EMRP 2013

ENG60 LNG II

Metrological support for LNG custody transfer and transport fuel applications

Report on the relevant physical quantities and current data used in enthalpy and calorific value calculations

(Task D4.4.2)

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1. Introduction

The work described in this report is part of the European Metrology Research Programme (EMRP) project for Liquefied Natural Gas (LNG) which is jointly funded by the European Commission and participating countries within Euramet and the European Union.

In this task, current data used in enthalpy and calorific-value calculations are examined with respect to the uncertainties and to check the traceability of the data. As well as density, composition of an LNG sample and the total amount of transferred LNG, the energy content is determined by the thermophysical quantities enthalpy and calorific value.

One task (among other tasks) of the preceding JRP ENG03 LNG [111] was to calculate the calorific values and enthalpies of formation of typical LNG samples. The result showed a difference in energy content between the LNG in the real liquid state (-160°C, several bar pressure) and at pipeline reference conditions (15 or 25°C, atmospheric pressure).

Another conclusion from the previous JRP ENG03 was the lack of uncertainty for many input quantities for calculations, such as heat capacities or enthalpies of formation. Therefore, some of these uncertainties are estimated, including the uncertainty for the calorific values of pure LNG components. This task will contribute to a firmer basis for these values in accordance with the GUM (Guide to the expression of Uncertainty in Measurement).

In the first part of this report, the ‘current data’ used for enthalpy and calorific-value calculations is identified. The second part deals with the aspect of traceability of the ‘current data’ and how literature data can be classified in the sense of traceability. The last part of the report contains surveys of the identified sources of the current data used for calorific value and enthalpy calculations and their classification.

Summary and conclusions of this report are part of the deliverable D4.4.3 ‘Guideline on the traceability of energy and enthalpy calculations’.
2. Identification of current data used in enthalpy and calorific value calculations

The identification of ‘current data’ should consider several aspects. One aspect is the question about the substances which should be considered. Examples of typical LNG samples will deliver this information. The second aspect deals with the kind of thermophysical quantities which have to be considered. In general, the task specifies enthalpy and calorific value. To go into detail, for example, the enthalpy of methane needs the knowledge of the standard enthalpy of formation of methane. But this is a derived thermophysical quantity and it requires the heat of combustion of methane and the enthalpies of formation of water and carbon dioxide at a certain temperature and pressure.

Identified thermophysical quantities are displayed in a matrix form. The columns (substances) contain the hydrocarbons from methane up to pentane, nitrogen, water, carbon dioxide and oxygen. The rows (thermophysical properties) comprise standard enthalpies of formation, heats of combustion (superior calorific value), enthalpies of fusion, sublimation and vaporisation and temperature-dependent heat capacities of the gas, liquid and solid state. The matrix indicates thermophysical properties which are necessary for the calculation of temperature-dependent enthalpies of an LNG sample.

The third aspect of the ‘current data’ identification is the question about what does the term ‘current’ include. The report checked the relevant ISO-standard [200], databases from NIST [267] and CODATA [74]. Scientific publications which deal with the development of equations of state (see section 0) for the identified relevant substances are also analysed.

2.1. Substances

In order to determine the relevant substances of current data, a set of LNG composition data is required. This experimental data was obtained from two open literature sources. The first source, Hynes [184], provided three sets of experimental data and the second source, Orrit [274], provided two more sets of data.

The above five examples of experimental data were taken over a range of methane content from 81% to 98%. The data and sources are given in Tables 1 and 2 below and denoted as examples A to E. The molecular weights of examples D and E were calculated using ISO 6976 as they were not provided in the source.

<table>
<thead>
<tr>
<th>Table 1: LNG composition for each open literature example [184, 274]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Component</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Methane</td>
</tr>
<tr>
<td>Ethane</td>
</tr>
<tr>
<td>Propane</td>
</tr>
<tr>
<td>Isobutane</td>
</tr>
<tr>
<td>n-Butane</td>
</tr>
<tr>
<td>Isopentane</td>
</tr>
<tr>
<td>n-Pentane</td>
</tr>
<tr>
<td>n-Hexane</td>
</tr>
<tr>
<td>Nitrogen</td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
</tbody>
</table>
Table 2: Experimental data for each open literature example [184, 274]

<table>
<thead>
<tr>
<th>Example</th>
<th>Example</th>
<th>Example</th>
<th>Example</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
</tr>
<tr>
<td>Molecular Weight, g/mol</td>
<td>20.070</td>
<td>19.358</td>
<td>17.902</td>
<td>17.095</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>112.37</td>
</tr>
<tr>
<td>Pressure, MPa</td>
<td>0.2214</td>
<td>0.1172</td>
<td>0.1456</td>
<td>0.134</td>
</tr>
<tr>
<td>Experimental density, kg/m³</td>
<td>490.851</td>
<td>477.311</td>
<td>454.001</td>
<td>441.600</td>
</tr>
<tr>
<td>Reported Uncertainty</td>
<td>±0.12%</td>
<td>±0.12%</td>
<td>±0.12%</td>
<td>±0.028%</td>
</tr>
</tbody>
</table>

The typical LNG samples from Haynes [184] and Orrit [274] indicate the following hydrocarbons: methane, ethane, propane, n- and iso-butane, n- and iso-pentane. Additionally, nitrogen is relevant.

### 2.2. Thermophysical properties of current data

Calorific values $H_s$ are determined, e.g., in open-flame calorimeters [87, 180, 287, 303, 331] at a certain temperature and pressure. In order to transform the values measured to standard conditions, they have to be calculated from Hess’s law, e.g. for methane

$$H_s = \left[\Delta_{CO2}H + \Delta_{H2O}H - \Delta_{CH4}H\right], \quad (1)$$

where $\Delta_{CO2}H$, $\Delta_{H2O}H$ and $\Delta_{CH4}H$ are the temperature-dependent enthalpies of carbon dioxide, water and methane at a given pressure.

$$\Delta_i H_i = \sum \Delta_{i,H_{comb,prod}} - \Delta_{comb,H_i}, \quad (2)$$

The equation expresses Hess’s law in general way. The enthalpy of formation of a species $i$ is the difference between the sum of the enthalpies of formation of reaction products minus the heat of combustion $\Delta_{comb}H_i$. The following enthalpy diagram illustrates Eq. (2).
Eq. (1) has two consequences. The first consequence is that calorific values at different temperatures can be calculated from the temperature dependence of the enthalpy components on the right-hand side of Eq. (1).

The second consequence of Eq. (1) is that at standard conditions the enthalpy of formation of methane is calculated in our example from the heat of combustion of methane and this is the relevant experimental measurement quantity. The standard enthalpies of formation of methane and all other hydrocarbons are derived quantities.

Therefore, this report focuses on the primary data and these are for the hydrocarbons the heats of combustion. The situation is different for water and carbon dioxide. The combustion of hydrogen and oxygen at standard conditions directly yields the enthalpy of formation of these substances. In that special case, the standard enthalpy of formation and heat of combustion are identical.

The representation of the temperature dependence of enthalpies of combustion products is more extensive. For example, the equation for the enthalpy of water and temperatures below the melting point is given by:

\[
\Delta_{\text{H}_2\text{O}} H = \Delta_{\text{H}_2\text{O}} H^\circ + \Delta_{\text{H}_2\text{O}} H(T_0 \rightarrow T_{\text{fus}}) + \Delta_{\text{fus, H}_2\text{O}} H + \int_{T_{\text{fus}}}^{T} c_p(\text{H}_2\text{O}, s) dT ,
\]

where \(\Delta_{\text{H}_2\text{O}} H^p\) is the standard enthalpy of formation of water at reference conditions and \(\Delta_{\text{H}_2\text{O}} H(T_0 \rightarrow T_{\text{fus}})\) is the change of enthalpy from standard temperature \(T_0\) to the freezing temperature \(T_{\text{fus}}\). With means of the temperature dependence of the isobaric heat capacity \(c_p\) of frozen water it is possible to calculate any enthalpy of frozen water at a given pressure.

The necessary quantities for deteremining of the temperature dependency of the enthalpies of water and carbon dioxide are: temperature-dependent heat capacities, standard enthalpies of formation and enthalpy of fusion for water and, for carbon dioxide, the enthalpy of sublimation at ambient pressures, respectively.

The results of the preceding sections are summarized in the following table:

<table>
<thead>
<tr>
<th></th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
<th>Butane</th>
<th>i-Butane</th>
<th>Pentane</th>
<th>i-Pentane</th>
<th>Nitrogen</th>
<th>Water</th>
<th>Carbon Dioxide</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard enthalpy of formation</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Heat of combustion/calorific value</td>
<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>x</td>
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<tr>
<td>Enthalpies of</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>fusion</td>
<td>x</td>
<td>x</td>
<td></td>
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<tr>
<td>sublimation</td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
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<tr>
<td>vaporisation</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
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<td></td>
<td>x</td>
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<tr>
<td>Heat capacity (temperature dependent)</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>gas</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>liquid</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>solid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>
2.3. Data sources of current data

In order to collect the relevant data sources in literature and follow the current development in the description of thermophysical properties of natural gases and LNG, it seems promising to analyse the literature in the research field of equations of state.

