ELSEVIER Thermochimica Acta 256 (1995) 9–16

thermochimica
acta

Accuracy analysis in flow calorimetry ☆

P.G. Grini[a], *, G.A. Owren[a], H.S. Mæhlum[b]

[a] *Norwegian Institute of Technology, Department of Refrigeration Engineering, 7034 Trondheim, Norway*

[b] *SINTEF Refrigeration Engineering, 7034 Trondheim, Norway*

Abstract

The accuracy claimed for calorimetric measurements should be given at a certain confidence level. This paper describes how the standard uncertainty of isobaric enthalpy increment measurements from a new cryogenic flow calorimeter is derived. The new calorimeter has several features that reduce the heat leakage better than previous designs. The temperature and pressure ranges covered by the calorimeter are 133–335 K and 0.17–14 MPa. The enthalpy increment measurements have an average standard uncertainty of 0.10 kJ kg^{-1} or 0.25% of the enthalpy increment.

Keywords: Accuracy; Calorimetry; Enthalpy; Flow calorimetry; Novel

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1. Introduction

The accuracy of measurements claimed by different laboratories varies both with the method used and in the reliability of the claimed result. Different methods have been in use, but the method based on the law of propagation of uncertainty usually gives the most nearly correct result.

A new cryogenic flow calorimeter for measurement of isobaric enthalpy increment and Joule–Thomson (J–T) effect has recently been thoroughly evaluated for finding the standard uncertainty in the measurements. The design of the calorimeter is based on that of Pieper at the Technische Universität Berlin [1] and incorporates several improvements to reduce heat leakage; these include thermal shields cooled by propane, a heat sink, and multilayer super-insulation on all tubing. Very accurate instrumentation is used to increase the accuracy of the measurements.

☆ Presented at the 14th Symposium on Thermal Analysis and Calorimetry, Oslo, Norway, 15–17 June 1994.

* Corresponding author. Fax number: + 47 73 593926

SSDI 0040-6031 (94) 02165-1

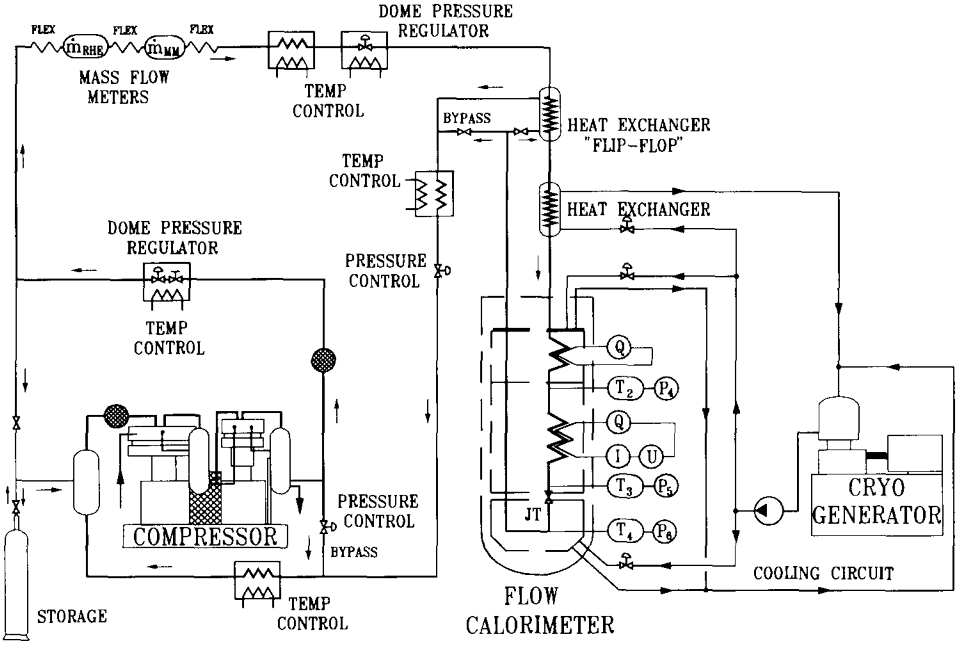

Fig. 1. Flow sheet of the SPUNG calorimeter.

