readings	Every minute during the reaction and every 2 min in fore and aft periods	Every 30 s	Every 3 s
Spark energy	Experiments conducted to determine spark energy	Short runs to correct for spark energy	Short runs to correct for spark energy

Each input quantity is analysed to calculate its uncertainty, $u(x_i)$. If equipment is calibrated by a UKAS registered laboratory (or international equivalent) then the certificate should state the uncertainty. Equipment needs to be calibrated frequently as values can drift with time.

For measurements taken during the experiment, the uncertainty should include figures for accuracy of the instrument, drift, and readability of the scale. These values should be found in the manufacturers' handbooks or they may have to be evaluated.

The individual uncertainties are combined using Eq. (4). This weights each uncertainty by an amount depending on the partial derivative of the equation relating f and x_i.

$$u_c^2(f) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) \qquad (4)$$

where f is the equation relating heat of combustion to the input values x_i, $u_c(f)$ the combined standard uncertainty on f, and $u(x_i)$ is the uncertainty on the input value x_i.

Listing the individual terms in the summation shows the relative sizes of the uncertainties. In the reference calorimeter, the largest uncertainty is due to the weighing of the gas cylinders.

For the reference calorimeter, the combined standard uncertainty, u_c, for a set of heat of combustion measurements for methane on a molar basis is 0.21 kJ mol^{-1}.

To check the reliability of the uncertainty analysis several sets of results for the same gas can be compared. This allows systematic factors, such as equipment drift and re-calibration, to affect the readings and give variability. The two sets of determinations which have been carried out using the reference calorimeter are 890.72 and 890.51 kJ mol^{-1}. The spread of these results about their mean is ± 0.1 kJ mol^{-1} which is consistent with the value given by the uncertainty analysis.

The individual results which make up the two sets of measurements carried out on the reference calorimeter show standard deviations of 0.13 kJ mol^{-1} on nine readings and 0.35 kJ mol^{-1} on 10 readings. These results give random uncertainties of $u_r = \mathrm{S.D.}/\sqrt{n} =$ 0.04 and 0.11 kJ mol^{-1}, respectively. The value of the random uncertainty, calculated as part of the overall combined standard uncertainty, is 0.06 kJ mol^{-1}. Lythall's results are consistent with this value, however, Dale's results show a greater spread.

7. Conclusion

The reference calorimeter is an accurate and precise instrument for measuring the superior heat of combustion of methane at 25 °C. The reference calorimeter gives a value of 890.61 kJ mol^{-1} with an uncertainty of 0.21 kJ mol^{-1}. This compares well with the value of 890.63 kJ mol^{-1} (with a random uncertainty based on 1 S.D. of 0.53 kJ mol^{-1}) in ISO6976: 1995.

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