An example is a generally accepted equation of state (EoS) the GERG 2004 wide-range equation of state for natural gases and other mixtures (ISO 20765-2, [225]). The Helmholtz free energy is the central core of the GERG 2004 and, therefore, used to calculate all other types of thermal and pressure-dependent gas properties, e.g. density, speed of sound, heat capacities and enthalpies, by classical partial derivatives known from fundamental thermodynamics.

To set up such an EoS like the GERG 2004, the input of caloric and thermal experimental data is necessary. The work of Jaeschke and Schley [202] yields the parameterized equations for the heat capacities. The equations recommended by Jeschke and Schley represent many available data sets in literature of the isobaric heat capacity of hydrocarbons (up to n-decane) and all types of impurities of natural gas as nitrogen, carbon dioxide, hydrogen, oxygen and so on.

Other sources for relevant literature were ISO-standards, NIST-database and the IUPAC monographs for certain substances. The following list gives an overview about the literate sources were considered:

- Calorific values: ISO 6976 [200] and technical report [201];
- Calorific values and other thermophysical properties (standard enthalpies of formation, enthalpies of fusion, vaporisation and sublimation): NIST Chemistry Webbook [269];
- Heat capacities for hydrocarbons, nitrogen and water: Jaeschke/Schley [202] and Schley et al. [330];
- The monograph ‘CODATA key values for thermodynamics’ [74];
- Collection of polar and non-polar fluids: Span/Wagner [349, 350, 351];

For special substances, the following literature sources were taken into account:

- Methane: Angus et al. [23], Setzmann/Wagner [334] and Wagner/Span [395];
- Ethane: Bücker/Wagner [61], Chao et al. [65] and Friend et al. [148];
- Propane: Chao et al. [65], Lemmon et al. [230] and Miyamoto/Watanabe [259];
- N-Butane/Isobutane: Bücker/Wagner [62] and Chen et al. [68];
- Pentane: Span/Wagner [350];
- Water/Steam: Sato et al. [327] and Wagner/Pruß [393];
- H2O-ice: Feistel/Wagner [141];
- CO2: Angus et al. [22] and Span/Wagner [348];
- O2: Stewart et al. [355], Wagner et al. [392] and Wagner et al. [394];
- N2: Angus et al. [24], Span et al. [347] and Wagner/Span [395];

If available, the literature collection was supplemented by the latest relevant publications.
3. Traceability and uncertainties of the current data

Traceability means ‘the property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty’ according to the BIPM (Bureau International des Poids et Mesures, http://www.bipm.org/en/bipm-services/calibrations/traceability.html).

Traceability requires (among others; see BIPM homepage) a documented uncertainty statement. This involves uncertainty statements for the measurement result, uncertainty statements for all input quantities which are measured, uncertainty statements for the calibration standards used and a documented measurement procedure. The assessment of the measurement uncertainty is explained in guides like GUM [178] or the EURACHEM/CITAC [133].

The question is now how to judge from a publication whether the measurement result of a certain publication is traceable or not. In any case, if an uncertainty is reported there was e. g. a calibrated measurement device or a reference material which guarantees the traceability chain. This is the basic assumption. If no uncertainties are reported or only claims of an uncertainty are given without an uncertainty analysis of the measurement process, the traceability chain is broken.

The analysed literature sources are classified into 3 categories: A, B and C.

3.1. Category A

Category A means a fully traceable measurement result.

This requires a complete report of the uncertainties of the input quantities measured (and not intermediate quantities, see description ‘category B’ below), a statement about the combined uncertainty of the measurement result and an uncertainty budget or a description by formulas or in a continuous text how the combined uncertainty is assessed.

From the given numerical values of the input quantities measured and the corresponding uncertainties, the description in the publication or the model equations it should be possible to recalculate the stated combined measurement uncertainty from scratch. This means the stated final combined uncertainty of the measurement results should be reproducible by any other researcher only given by the information in the considered publication or by an available supplementary publication.

There should be not too much time elapse between the dissemination of the considered publication and supplementary publications (less than two years) because, e. g., the validity of calibration certificates of the measurement devices used expire. The supplementary publication should also directly refer to the measurement range and the used and unchanged measurement set-up. The measurement range is not only temperature and pressure but also refers to the measurement ranges of all input quantities.

3.2. Category B

In category B all publications are collected which are close to category A but with a few limitations. Limitations are
• Reporting of intermediate uncertainties in a smaller number (less than 50% arbitrary chosen). An intermediate uncertainty belongs not to a directly measurable quantity. They are derived from uncertainties of directly measurable quantities by the researcher but the uncertainties of the directly measurable quantities are not reported. For example, the uncertainty of the electrical heating power in a calorimetric experiment is such an intermediate uncertainty as voltage and current are measured in most cases (sometimes the current is determined by a reference resistor and the voltage drop at this resistor) to determine the electrical heating power.

• Missing uncertainties of minor correction terms which are applied to calculate the measurement result. If an uncorrected bias is recognised in a measurement, it should be taken into account by an uncertainty contribution to the final combined uncertainty of the measurement result. In case there is a correction of the later bias applied, the correction has also an uncertainty and the uncertainty of the bias correction also contributes to the final combined uncertainty of the measurement result.

• Reporting of relative uncertainties of the input quantities of a measurement without reporting numerical values of the sensitivity coefficients or without reporting a model equation and the absolute numerical values of the measured input quantities.

3.3. Category C

The final category C classifies all publications without an uncertainty statement. This category also contains data sources which only make a statement of the measurement uncertainty without a further analysis or discussion. Uncertainties of measurement which only consist of the standard deviation of multiple measurement results are treated as category C.
4. Thermodynamic data references/sources:

This chapter contains all considered literature sources of thermophysical properties and substances. The chapter is divided into subsections for each single substance. The discussion of the thermophysical properties takes place in the special subsections for each substance.

4.1. Methane:

4.1.1. Methane: Heat of combustion/calorific value:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Traceability category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rossini</td>
<td>1931</td>
<td>304</td>
<td>C</td>
</tr>
<tr>
<td>Roth/Banse</td>
<td>1932</td>
<td>312</td>
<td>C</td>
</tr>
<tr>
<td>Prosen/Rossini</td>
<td>1945</td>
<td>294</td>
<td>C</td>
</tr>
<tr>
<td>Pittam/Pilcher</td>
<td>1972</td>
<td>287</td>
<td>C</td>
</tr>
<tr>
<td>Alexandrov</td>
<td>2002</td>
<td>9</td>
<td>A</td>
</tr>
<tr>
<td>Dale et al.</td>
<td>2002</td>
<td>87</td>
<td>C</td>
</tr>
<tr>
<td>Schley et al.</td>
<td>2010</td>
<td>331</td>
<td>C</td>
</tr>
<tr>
<td>Haloua et al.</td>
<td>2015</td>
<td>180</td>
<td>A</td>
</tr>
</tbody>
</table>

Rossini (1931): ‘Heats of combustion of methane and carbon monoxide’ [304].
Traceability category: C.
The procedure applied to estimate uncertainties is the same as in Rossini [303] and discussed in the section 4.7.1 ‘Water: Standard enthalpy of formation’.

Roth/Banse (1932): ‘Die Verbrennungs- und Bildungswärme von Kohlenoxyd und Methan’ [312].
Traceability category: C.
The reported result of the bomb calorimetric investigation is accompanied by an uncertainty (page 3, right table). It is unclear how this uncertainty value is determined.

Traceability category: C.
This work contains no new experimental values and it is considered because the NIST Chemistry webbook [269] mentioned it in the tables for calorific values of methane. The NIST Chemistry webbook comments value in the table with ‘(calorific value) derived from Heat of Hydrogenation’. The calculation is, e. g., based on enthalpy of formation of water determined by Rossini [303] and, therefore, not traceable.

Pittam/Pilcher (1972): ‘Measurements of heats of combustion by flame calorimetry’ [287].
Traceability category: C.
The authors determined the calorific values of the hydrocarbons methane, ethane, propane, n-butane and 2-methylpropane in a flame calorimeter. The calorimeter was calibrated with the heat of combustion of hydrogen determined by Rossini [303] and the amount of burned substance is gravimetrically determined by the amount of produced carbon dioxide. The authors’ statement about the uncertainty on page 2227 is: ‘The errors …are twice the standard
deviation of the mean including the uncertainties in calibration, measurement, determination of the ignition energy ...'. Despite the fact that the system is calibrated with hydrogen, there should be a deeper uncertainty analysis of the measurement process of the produced mass of carbon monoxide, at least.

Traceability category: A.
The author presents a seemingly complete uncertainty analysis which fulfills the criterions for traceability category A.

Dale et al. (2002): ‘High precision calorimetry to determine the enthalpy of combustion of methane’ [87].
Traceability category: C.
At page 53 Dale et al. start a discussion about the uncertainty analysis. The explanation remains vague and general. The final reported measurement uncertainty cannot be recalculated by the reader.

Traceability category: C.
The paper contains a statement about the final measurement results. No uncertainty analysis of the measurement process and the evaluation procedures is given.

Haloua et al. (2015): ‘Traceable measurement and uncertainty analysis of the gross calorific value of methane determined by isoperibolic calorimetry’ [180].
Traceability category: A.
Haloua et al. examined in detail the introduced experimental results and performed a state of the art uncertainty analysis.