A flow sheet of the calorimeter is shown in Fig. 1. The measurements of interest are made inside the "calorimeter container". The temperature and pressure are measured before (T_2, p_4) and after (T_3, p_5) the isobaric heating section. The power Q to the heating section is measured by the applied voltage U and the current I. From the heating section the medium passes through an adjustable J-T valve and the temperature and pressure are measured again (T_4, p_6). An example of the measurements performed is given in Table 1.

The flow calorimeter has been used for measurements on pure methane, ethane and nitrogen, and binary mixtures of these components and also propane. The temperature and pressure ranges covered by the calorimeter are 133-335 K and 0.17-14 MPa. All measured data except the mass flow are recorded directly on a PC. These data are transferred to a database, converted into SI units and corrected through calibration factors. The database contains about 900 of our own measure-

Table 1
Measured enthalpy increment Δh_{Exp} on a mixture of 68.32% methane and 31.68% propane

Run No.	T_2 in K	T_3 in K	P_4 in MPa	P_5 in MPa	Δh_{Exp} in kJ kg^{-1}
654	284.87	301.73	1.0186	1.0080	34.23
670	329.00	339.15	13.9509	13.9502	36.47
1020	143.22	155.12	14.0365	14.0358	30.26
1026	253.24	270.72	11.0233	11.0222	63.27

ments and 2600 measurements from the published literature. The flow calorimeter and database are fully described elsewhere [2,3]. The calculation of the accuracy of the measurements given in the project report [2] is less precise than the calculation of the standard uncertainty of the measurements described in this paper.

This paper describes the results of the heat leakage evaluation and the evaluation of the standard uncertainty in the individual measurements. The combination of the individual standard uncertainties to give the standard uncertainty of the measured enthalpy increment Δh is shown. Results of a consistency test and a precision test are also shown.

2. Results and discussion

2.1. *Accuracy of the measurements*

The uncertainty analysis is done in accordance with the guidelines given by the National Institute of Standards and Technology (NIST) [4]. All uncertainties are treated as so called "Type B", where the standard uncertainty is estimated by other means than statistical methods on a large population. The term standard uncertainty $u(x_i)$ is used for each component of uncertainty that contributes to the uncertainty of a measurement result by an estimated standard deviation.

All uncertainties are considered to be normally distributed and, even if some uncertainties have a different distribution, one gets a normally distributed error in the measured enthalpy increment owing to the central limit effect [5]. The assumption of normal distribution is not correct for some of the heat leakages, but because of the small influence of these sources on the measurement result all the heat leakages are treated as normally distributed.

2.2. *Heat leakage*

Extensive experimental test runs and theoretical evaluations have been performed to find the heat leakage by radiation, conduction into the calorimeter, and conduction along the internal flow tubes. In order to get comparable numbers, all calculations have been performed at level ± 1 standard deviation. The condition of maximum heat transfer is set to be at level ± 3 standard deviations.

The heat leakages at level ± 1 standard deviation to the isobaric section of the calorimeter are given in Table 2. The electrical power UI has been corrected for heat leakage through the power supply lines and the voltage measuring lines and heat generation in the power supply lines. The largest correction in the enthalpy increment measurements is 0.084% of the electrical heat input. The reason why not all heat leakages are included in the correction term is that the uncertainty of their quantity was considered to be too high. The measured heat leakage under "ideal conditions" means that there was no temperature difference between the test fluid and the radiation shields and heat sinks.

Table 2
Heat leakages to the isobaric section of the flow calorimeter

Heat leakage by:	Q in W
Radiation	4.7×10^{-3}
Total conduction into the calorimeter	24.0×10^{-3}
Conduction into the calorimeter (after correction)	1.9×10^{-3}
Conduction along internal flow tubes	6.0×10^{-3}
Measured heat leakage at "ideal conditions"	16.0×10^{-3}
Standard uncertainty in correction term for heat generation in power supply lines	1.0×10^{-3}
Total heat leakage after correction	29.0×10^{-3}

2.3. Combination of individual uncertainties

The standard uncertainty cannot be given as a fixed value for all the test runs because the measured enthalpy increment and J–T effect are a function of several parameters of varying importance in different temperature and pressure regions. The standard uncertainties in the individual measurements are given in Table 3.