4.1.2. Methane: Enthalpies of vaporisation:

<table>
<thead>
<tr>
<th>Methane: Heat of vaporisation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Authors</strong></td>
</tr>
<tr>
<td>Eucken/Berger</td>
</tr>
<tr>
<td>Frank/Clusius</td>
</tr>
<tr>
<td>Frank/Clusius</td>
</tr>
<tr>
<td>Jones et al.</td>
</tr>
<tr>
<td>Colwell et al.</td>
</tr>
<tr>
<td>Cutler/Morrison</td>
</tr>
</tbody>
</table>

Eucken/Berger (1934): ‘Das I-T-Diagramm des Methans’ [130].
Traceability category: C.
At page 151, the claimed uncertainty is not supported by further explanations.

Traceability category: C.
The authors report an uncertainty for the determined heat of vaporisation of methane, but a deeper analysis of the uncertainty is omitted. The heat capacities of methane are reported without uncertainty statements.

Frank/Clusius (1939): ‘Präzisionsmessungen der Verdampfungswärme der Gase O₂, H₂S, PH₃, A, COS, CH₄ und CH₃D’ [146].
Traceability category: B.
In Chapter 4 (p. 403 ff), Frank and Clusius present their working equations, make statements about the used uncertainties of the measurable quantities. The uncertainty statement for the evaporated number of moles is about an intermediate quantity and not the measured input quantities. Also, uncertainty statements of the corrections for radiation and heat leak (e.g. lead wires and tubes) are missing. Nevertheless, the uncertainty considerations of Frank and Clusius are much more as one could expect at that time.

Jones et al. (1963): ‘Measurement of the thermodynamic properties of gases at low temperature and high pressure – methane’ [204].
Traceability category: C.
The work of Jones et al. also reports enthalpies of methane with uncertainties. Heat capacities and enthalpies of vaporisation are given without uncertainties, although Jones et al. list several uncertainties for input measurements (e.g. temperature, heat input, flow rate and pressures). A working equation and sensitivity coefficients are not reported.

Traceability category: C.
This publication is a correction of the preceding work of the same authors [76]. In the later publication, the uncertainty is only a general estimation.

Cutler and Morrison (1965): ‘Excess Thermodynamic Functions for Liquid Mixtures of Methane +Propane’ [82].
Traceability category: C.
The authors report several uncertainties of their input measurements, but it is unclear how the uncertainty of the heat capacities and enthalpies of vaporisation were determined.
4.1.3. Methane: Heat capacities (liquid/gaseous) and enthalpies:

### Methane: Heat capacity and enthalpy

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Quantity</th>
<th>Phase</th>
<th>T / K</th>
<th>Traceability category</th>
</tr>
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<tr>
<td>Millar</td>
<td>1923</td>
<td>258</td>
<td>$c_p$</td>
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<td>151</td>
<td>$c_V$</td>
<td>g</td>
<td>83-278</td>
<td>C</td>
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<td>Clusius</td>
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<td>Sage et al.</td>
<td>1937</td>
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<td>$c_p$</td>
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<td>328-378</td>
<td>C</td>
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<td>Thompson</td>
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<td>367</td>
<td>$c_{p0}$</td>
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<td>291-1500</td>
<td>C</td>
</tr>
<tr>
<td>Pitzer</td>
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<td>$c_p$</td>
<td>g</td>
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<tr>
<td>Hujsak et al.</td>
<td>1963</td>
<td>198</td>
<td>$c_p$</td>
<td>g</td>
<td>244-300</td>
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<tr>
<td>Jones et al.</td>
<td>1963</td>
<td>204</td>
<td>$c_p$</td>
<td>lq/g</td>
<td>283-394</td>
<td>C</td>
</tr>
<tr>
<td>Cutler/Morrison</td>
<td>1965</td>
<td>82</td>
<td>$c_p$</td>
<td>lq</td>
<td>94-107</td>
<td>C</td>
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<tr>
<td>Ewing/Goodwin</td>
<td>1992</td>
<td>134</td>
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<td>g</td>
<td>255-300</td>
<td>C</td>
</tr>
<tr>
<td>Trusler et al.</td>
<td>1993</td>
<td>373</td>
<td>$c_{p0}$</td>
<td>g</td>
<td>280-375</td>
<td>C</td>
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<tr>
<td>Esper et al.</td>
<td>1995</td>
<td>119</td>
<td>$c_{p0}$</td>
<td>g</td>
<td>250-350</td>
<td>C</td>
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<tr>
<td>Trusler/Zarari</td>
<td>1995</td>
<td>376</td>
<td>$c_{p0}$</td>
<td>g</td>
<td>125-250</td>
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#### Enthalpy

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>$\Delta H$</th>
<th>Phase</th>
<th>T / K</th>
<th>Traceability category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pitzer</td>
<td>1944</td>
<td>288</td>
<td>$\Delta H$</td>
<td>g</td>
<td>298-1500</td>
<td>C</td>
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<tr>
<td>Sahgal et al.</td>
<td>1964</td>
<td>326</td>
<td>$\Delta H$</td>
<td>g</td>
<td>122-228</td>
<td>A</td>
</tr>
<tr>
<td>Dillard et al.</td>
<td>1968</td>
<td>104</td>
<td>$\Delta H$</td>
<td>g</td>
<td>339</td>
<td>C</td>
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<tr>
<td>Laverman et al.</td>
<td>1968</td>
<td>228</td>
<td>$\Delta H$</td>
<td>g</td>
<td>184-208</td>
<td>C</td>
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<tr>
<td>Banks/Haselden</td>
<td>1969</td>
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<td>$\Delta H$</td>
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<td>153-373</td>
<td>B</td>
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<tr>
<td>Mather et al.</td>
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<td>$\Delta H$</td>
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<td>240-366</td>
<td>C</td>
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<tr>
<td>Dawe/Snowdon</td>
<td>1974</td>
<td>91</td>
<td>$\Delta H$</td>
<td>g</td>
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<tr>
<td>Ashton/Haselden</td>
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<td>$\Delta H$</td>
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<td>153-370</td>
<td>C</td>
</tr>
<tr>
<td>Day et al.</td>
<td>1997</td>
<td>96</td>
<td>$\Delta H$</td>
<td>g</td>
<td>295-580</td>
<td>B</td>
</tr>
</tbody>
</table>

**Millar (1923):** 'The specific heats of polyatomic gases at low temperatures' [258].

Traceability Category: C.

There is no uncertainty assessed.

**Giacomini (1925):** 'The temperature dependency of the molecular heats of gases, especially of ammonia, methane, and hydrogen, at low temperatures' [151].

Traceability category: C.

At page 147, the author refuses ('No claims are mad for the applicability of this method to measurements of precision on the absolute values of $C_V$.') any statements about an uncertainty of his measurements if his words could be interpreted in that way.
Clusius (1929): ‘Über die spezifische Wärme einiger kondensierter Gase zwischen 10° abs. und ihrem Tripelpunkt.’ [71]
Traceability category: C.
In a special section of his publication, Clusius discusses possible sources of uncertainty. The final estimation of the final uncertainty is not directly connected to the discussion of the uncertainties of the input quantities.

Traceability category: B.
At page 435 of the publication by Eucken/Lüde, a relatively complete discussion of uncertainties is introduced and supplemented by model equation for the evaluation of the measurements. The reported relative uncertainties spoil the traceability category from grade A to B.

Sage et al. (1937): ‘… XX. Isobaric Heat Capacity of Gaseous Propane, n-Butane, Isobutane and n-Pentane’ [323].
Traceability Category: C.
Some uncertainties are missing (p. 1312), e.g. of the compressibility-temperature coefficient and of the Joule-Thomson coefficients, and, therefore the stated uncertainty of the reported isobaric heat capacities is questionable.

Thompson (1941): ‘The free energy of methyl cyanide, and equilibrium constants of some related reactions’ [367].
Traceability Category: C.
Specific heat capacities were represented obtained by statistical calculations. Despite the fact, that the paper reports the results of theoretical considerations, relevant input quantities (e.g. vibration frequencies) are based on experimental work. Nevertheless, uncertainties are not presented.

Traceability category: C.
Among other thermodynamic properties the specific heat and enthalpy for methane, ethane, propane, butane and pentane were calculated. Only for the specific heat calculation the author claims an uncertainty without further discussion of details.

Sahgal et al. (1960): ‘A new high-pressure flow calorimeter for accurate measurement of enthalpy data’ [323].
Traceability category: A.
Even though there is no working or model equation introduced by the authors, the uncertainty considerations on page 229 show a complete uncertainty estimation and, therefore, a prerequisite for full traceability.

Huisak et al. (1963): ‘The specific heat of a natural gas and methane at 69 and 103 atmospheres’ [198].
Traceability category: C.
The stated uncertainty of the specific heat seems to be derived from the ‘reproducibility of calibration corrections’ (see page 90, right column, last sentence, second paragraph of [198]).

Jones et al. (1963): See section ‘Methane: Enthalpies of vaporisation’.

LNG II - Task D4.4.2 - Report on the relevant physical quantities and current data used in enthalpy and calorific value calculations.

Dillard et al. (1968): ‘Calorimetric Determination of the Isothermal Effect of Pressure on the Enthalpy of Methane and Two Methane-Propane Mixtures’ [104].
Traceability category: C.
Without further explanations, the authors state an uncertainty (‘The results are believed to be precise to within ...’, p. 928).

Laverman et al. (1968): ‘Calorimeter Helps Design Better LNG Liquefaction Cycles’ [228].
Traceability category: C.
There is no uncertainty reported for the reported change in enthalpies.

Traceability category: B.
On page 125, the authors present a budget with several uncertainty contributions, but there is no model equation reported and the contribution of the shift in the sample concentration (p. 124) is not part of the uncertainty considerations.

Mather et al. (1969): ‘The Direct Determination of the Effect of Pressure on Enthalpy of a Mixture of Methane and Propane’ [249].
Traceability category: C.
The pressure dependence of the enthalpy in a mixture of methane with 5 mol% propane was investigated with a throttling flow calorimeter. Uncertainties of measurement were only depicted in the figures 3 and 4 but were not given as values or by an uncertainty analysis.

Dawe/Snowdon (1974): ‘Enthalpy of Gaseous Methane in Range 224.00-366.70 K and 1-100 bar’ [91].
Traceability category: B.
Dawe and Snowdon discuss in their work several uncertainty sources. For the analysis of the measurements, a correction has to be applied but its uncertainty is not given. Also, the evaluation of equation (2) is not clear. These two reasons spoil a grade A traceability category.

Ashton/Haselden (1980): ‘Measurements of enthalpy and phase equilibrium for simulated natural gas mixtures and correlation of the results by a Starling equation’ [30].
Traceability category: C.
The combined uncertainty for the investigated enthalpies could not be derived from reported uncertainties (temperature, pressure, composition and heat leak).

Ewing/Goodwin (1992): ‘Speeds of sound, perfect-gas heat capacities, and acoustic virial coefficients for methane determined using a spherical resonator at temperatures between 255 K and 300 K and pressures in the range 171 kPa to 7.1 MPa’ [134].
Traceability category: C.
The authors mention many uncertainty contributions to their final results. The uncertainty assessment for the ideal heat capacity cannot be recalculated from the information given in the paper. For example, the uncertainty of the radius of the resonator is missing.

Trusler et al. (1993): ‘The speed of sound in a gaseous mixture of methane and propane’ [373].
Traceability Category: C
There is no uncertainty statement for the determined ideal heat capacities.

Traceability Category: C.
The authors reported only the uncertainty statements given in literature (p. 174). An independent uncertainty statement for the experimental results was omitted, but uncertainties for temperature and pressure are reported.
Traceability category: C.
The uncertainty of the measured pressure is not given.

Day et al. (1997): ‘A new flow calorimeter for the measurement of the isobaric enthalpy increment and the isenthalpic Joule-Thomson effect. Results for methane and (methane+ethane)’ [94].
Traceability category: B.
The authors make a general statement of the maximum uncertainty of 0.9 %. In tables 1 and 2 absolute values of the measured quantities are given and uncertainties are reported which are distinguished in type A and B (comparable to GUM [178]). A model equation is not described in the publication and how the combined uncertainty is derived.

4.2. Ethane:

4.2.1. Ethane: Heat of combustion/calorific value:

<table>
<thead>
<tr>
<th>Ethane: Calorific value</th>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Traceability category</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rossini</td>
<td>1934</td>
<td>304</td>
<td>C</td>
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<tr>
<td></td>
<td>Prosen/Rossini</td>
<td>1945</td>
<td>293</td>
<td>C</td>
</tr>
<tr>
<td></td>
<td>Pittam/Pilcher</td>
<td>1972</td>
<td>285</td>
<td>C</td>
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</tbody>
</table>

Rossini (1934): Calorimetric determination of the heats of combustion of ethane, propane, normal butane, and normal pentane’ [306].
Traceability category: C.
The combined uncertainty of the determined calorific value (p. 746) is calculated as twice the root of the squared sum of standard deviations (electrical calibration and the combustion experiment) and ‘error estimation’ due to impurities and other causes. A detailed analysis of the electrical calibration and the combustion experiment is not performed in the sense of a state-of-the-art uncertainty analysis.


### 4.2.2. Ethane: Enthalpies of fusion and vaporisation:

**Ethane: Enthalpy of fusion/vaporisation**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>$T / K$</th>
<th>Traceability category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wiebe et al.</td>
<td>1930</td>
<td>398</td>
<td>87-91</td>
<td>C</td>
</tr>
<tr>
<td>Witt/Kemp</td>
<td>1937</td>
<td>407</td>
<td>87-92</td>
<td>C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>$T / K$</th>
<th>Traceability category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Witt/Kemp</td>
<td>1937</td>
<td>407</td>
<td>184</td>
<td>C</td>
</tr>
<tr>
<td>Miyazaki et al.</td>
<td>1980</td>
<td>260</td>
<td>289/301</td>
<td>B</td>
</tr>
</tbody>
</table>

### Enthalpy of fusion

**Wiebe et al. (1930):** 'The heat capacity of saturated liquid ethane from the boiling point to the critical temperature and heat of fusion of the solid' [398].

Traceability category: C.

Most of the uncertainties of the input quantities are missing, e.g., sample mass and temperature.

**Witt/Kemp (1937):** 'The Heat Capacity of Ethane from 15 K to the Boiling Point. The Heat of Fusion and the Heat of Vaporization' [407].

Traceability category: C.

The stated uncertainties are not supported by any kind of evaluation of the uncertainties of the relevant input quantities.

**Miyazaki et al. (1980):** 'A new high-pressure recycle-flow calorimeter and results of determinations with ethane' [260].

Traceability category: B.

In a table at page 112 of their publication, the authors show which kind of instruments they used, where the measurement devices were calibrated and the estimated accuracy. Nevertheless, for a fully traceable measurement result, the sensitivity coefficients should be at least reported to allow a recalculation of the stated uncertainty.
4.2.3. Ethane: Heat capacities (solid/liquid/gaseous):

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Quantity</th>
<th>Phase</th>
<th>$T / K$</th>
<th>Traceability Category</th>
</tr>
</thead>
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<tr>
<td>Eucken/Hauck</td>
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<td>100-270</td>
<td>C</td>
</tr>
<tr>
<td>Thayer/Stegeman</td>
<td>1930</td>
<td>366</td>
<td>$c_p$</td>
<td>g</td>
<td>275-337</td>
<td>C</td>
</tr>
<tr>
<td>Wiebe et al.</td>
<td>1930</td>
<td>399</td>
<td>$c_p$</td>
<td>s/lq/g</td>
<td>67-305</td>
<td>C</td>
</tr>
<tr>
<td>Eucken/Parts</td>
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<td>128</td>
<td>$c_p$</td>
<td>lq/g</td>
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<td>C</td>
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<td>Eucken/Weigert</td>
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<td>129</td>
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<td>Witt/Kemp</td>
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<td>s/lq/g</td>
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<td>g</td>
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<td>C</td>
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<tr>
<td>Kistiakowsky et al.</td>
<td>1939</td>
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<td>C</td>
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<tr>
<td>Thompson</td>
<td>1941</td>
<td>367</td>
<td>$c_{p0}$</td>
<td>g</td>
<td>291-1000</td>
<td>C</td>
</tr>
<tr>
<td>Dailey/Felsing</td>
<td>1943</td>
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<td>C</td>
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<tr>
<td>Pitzer</td>
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<td>288</td>
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<td>g</td>
<td>298-1500</td>
<td>C</td>
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<tr>
<td>Bier et al.</td>
<td>1976</td>
<td>49</td>
<td>$c_p$</td>
<td>g</td>
<td>283-473</td>
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<tr>
<td>Esper et al.</td>
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<td>119</td>
<td>$c_{p0}$</td>
<td>g</td>
<td>223-350</td>
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<tr>
<td>Abdulagatov et al.</td>
<td>1996</td>
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<td>lq/g</td>
<td>292-376</td>
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<td>$c_V$</td>
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<tr>
<td>Mu et al.</td>
<td>2003</td>
<td>264</td>
<td>$c_V$</td>
<td></td>
<td>309</td>
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<td>Miyazaki et al.</td>
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<td>260</td>
<td>$\Delta H$</td>
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<td>275-313</td>
<td>B</td>
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<tr>
<td>Pitzer</td>
<td>1944</td>
<td>288</td>
<td>$\Delta H$</td>
<td>g</td>
<td>298-1500</td>
<td>C</td>
</tr>
</tbody>
</table>

Eucken/Hauck (1928): ‘Die spezifischen Wärmen $c_p$ und $c_v$ einiger Stoffe im festen, flüssigen und hyperkritischen Gebiet zwischen 80° und 320° abs’ [126].
Traceability category: C.
The claimed uncertainty of measurement on page 166 cannot be reproduced from the information given in the text.

Thayer/Stegeman (1930): ‘The heat capacity and free energy of formation of ethane gas’ [366].
Traceability category: C.
There is no uncertainty statement.

Wiebe et al. (1930): See section ‘Ethane: Heat of fusion and vaporization’.