The influence of the individual variables and their standard uncertainty on the isobaric enthalpy increment in the calorimeter Δh is given by

$$\begin{aligned}
&\Delta h[T_2 + u(T_2),\ T_3 + u(T_3),\ p_4 + u(p_4),\ p_5 + u(p_5),\ z_i + u(z_i)] \\
&\quad = h[T_3 + u(T_3),\ p_5 + u(p_5),\ z_i + u(z_i)] - h[T_2 + u(T_2),\ p_4 + u(p_4),\ z_i + u(z_i)] \\
&\quad = \frac{[U + u(U)][I + u(I)] + u(Q_{\text{leakage}})}{[\dot{m} + u(\dot{m})]}
\end{aligned} \tag{1}$$

Table 3
Standard uncertainties in the individual measurements

Unit	Standard uncertainty $u(x_i)$
$u(T_2)$, $u(T_3)$, $u(T_4)$	± 0.013 K
$u(p_4)$	± 0.0016 MPa
$u(p_5)$	$\pm 0.0016 + 8.5 \times 10^{-6}$ MPa
$u(p_6)$	± 0.0011 MPa
$u(I)$	$\pm 0.0167\%$ of reading $+ 13.3 \times 10^{-6}$ A, $I < 1.0$ A
	$+0.033\%$ of reading $+ 13.3 \times 10^{-6}$ A, $I > 1.0$ A
$u(U)$	$+0.002\%$ of reading ± 1.0 mV
$u(\dot{m}_{\text{MM}})$	$\pm 0.11\%$ of reading
$u(\dot{m}_{\text{RHE}})$	$\pm 0.17\%$ of reading
$u(Q_{\text{leakage, isobar-s}})$	29×10^{-3} W
$u(Q_{\text{leakage, JT-s}})$	5.1×10^{-3} W
$u(\Delta E_{\text{kinetic}})$	$+0.014$ kJ kg^{-1} if P6 < 0.5 MPa and gas phase; otherwise negligible
$u(z_i)$	± 1.0 g/gas cylinder

In Eq. (1), z_i is the molar fraction of component i in the gas, $u(Q_{\text{leakage}})$ is the heat leakage to the isobaric section, and $\dot{m}$ is the mass flow rate of the test fluid.

The variables have to be divided into two groups: the variables which influence the accuracy of the experimental enthalpy increment: (U, I, $\dot{m}$, Q_{leakage}), giving the standard uncertainty $u(\Delta h)_{\text{Exp}}$, and the variables which have to be considered when evaluating the calculated enthalpy increment: (T, p, z_i), giving the standard uncertainty $u(\Delta h)_{\text{Calc}}$.

The contributions of the individual standard uncertainties to $u(\Delta h)_{\text{Exp}}$ and $u(\Delta h)_{\text{Calc}}$ are given by Eqs. (2) and (3)

$$
\begin{aligned}
u(\Delta h)_{\text{Exp}} = \Bigg[& \left(u(I)\frac{\partial \Delta h_{\text{Exp}}}{\partial I} \right)^2 + \left(u(U)\frac{\partial \Delta h_{\text{Exp}}}{\partial U} \right)^2 \\
& + \left(u(m)\frac{\partial \Delta h_{\text{Exp}}}{\partial m} \right)^2 \\
& + \left(u(Q_{\text{leak}})\frac{\partial \Delta h_{\text{Exp}}}{\partial Q_{\text{leak}}} \right)^2 \Bigg]^{1/2}
\end{aligned} \tag{2}
$$

The dominant term in Eq. (2) is the one concerning the mass flow rate $\dot{m}$.