Eucken/Parts (1933): ‘Die Molwärmen und Normalschwingungen des Äthans und Äthylens’ [128].
Traceability category: C.
The uncertainty of the determined heat capacity of ethane could not be reproduced by the information given in the publication.

Eucken/Weigert (1933): ‘Eine Bestimmung der inneren Rotationswärme des Äthans’ [129].
Traceability category: C.
The authors claim an uncertainty between 0.5 and 1%. The description of the experiments makes the latter statement not transparent.


Traceability category: C.
The authors derive no uncertainty statement for their measurement results.

Kistiakowsky et al. (1939): ‘The Low Temperature Gaseous Heat Capacities of C2H6 and C2D6’ [216].
Traceability category: C.
In the whole publication, the discussion of uncertainties is avoided.

Thompson (1941): See section 'Methane: Heat capacity ...'.

Dailey/Felsing (1943): ‘The Heat Capacities at Higher Temperatures of Ethane and Propane’ [85].
Traceability category: C.
With an adiabatic flow calorimeter, heat capacities were determined over a temperature range of 340-700 K. An uncertainty (‘accuracy’, p. 42) is claimed but not supported by a detailed uncertainty analysis.

Pitzer (1944): See section 4.1.3 ‘Methane: heat capacity and enthalpy’.

Bier et al. (1976): ‘Experimental Results for Heat Capacity and Joule-Thomson Coefficient of Ethane at Zero Pressure’ [49]
Traceability category: C.
Isobaric heat capacities were measured with a flow calorimeter. The stated measurement uncertainty of 0.1% for \( c_p \) is not supported by an uncertainty analysis. Only the purity of the sample is mentioned and could be identified as possible uncertainty contribution.

Miyazaki et al. (1980): See section 4.2.1 ‘Ethane: Enthalpies of fusion and vaporisation’.


Abdulagatov et al. (1996): ‘Experimental and Theoretical Studies of the Crossover Behaviour of the Specific Heat \( C_{V,X} \) of Ethane, Propane, and Their Mixture at Critical Isochores’ [5].
Traceability Category: B.
The uncertainty of the heat capacity of the empty calorimeter is not presented. Additionally, uncertainties of the current and voltage are missing. Absolute values of the input quantities would also be useful to recalculate the stated uncertainty of the heat capacities by the reader.

Mu et al. (2003): ‘Effect of phase behaviour, density, and isothermal compressibility on the constant-volume heat capacity of ethane + n-pentane mixed fluids in different phase regions’ [264].
Traceability Category C:
The stated measurement uncertainty for \( C_V \) cannot be derived from the information given in the publication. Some uncertainties of input quantities (e.g. volume of calorimetric cell and density of the fluid) and the sensitivity coefficients are missing.
4.3. Propane:

4.3.1. Propane: Heat of combustion/Calorific value:

<table>
<thead>
<tr>
<th>Propane: Calorific value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Authors</strong></td>
</tr>
<tr>
<td>Rossini</td>
</tr>
<tr>
<td>Prosen/Rossini</td>
</tr>
<tr>
<td>Pittam/Pilcher</td>
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</table>


4.3.2. Propane: Enthalpies of fusion/vaporisation:

<table>
<thead>
<tr>
<th>Propane: Enthalpy of fusion/vaporisation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Authors</strong></td>
</tr>
<tr>
<td>Kemp/Egan</td>
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<td>Sage et al.</td>
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<td>Sage et al.</td>
</tr>
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<td>Cutler</td>
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<td>Helgeson/Sage</td>
</tr>
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<td>Abdulagatov et al.</td>
</tr>
<tr>
<td>Perkins et al.</td>
</tr>
</tbody>
</table>


Traceability category: C.

There is no uncertainty assessment for the reported enthalpies, enthalpies of vaporisation and heat capacities.


Traceability Category: C.
There are uncertainty statements for the heat of fusion and vaporisation but there are no further explanations how this uncertainty values are determined. No uncertainty is given for the reported heat capacities.

**Sage et al. (1939):** ‘... Latent Heat of Vaporization of Propane and n-Pentane’ [325].
*Traceability Category: B.*
Uncertainties for the measured electrical quantities voltage and current are not reported. The authors also admit a contradiction between precision of the directly measured quantities and the final experimental results. This indicates some neglected or not recognisable uncertainty contributions to the result.

**Cutler and Morrison (1965):** See section 4.1.2 ‘Methane: Enthalpies of vaporisation’.

*Traceability Category: C*
The stated uncertainty is the deviation from a reference equation.

**Abdulagatov et al. (1995):** ‘Thermodynamic properties of propane in the critical region’ [4].
*Traceability Category: C (for the quantity enthalpy of vaporisation).*
For the enthalpy of vaporisation, no uncertainty is reported.

**Perkins et al. (2009):** See section 4.3.3 ‘Propane: Heat capacities ...’.
4.3.3. Propane: Heat capacities (liquid/gaseous):

Propane: Heat capacity and enthalpy

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Quantity</th>
<th>Phase</th>
<th>$T / K$</th>
<th>Traceability category</th>
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<tr>
<td>Sage et al.</td>
<td>1934</td>
<td>316</td>
<td>$c_p$</td>
<td>294-378</td>
<td>C</td>
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<tr>
<td>Sage/Lacey</td>
<td>1935</td>
<td>318</td>
<td>$c_p$</td>
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<td>289-378</td>
<td>C</td>
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<tr>
<td>Sage et al.</td>
<td>1937</td>
<td>323</td>
<td>$c_p$</td>
<td>g</td>
<td>294-444</td>
<td>C</td>
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<td>Kemp/Egan</td>
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<td>s/lq/g</td>
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<tr>
<td>Pitzer</td>
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<td>289</td>
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<td>Cutler/Morrison</td>
<td>1965</td>
<td>82</td>
<td>$c_p$</td>
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<td>C</td>
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<tr>
<td>Ernst</td>
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<td>g</td>
<td>293-363</td>
<td>B</td>
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<td>Ernst/Büsser</td>
<td>1970</td>
<td>113</td>
<td>$c_p$</td>
<td>g</td>
<td>293-353</td>
<td>C</td>
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<td>Esper et al.</td>
<td>1995</td>
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<td>230-350</td>
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<tr>
<td>Abdulagatov et al.</td>
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<td>Abdulagatov et al.</td>
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<td>Trusler/Zarari</td>
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<td>He et al.</td>
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<td>Perkins et al.</td>
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</table>

Sage et al. (1934): See section 4.3.2 ‘Propane: Enthalpy of vaporisation’.

Sage/Lacey (1935): ‘Phase Equilibria in Hydrocarbon Systems IX. Specific Heats of n-Butane and Propane’ [318].
Traceability category: C.
For the presented specific heat capacities Sage/Lacey make a general statement about the uncertainty (p.1486). An uncertainty analysis is not presented to assess the combined uncertainty.

Sage et al. (1937): See section 4.1.2 ‘Methane: Enthalpies of vaporisation’.

Kemp/Egan (1938): See section 4.3.2 ‘Propane: Enthalpy of fusion and vaporisation’.

Dailey/Felsing (1943): See section 4.2.3 ‘Ethane: Heat capacities …’.

Pitzer (1944)a/b: See section 4.1.3 ‘Methane: Heat capacity and enthalpy’.


Sage et al. (1934) 316 $\Delta H$ 294-378 C
Pitzer (1944) 288 $\Delta H$ 298-1500 C
Pitzer (1944b) 289 $\Delta H$ 180-1500 C
Traceability category: B.
The determined specific heat constant values have a traceability close to category A. Only the
electric heating power is given as intermediate values and the extrapolation of mass flow to
zero is applied as a correction without an uncertainty contribution.

Ernst/Büsser (1970): 'Ideal and real gas state heat capacities $C_P$ of C$_3$H$_8$, i-C$_4$H$_{10}$, C$_3$F$_3$Cl,
CH$_2$ClCF$_3$, CF$_2$ClFCCl$_2$, and CHF$_2$Cl' [113].
Traceability Category: C.
The model equation and several input quantities are missing. Uncertainties for voltage and
current to satisfy the stated uncertainty of the electric heating power should be communicated.
The uncertainty and sensitivity coefficients for the important thermodynamic property
‘pressure’ are not reported.


Abdulagatov et al. (1995): See section 4.2.3 ‘Ethane: Heat capacities …’; reference
Abdulagatov et al. [5].

Abdulagatov et al. (1996): See section 4.2.3 ‘Ethane: Heat capacities …’.

Trusler/Zarari (1996): ‘The speed of sound in gaseous propane at temperatures between 225
K and 375 K and at pressures up to 0.8 MPa’ [377].
Traceability category: B.
The uncertainty of ($u/a_0$) should be explained more in detail as it is a key element of the
experimental work. Some other uncertainties are missing, e.g. uncertainties for applied
corrections (p. 330), amount-of-substance and parameters ($a$, $b$ and $c$) of Eq. (3).

He et al. (2002): ‘Measurement of Speed of Sound with a Spherical Resonator: HCFC-22,
HFC-152a, HFC-143a, and Propane’ [185].
Traceability category: C.
For the speed of sound measurements, an uncertainty is reported and uncertainties for the
input quantities are given. The uncertainty statement for the ideal heat capacities is missing.