$$
\begin{aligned}
u(\Delta h)_{\text{Calc}} = \Bigg[& \left(u(T_2)\frac{\partial \Delta h_{\text{Calc}}}{\partial T_2} \right)^2 + \left(u(T_3)\frac{\partial \Delta h_{\text{Calc}}}{\partial T_3} \right)^2 \\
& + \left(u(p_4)\frac{\partial \Delta h_{\text{Calc}}}{\partial p_4} \right)^2 + \left(u(p_5)\frac{\partial \Delta h_{\text{Calc}}}{\partial p_5} \right)^2 \\
& + \sum_{i=1}^{n-1} \left(u(z_i)\frac{\partial \Delta h_{\text{Calc}}}{\partial z_i} \right)^2 \Bigg]^{1/2}
\end{aligned} \tag{3}
$$

The most important terms in Eq. (3) are those which concern the influence of the standard uncertainty of the temperature measurements. It can be shown from the Leibniz rule that

$$\left.\frac{\partial \Delta h_{\text{Calc}}}{\partial T_2}\right|_{p,z_i} - c_p\big|_{T_2}$$

and that

$$\left.\frac{\partial \Delta h_{\text{Calc}}}{\partial T_3}\right|_{p,z_i} = c_p\big|_{T_3}$$

where c_p is the specific heat capacity at constant pressure.

The total standard uncertainty from the measurements $u(\Delta h)_{\text{Tot}}$, when comparing different models or equations with the measured enthalpy increment, is given as the combination of Eqs. (2) and (3)

$$u(\Delta h)_{\text{Tot}} = \sqrt{u(\Delta h)^2_{\text{Exp}} + u(\Delta h)^2_{\text{Calc}}} \tag{4}$$

From Eq. (4), the average standard uncertainty when comparing equations with the measured isobaric enthalpy increment $u(\Delta h)_{\mathrm{Tot}}$ is ± 0.10 kJ kg^{-1}, or $\pm 0.25\%$ of the enthalpy increment.

A similar analysis is performed for the J–T effect measurements, except that the change in kinetic energy has to be considered and the mass flow rate is without influence. The calculations give an average value of the standard uncertainty, referred to enthalpy, equal to ± 0.08 kJ kg^{-1}. The temperature change $T_4 - T_3$ and the pressure drop $p_6 - p_5$ are measured with a standard uncertainty of 0.018 K and 0.0019 MPa respectively.

2.4. Consistency check

A test of consistency, in the form of a loop check, is performed to confirm the claimed accuracy. In the loop check the measurements are performed such that they form a closed thermodynamic cycle. Two isobars and two isenthalps are chosen to form the loop. The consistency of the measurements is evaluated by Eq. (5) [6], where "Deviation" is the experimental inconsistency.

$$\text{Deviation} = \frac{\sum \Delta h_i}{\sum |\Delta h_i|} \times 100\% \tag{5}$$

Two of the paths in the loop are isenthalpic and make no direct contribution to Eq. (5), but any heat leak will contribute to the deviation between the two isobaric paths. It is impossible to fit the starting conditions (T, p, $\dot{m}$) in one run exactly to the end conditions in the next. A correction term must therefore be used to get comparable conditions that can be evaluated. Three loop tests were performed and the results are consistent with an average deviation of 0.076 kJ kg^{-1} or 0.125% of the total absolute enthalpy change.

The loop consists of four paths, but one of the measurements covers one isobar and one isenthalp, giving a total of three individual measurements. The average standard uncertainty calculated is 0.13 kJ kg^{-1} for the combined isobaric/isenthalpic measurement, 0.08 kJ kg^{-1} for the isenthalpic measurement, and 0.10 kJ kg^{-1} for the isobaric measurement. If these standard uncertainties are combined, the standard uncertainty around the loop should be 0.18 kJ kg^{-1}. Compared with the measured average inconsistency of 0.076 kJ kg^{-1}, the calculated standard uncertainty seems conservative.

2.5. Evaluation of precision

The precision or repeatability of the calorimeter was evaluated by eight independent repetitions at one test condition. The different variables (mass flow rate, heat input, and stop/start) were respectively given a deviation from the set point, stabilized at this new condition, and then brought back to the set point. This was done to check whether the previous setting would influence the measurements, but no such influence was detected. The precision of the isobaric enthalpy increment measurements from this test is ± 0.0028 kJ kg^{-1} at level $\pm$ one standard deviation. The measured precision is acceptable compared with the standard uncertainty in the measurements of 0.10 kJ kg^{-1}.