Constant Volume from (85 to 345) K with Pressures up to 35 MPa’ [283].
Traceability Category: B.
With an adiabatic calorimeter (originally described by Goodwin [161]) isochoric heat capacities
and enthalpies of fusion were determined. The authors give a model equation (see [283], Eq.
(2)) and discuss in detail all uncertainty sources in relative quantities in a special section about
‘Assessment of Uncertainty’ (p. 3199 ff). This discussion of relative uncertainties makes it
difficult to recognise the absolute values of the input quantities measured and, therefore, a
calculation of the stated uncertainty starting with the model equation given by the authors is
not possible. Also, for a fully traceable measurement result it is necessary to report absolute
measured quantities as the comparisons in the traceability chain depend in most cases on the
measurement range to which standard the measurement has to be related.
4.4. Butane and Iso-Butane:

4.4.1. Butane and Iso-Butane: Heat of combustion/calorific value:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Traceability category</th>
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<tbody>
<tr>
<td>Rossini</td>
<td>1934</td>
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<td>C</td>
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<tr>
<td>Prosen et al.</td>
<td>1951</td>
<td>297</td>
<td>C</td>
</tr>
<tr>
<td>Pittam/Pilcher</td>
<td>1972</td>
<td>287</td>
<td>C</td>
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</table>


Prosen et al. refer to reference No. 1 [296] for their method of assigning uncertainties. In that reference, the authors refer (now its reference No. 5) to another paper [311]. That publication of Rossini/Deming (1939) explains how the uncertainties are assessed in principle. The uncertainties are the standard deviation of the mean value measured.


4.4.2. Butane and Iso-Butane: Enthalpies of vaporisation:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>$T / K$</th>
<th>Traceability category</th>
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</thead>
<tbody>
<tr>
<td>Perkins/Magee</td>
<td>2009</td>
<td>282</td>
<td>114</td>
<td>B</td>
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</tbody>
</table>

The authors discuss apparently most of the import uncertainty contributions. A model equation is given and uncertainties of the enthalpy and enthalpy of vaporisation are assessed.

Sage et al. (1938): See section 4.4.3 ‘Butan and Iso-Butane: Heat capacities …’.

Perkins/Magee (2009): See section ‘4.4.3 Butan and Iso-Butane: Heat capacities …’.

### 4.4.3. Butane and Iso-Butane: Heat capacities (liquid/gaseous):

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Quantity</th>
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<th>Traceability Category</th>
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<td>1935</td>
<td>318</td>
<td>$c_p$</td>
<td>lq</td>
<td>289-378</td>
<td>C</td>
</tr>
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<td>Sage et al.</td>
<td>1937a</td>
<td>323</td>
<td>$c_p$</td>
<td>g</td>
<td>294-394</td>
<td>C</td>
</tr>
<tr>
<td>Sage et al.</td>
<td>1937b</td>
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<td>C</td>
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<td>Dailey/Felsing</td>
<td>1943</td>
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<td>345-693</td>
<td>C</td>
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<tr>
<td>Pitzer</td>
<td>1944</td>
<td>288</td>
<td>$c_p$</td>
<td>g</td>
<td>298-1500</td>
<td>C</td>
</tr>
<tr>
<td>Ewing et al.</td>
<td>1988</td>
<td>137</td>
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<td>g</td>
<td>250-320</td>
<td>C</td>
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<tr>
<td>Colgate et al.</td>
<td>1990</td>
<td>75</td>
<td>$c_{p0}$</td>
<td>g</td>
<td>298-348</td>
<td>C</td>
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<tr>
<td>Magee/Lüddecke</td>
<td>1998</td>
<td>245</td>
<td>$c_V$</td>
<td>lq</td>
<td>141-342</td>
<td>C</td>
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<tr>
<td>Iso-Butane</td>
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<tr>
<td>Sage et al.</td>
<td>1937b</td>
<td>322</td>
<td>$c_p$</td>
<td>g</td>
<td>294-444</td>
<td>C</td>
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<tr>
<td>Sage et al.</td>
<td>1938</td>
<td>324</td>
<td>$c_p$</td>
<td>g</td>
<td>294-394</td>
<td>C</td>
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<tr>
<td>Dailey/Felsing</td>
<td>1943</td>
<td>86</td>
<td>$c_p$</td>
<td>g</td>
<td>348-693</td>
<td>C</td>
</tr>
<tr>
<td>Ernst/Büsser</td>
<td>1970</td>
<td>114</td>
<td>$c_p$</td>
<td>g</td>
<td>293-353</td>
<td>C</td>
</tr>
<tr>
<td>Colgate et al.</td>
<td>1990</td>
<td>75</td>
<td>$c_{p0}$</td>
<td>g</td>
<td>298-348</td>
<td>C</td>
</tr>
<tr>
<td>Ewing/Goodwin</td>
<td>1991</td>
<td>138</td>
<td>$c_{p0}$</td>
<td>g</td>
<td>251-320</td>
<td>C</td>
</tr>
<tr>
<td>Perkins/Magee</td>
<td>2009</td>
<td>282</td>
<td>$c_V$</td>
<td>s/lq</td>
<td>114-345</td>
<td>B</td>
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<tr>
<td>Liu et al.</td>
<td>2017</td>
<td>237</td>
<td>$c_p$</td>
<td>lq</td>
<td>303-413</td>
<td>B</td>
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</table>

Sage et al. (1935): See section 4.3.3 ‘Propane: Heat capacity …’.

Sage et al. (1937a): See section 4.4.2 ‘Butane and Iso-Butane: Enthalpy of vaporisation’.

Sage et al. (1937b): See section 4.1.3 'Methane: Heat capacities ...'.


In the temperature range from 121 K to 394 K several thermodynamic properties (specific volume, vapour pressure, heat capacities, Joule-Thomson coefficient and latent heat of vaporisation) of Iso-Butane were investigated. The authors made statements about the uncertainties of the heat capacity (p. 674, left column: ‘It is believed that the heat capacity data … are not in error by more than 1 per cent …’) and for latent heats of vaporisation (p. 674, right column: ‘… uncertainty of less than 1.0 per cent …’). The derivation of this uncertainty...
statements is not given. Nevertheless, in case of the pressure-volume-temperature measurements (p. 673, right column) uncertainties for important measurable input quantities (pressure, temperature, sample volume and mass, purity grade of the sample) are reported.

Dailey/Felsing (1943): ‘Heat Capacities of and Hindered Rotation in n-Butane and Isobutane’ [86].
Traceability category: C.
The ‘estimated maximum experimental error …’ (p. 45) is claimed but not further analysed.

Pitzer (1944): See section 4.2.3 ‘Methane: Heat capacities …’.

Ernst/Büsser (1970): See section 4.3.3 ‘Propane: heat capacities …’.

Ewing et al. (1988): ‘Thermophysical properties of alkanes from speed of sound determined using a spherical resonator; 2. n-Butane’ [137].
Traceability category: C.
The authors discuss several uncertainties of the input quantities despite the fact that some of these values are missing (e.g. temperature, viscosity, density and radius of the resonator). Additionally, the uncertainty statement for the ideal (or perfect) gas heat capacity is not given.

Ewing/Goodwin (1991): ‘Thermophysical properties of alkanes from speeds of sound determined using a spherical resonator 4. 2-Methylpropane at temperatures in the range 251 K to 320 K and pressures in the range 5 kPa to 114 kPa’ [138].
Traceability category: C.
The combined uncertainty could not be reproduced form the information given in the publication.

Colgate et al. (1990): ‘Experimental Ideal Gas Reference State Heat Capacities of Gases’ [75].
Traceability category: C.
The ideal heat capacities are derived from speed of sound measurements (SOS) and several uncertainties are reported. An uncertainty for the ideal heat capacity is not reported.

Magee/Lüddecke (1998): ‘Molar Heat Capacity at Volume of n-Butane at Temperatures from 141 to 342 K and at Pressures at 33 MPa’ [245].
Traceability category: C.
At page 140, the authors refer to their reference No. 15 (Lüddecke T. O. and Magee J. W., Int. J. Thermophys. 17, 823 (1996)) where a detailed discussion of the uncertainties should be available. The latter reference is about heat capacity measurements of difluoromethane and pentafluoroethane but not of n-Butane.

Perkins/Magee (2009): ‘Molar Heat Capacity at Constant Volume for Isobutane at Temperatures from (114 to 345) K and at Pressures to 35 MPa’ [282].
Traceability category: B.
The discussion is similar to Perkings et al. [283] (see section 4.3.3 ‘Propane: Heat capacities …’).

Liu et al. (2017): ‘Heat capacity of isobutane in liquid phase at temperatures from 303 K to 413 K and pressures up to 12 MPa’ [237].
Traceability category: B.
Liu et al. only report the uncertainty of the heat flux Q (p. 266, right column) being an intermediate quantity. The uncertainties of the input measurements, as written in the paper (‘The voltage and current could be measured by a multimeter.’), voltage and current are not given. Also, the uncertainty contribution of the extrapolation procedure of the sample mass \(1/m \rightarrow 0\) to the expanded uncertainty in Eq. (3) is missing.
4.5. Pentane and Iso-Pentane:

4.5.1. Pentane and Iso-Pentane: Heat of combustion/Calorific value:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Traceability category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rossini</td>
<td>1934</td>
<td>306</td>
<td>C</td>
</tr>
<tr>
<td>Prosen/Rossini</td>
<td>1944</td>
<td>293</td>
<td>C</td>
</tr>
<tr>
<td>Pilcher/Chadwick</td>
<td>1967</td>
<td>286</td>
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<tr>
<td>Good</td>
<td>1970</td>
<td>160</td>
<td>C</td>
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</tbody>
</table>

Pentane und Iso-Pentane: Calorific value

Rossini (1934): See section 4.2.1 ‘Ethane: Heat of combustion …’.

Traceability category: C.
It is unclear how the stated uncertainty of the measurement result is derived, e. g. the uncertainty of the calorific value of the used benzoic acid calibration is missing. Several corrections are applied (temperature and pressure) but no uncertainties are estimated for these corrections.

Knowlton/Rossini (1939): ‘Heats of combustion of tetramethylmethane and 2-methylbutane’ [220].
Traceability category: C.
The measurement results are accompanied by numerical uncertainty values. The origin of these values is unclear.

Traceability category: C.
The uncertainties reported are twice the standard deviation of the mean.

Traceability category: C.
The used bomb calorimeter is calibrated with a standard reference material with a known uncertainty of the energy content. Nevertheless, it is not comprehensible how the final uncertainties of the measurement results were assessed.

### 4.5.2. Pentane and Iso-Pentane: Enthalpies of vaporisation:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>$T$ / K</th>
<th>Traceability Category</th>
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</thead>
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<td>170</td>
<td>255-298</td>
<td>C</td>
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<tr>
<td>Sage et al.</td>
<td>1939</td>
<td>325</td>
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<td>Messerly/Kennedy</td>
<td>1940</td>
<td>255</td>
<td>293</td>
<td>C</td>
</tr>
<tr>
<td>Hossenlopp/Scott</td>
<td>1981</td>
<td>195</td>
<td>259-290</td>
<td>C</td>
</tr>
</tbody>
</table>

Griffiths/Awbery (1932): ‘The latent heat of some refrigerants’ [170].
Traceability category: C.
No uncertainty statement is given by the authors.

Sage et al. (1939): See section ‘Propane: Enthalpy of vaporisation’.

Messerly/Kennedy (1940): ‘The heat Capacity and Entropy, Heats of Fusion and Vaporization and the Vapor Pressure of n-Pentane’ [255].
Traceability category: C.
For all three quantities investigated in the publication uncertainties are given but it is unclear how these uncertainties were assessed.

Traceability category: C.
The authors make only a general statement about the experimental uncertainty (p. 417) without further considerations. This publication belongs to a series of publications [194, 195, 196] and Todd et al. [368]. In the first publication of Todd et al. [368], one gets the impression that for the authors ‘precision’ is the same as uncertainty if one considers the statement ‘Temperatures were measured with a precision of 0.001 or 0.002 K’ (p. 643). On the other side, ‘precision’ is deduced as deviation of the experimental values from a fit.
4.5.3. Pentane and Iso-Pentane: Heat capacities (liquid/gaseous):

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Quantity</th>
<th>Phase</th>
<th>T / K</th>
<th>Traceability Category</th>
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<tr>
<td>Sage et al.</td>
<td>1935</td>
<td>317</td>
<td>(c_p)</td>
<td>g</td>
<td>294-377</td>
<td>C</td>
</tr>
<tr>
<td>Sage et al.</td>
<td>1937</td>
<td>323</td>
<td>(c_p)</td>
<td>g</td>
<td>311-428</td>
<td>C</td>
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<tr>
<td>Messerly/Kennedy</td>
<td>1940</td>
<td>255</td>
<td>(c_p)</td>
<td>s/lq</td>
<td>12-286</td>
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<tr>
<td>Pitzer</td>
<td>1944</td>
<td>288</td>
<td>(c_p)</td>
<td>g</td>
<td>298-1500</td>
<td>C</td>
</tr>
<tr>
<td>Hossenlopp/Scott</td>
<td>1981</td>
<td>195</td>
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<td>g</td>
<td>298-523</td>
<td>C</td>
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<tr>
<td>Ewing et al.</td>
<td>1989</td>
<td>137</td>
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<td>C</td>
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<td>Guthrie et al.</td>
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<td>s/lq</td>
<td>13-300</td>
<td>C</td>
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</tbody>
</table>

Traceability category: C.
The uncertainty is only stated without further analysis.

Sage et al. (1937): See section 4.1.3 ‘Methane: Heat capacities …’.

Messerly/Kennedy (1940): See section 4.5.2 ‘Pentane and Iso-Pentane: enthalpy of vaporisation’.

Guthrie et al. (1943): ‘Thermal Data. XVI. The heat capacity and entropy of isopentane. The absence of a reported anomaly’ [176].
Traceability category: C.
No uncertainty is presented for the heat capacity of Iso-pentane.

Pitzer (1944): See section 4.1.3 ‘Methane: Heat capacities …’.


Ewing et al. (1989): ‘Thermophysical properties of alkanes from speeds of sound determined using a spherical resonator 3. n-Pentane’ [137].
Traceability category: C.
The uncertainty estimation is not comprehensible, and values of important uncertainty contributions are missing (e.g. radius of the resonator).
4.6. Nitrogen:

4.6.1. Nitrogen: Enthalpy of vaporisation:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>$T / K$</th>
<th>Traceability category</th>
</tr>
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<tbody>
<tr>
<td>Alt</td>
<td>1906</td>
<td>11</td>
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<tr>
<td>Witt</td>
<td>1912</td>
<td>406</td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Eucken</td>
<td>1916</td>
<td>124</td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Giauque/Clayton</td>
<td>1933</td>
<td>154</td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Furukawa/McCoskey</td>
<td>1953</td>
<td>150</td>
<td>62-78</td>
<td>C</td>
</tr>
<tr>
<td>Mage et al.</td>
<td>1963</td>
<td>240</td>
<td>119-124</td>
<td>C</td>
</tr>
</tbody>
</table>

Traceability category: C.
On page 764, the author claims an uncertainty of zero for all input quantities measured with one exception. This exception leads the author to the estimation of a 1% uncertainty of his measurements.

Witt (1912): ‘Über die Verdampfungswärme flüssiger Luft’ [406].
Traceability category: C.
There is no uncertainty statement for the determined heat of vaporisation.

Eucken (1916): ‘Über das thermische Verhalten einiger komprimierter und kondensierter Gase bei tiefen Temperaturen’ [124].
Traceability category: C.
The publication reports no uncertainty statement for the determined heat capacities and enthalpies of vaporisation for nitrogen and oxygen.

Giauque/Clayton (1933): ‘The Heat Capacity and Entropy of Nitrogen. Heat of Vaporization. Vapor Pressures of Solid and Liquid. The Reaction $\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$ from Spectroscopic Data’ [154].
Traceability category: C.
The authors make no uncertainty statements for the determined heat of vaporization and heat capacity of nitrogen.

Furukawa/McCoskey (1953): ‘The condensation line of air and the heats of vaporisation of oxygen and nitrogen’ [150].
Traceability category: C.
The authors compare their results with the findings of other researchers. An uncertainty statement is missing.


Giauque/Clayton (1933): ‘The Heat Capacity and Entropy of Nitrogen. Heat of Vaporization. Vapor Pressures of Solid and Liquid. The Reaction $\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$ from Spectroscopic Data’ [154].
4.6.2. Nitrogen: Heat capacities:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Quantity Phase</th>
<th>T / K</th>
<th>Traceability Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheel/Heuse</td>
<td>1913</td>
<td>329</td>
<td>$c_p$</td>
<td>g</td>
<td>90/291</td>
</tr>
<tr>
<td>Eucken</td>
<td>1916</td>
<td>124</td>
<td>$c_p$</td>
<td>s/lq/g</td>
<td>16-73</td>
</tr>
<tr>
<td>Keesom/Kamerlingh Onnes</td>
<td>1916</td>
<td>206</td>
<td>$c_p$</td>
<td>g</td>
<td>15-62</td>
</tr>
<tr>
<td>Shilling/Partington</td>
<td>1928</td>
<td>337</td>
<td>$c_V$</td>
<td>g</td>
<td>273-1273</td>
</tr>
<tr>
<td>Clusius</td>
<td>1929</td>
<td>71</td>
<td>$c_p$</td>
<td>s/lq/g</td>
<td>10-74</td>
</tr>
<tr>
<td>Eucken/Lüde</td>
<td>1929</td>
<td>127</td>
<td>$c_p$</td>
<td>g</td>
<td>304-479</td>
</tr>
<tr>
<td>Krase/Mackey</td>
<td>1930a</td>
<td>222</td>
<td>$c_p$</td>
<td>g</td>
<td>303</td>
</tr>
<tr>
<td>Krase/Mackey</td>
<td>1930b</td>
<td>223</td>
<td>$c_p$</td>
<td>g</td>
<td>303-423</td>
</tr>
<tr>
<td>Mackey/Krase</td>
<td>1930</td>
<td>239</td>
<td>$c_p$</td>
<td>g</td>
<td>303-423</td>
</tr>
<tr>
<td>Giauque/Clayton</td>
<td>1933</td>
<td>154</td>
<td>$c_p$</td>
<td>s/lq</td>
<td>16-78</td>
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<tr>
<td>Reobuck et al.</td>
<td>1935</td>
<td>302</td>
<td>$c_p$</td>
<td>g</td>
<td>173-573</td>
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<tr>
<td>Mage et al.</td>
<td>1963</td>
<td>240</td>
<td>$c_p$</td>
<td>lq/g</td>
<td>125-280</td>
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<tr>
<td>Voronel et al.</td>
<td>1966</td>
<td>383</td>
<td>$c_V$</td>
<td>lq</td>
<td>106-126</td>
</tr>
<tr>
<td>Magee</td>
<td>1991</td>
<td>241</td>
<td>$c_V$</td>
<td>lq/g</td>
<td>65-300</td>
</tr>
<tr>
<td>Perkins et al.</td>
<td>1991</td>
<td>281</td>
<td>$c_p$</td>
<td>g</td>
<td>102-303</td>
</tr>
<tr>
<td>Ewing/Trusler</td>
<td>1992</td>
<td>139</td>
<td>$c_p$</td>
<td>g</td>
<td>80-373</td>
</tr>
<tr>
<td>Esper et al.</td>
<td>1995</td>
<td>119</td>
<td>$c_p$</td>
<td>g</td>
<td>232-350</td>
</tr>
</tbody>
</table>