2.6. Database

A computer program that calculates $u(\Delta h_{\mathrm{Tot}})$, $u(\Delta h_{\mathrm{Exp}})$ and $u(\Delta h_{\mathrm{Calc}})$ is created and implemented in the database. The program also calculates the influence on $u(\Delta h)$ of every individual standard uncertainty $u(x_i)$ in the instrumentation, called $u_{\Delta h}[u(x_i)]$, where

$$u_{\Delta h}[u(x_i)] = \frac{\partial \Delta h}{\partial x_i} u(x_i)$$

as shown in Eqs. (2) and (3).

Table 4
Standard uncertainties in the individual measurements regarding $u(\Delta h)_{\mathrm{Exp}}$

Run No.	$u_{\Delta h}[u(I)]$ in kJ kg^{-1}	$u_{\Delta h}[u(U)]$ in kJ kg^{-1}	$u_{\Delta h}[u(\dot{m})]$ in kJ kg^{-1}	$u_{\Delta h}[u(Q_{\mathrm{leak}})]$ in kJ kg^{-1}	$u(\Delta h)_{\mathrm{Exp}}$ in kJ kg^{-1}
654	0.012	0.002	0.038	0.022	0.045
670	0.011	0.002	0.040	0.023	0.048
1020	0.010	0.001	0.033	0.020	0.048
1026	0.021	0.003	0.070	0.020	0.075

Table 5
Standard uncertainties in the individual measurements regarding $u(\Delta h)_{\mathrm{Calc}}$

Run No.	$u_{\Delta h}[u(T_2)]$ in kJ kg^{-1}	$u_{\Delta h}[u(T_3)]$ in kJ kg^{-1}	$u_{\Delta h}[u(p_4)]$ in kJ kg^{-1}	$u_{\Delta h}[u(p_5)]$ in kJ kg^{-1}	$u_{\Delta h}[u(z)]$ in kJ kg^{-1}	$u(\Delta h)_{\mathrm{Calc}}$ in kJ kg^{-1}
654	0.026	0.026	0.028	0.025	0.005	0.053
670	0.048	0.046	0.015	0.015	0.012	0.085
1020	0.033	0.034	0.022	0.021	0.002	0.048
1026	0.048	0.054	0.004	0.009	0.008	0.073

Table 6
Standard uncertainties in the individual measurements

Run No.	$u(\Delta h)_{\mathrm{Exp}}$ in kJ kg^{-1}	$u(\Delta h)_{\mathrm{Calc}}$ in kJ kg^{-1}	$u(\Delta h)_{\mathrm{Tot}}$ in kJ kg^{-1}	$u(\Delta h)_{\mathrm{Tot}}$ in % of Δh_{Exp}
654	0.045	0.053	0.069	0.20
670	0.048	0.071	0.085	0.23
1020	0.040	0.048	0.062	0.21
1026	0.075	0.073	0.105	0.16

Every test run on the calorimeter is linked to a certain calibration set in the database. When some instrumentation on the calorimeter is changed or recalibrated, a new calibration set is made for the database and the accuracy of each measurement is calculated. Some examples of these calculations are given in Table 4 for the inaccuracies that contribute to $u(\Delta h_{\mathrm{Exp}})$, in Table 5 for the inaccuracies that contribute to $u(\Delta h_{\mathrm{Calc}})$, and in Table 6 for $u(\Delta h)_{\mathrm{Tot}}$.

3. Conclusions

High accuracy can be reached in flow calorimetry by good design and careful operation. The accuracy analysis presented gives a heat leakage of 29.0×10^{-3} W and an average standard uncertainty of the enthalpy increment measurements of 0.10 kJ kg^{-1}.

Acknowledgements

The project was financed by the Research Council of Norway (NFR) through The State R&D Program for Utilization of Natural Gas (SPUNG). Svein Puntervold developed the database application.

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