**Enthalpy**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>$\Delta H$</th>
<th>Traceability Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sahgal et al.</td>
<td>1964</td>
<td>326</td>
<td>$\Delta H$</td>
<td>g 122-228 A</td>
</tr>
<tr>
<td>Dawe/Snowdon</td>
<td>1974</td>
<td>92</td>
<td>$\Delta H$</td>
<td>g 150-450 C</td>
</tr>
<tr>
<td>Dawe/Snowdon</td>
<td>1974</td>
<td>93</td>
<td>$\Delta H$</td>
<td>g 273-373 C</td>
</tr>
</tbody>
</table>

Traceability category: C.
An uncertainty of the heat capacities measured is estimated (p. 485) and a model equation for the evaluation of the experiments is given (p. 477), but a discussion of uncertainty contributions does not take place.


Keesom/Kamerlingh Onnes (1916): ‘The specific heat at low temperatures. III. Measurements of the specific heat of solid nitrogen between 14° K and the triple point and of liquid nitrogen between the triple point and the boiling point’ [206].
Traceability category: C.
In the publication, no uncertainty statement is given for the investigated specific heat.

Shilling/Partington (1928): ‘Measurements of the Velocity of Sound in Air, Nitrogen, and Oxygen, with Special Reference to the Temperature Coefficients of the Molecular Heats’ [337].
Traceability category: C.
The heat capacities determined are presented without uncertainty statements.
Clusius (1929): See section 4.1.3 'Methane: heat capacities ...'.

Eucken/Lüde (1929): See section 4.1.3 'Methane: heat capacities ...'.

Krase/Mackey (1930a): ‘The specific heats of gases at high pressures. I. Method and apparatus at room temperature’ [222].
Traceability category: C
The uncertainties of the measurements with adiabatic constant temperature flow calorimeter are extensively discussed (p.113 ff). A model equation is not reported and it is not clear if the authors’ statement ‘the results are reproducible ... better than 0.5% ...’ (p. 115) can be interpreted as the combined uncertainty.

Krase/Mackey (1930b): ‘The specific heats of gases at high pressures. II. Method and apparatus at high temperatures’ [223].
Traceability category: C
There is no statement about the uncertainty of the measured heat capacities.

Mackey/Krase (1930): ‘Specific Heats of Gases at High pressures III-Results for Nitrogen to 150° C and 700 Atmospheres’ [239].
Traceability category: B.
The authors apparently discuss all relevant uncertainties of the input quantities to determine the heat capacities with the presented experiment. The model equation is described in an acceptable way in a continuous text (and not by a formula). Due to the missing absolute values of the sensitivity coefficients it is not possible to recalculate the state uncertainty. This last drawback spoils the grade A.


Traceability category: C.
Uncertainties for the reported heat capacities are not given in the paper. There is only a hint on some uncertainty considerations by the authors on page 457: ‘Examination of the Table V shows agreement within the expected error’.

Mage et al. (1963): ‘Experimental enthalpies for nitrogen’ [240].
Traceability category: C.
In the publication, no uncertainty budget is given for the measurement results of table 1 and 2. The stated uncertainty in the abstract refers to calculated enthalpies in the pressure-enthalpy chart.

Sahgal et al. (1964): See section 4.1.3 'Methane: heat capacities ...'.

Voronel et al. (1966): ‘Specific heat of nitrogen near the critical point’ [383].
Traceability category: C.
The specific heat $C_V$ of nitrogen was measured with a calorimeter near the critical point. The authors make a general statement about the uncertainty of their $C_V$ measurements (see abstract: ‘... experimental errors do no exceed 5 %.’). The uncertainty of the purity of the investigated sample is given (see abstract: ‘...accuracy to ≈0.02%.’) also, but no further important uncertainties of the calorimetric investigation are reported, e. g. the amount of heat released in the calorimeter or the temperature rise.

Traceability category: C.
The authors determined with a Joule-Thomson expansions apparatus the enthalpy change of nitrogen and state a general uncertainty of ±3 J/mol. The uncertainty statement cannot be recalculated from the information given in the publication.

Dawe/Snowdon (1974): 'Experimental high-pressure enthalpies of N₂(g) and CO₂(g) in the range 273.15 to 373.15 K' [93].
Traceability category: C.

Enthalpy changes were determined by the measurement of the Joule-Thomson effect (10 isotherms). Dawe/Snowdon report typical experimental parameters (table 1) but omit the uncertainties of these parameters. The uncertainty for the enthalpy remains a mere statement despite the explanation 'After a close examination of the experimental measurements, the deviations from the polynomial fittings and the accuracy of the enthalpies at atmospheric pressure ...' (p. 300).

Magee (1991): 'Molar Heat Capacity \((C_V)\) for Saturated and Compressed Liquid and Vapor Nitrogen from 65 to 300 K at Pressures to 35 MPa' [241].
Traceability category: B.

The work by Magee used the automated adiabatic calorimeter from Goodwin (1961, [161]) with unchanged mechanical details but with some changes in the instrumentation (electronic versions). Magee used a model equation (eq. 2) and discussed in detail uncertainty sources (pages 727 ff, 729 and 739). At page 739, a complete section is devoted to the discussion of the 'Analysis of Errors'. There seems to be only the uncertainties for voltage and current measurement missing which are necessary to calculate the applied heating power. This is work is very close to category A.

Traceability category: C.

With a hot-wire technique, the thermal diffusivity \(D_{th}\) and thermal conductivity \(\lambda\) are determined. The isobaric heat capacity is calculated from the relation

\[ D_{th} = \frac{\lambda}{\rho \cdot C_p}. \]

The authors make statements about uncertainties of the thermal diffusivity and thermal conductivity but they did not perform an uncertainty analysis based on the working equations (1 and 2) given in the paper. Also, these statements only seem to reflect the scattering of the measured data if we take into account the statement of the authors on page 345: 'Considering the variation in applied powers, the uncertainty in thermal conductivity is ...'. Furthermore, uncertainties for density and 'applied powers' are not reported.

Traceability category: A.

The publication discusses all relevant uncertainty contributions and describes in Eq. 8 how the combined uncertainty is calculated.

Esper et al. (1995): See section 4.1.3 'Methane: Heat capacities ...'.
4.7. Water:

4.7.1. Water: Standard enthalpy of formation:

**Water: Standard enthalpy of formation**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Traceability category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rossini</td>
<td>1931</td>
<td>303</td>
<td>C</td>
</tr>
<tr>
<td>King/Armstrong</td>
<td>1968</td>
<td>213</td>
<td>B</td>
</tr>
</tbody>
</table>

Rossini (1931): ‘The heat of formation of water’ [303].
Traceability category: C
Rossini determined the uncertainty by calculating the standard deviation of the measured mean values. This calculation procedure does not comply with current accepted procedures to estimate uncertainties of measurement like GUM (Guide to the expression of uncertainty in measurement [178]), e.g. reporting an uncertainty budget.

King/Armstrong (1969): ‘Constant pressure flame calorimetry with fluorine II. The heat of formation of oxygen Diflouride’ [213].
Traceability category: B.
In table 11 of the publication by King/Armstrong, an uncertainty budget is presented. The electrical calibration is only contributing with a statistical calculated uncertainty. A more detailed uncertainty analysis of the electrical calibration procedure would improve the traceability value of this work.

4.7.2. Water: Enthalpy of fusion:

**Water: Enthalpy of fusion**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Quantity</th>
<th>Traceability category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Giauque/Stout</td>
<td>1936</td>
<td>155</td>
<td>$\Delta_{\text{fus}}H$</td>
<td>C</td>
</tr>
<tr>
<td>Osborne</td>
<td>1939</td>
<td>272</td>
<td>$\Delta_{\text{fus}}H$</td>
<td>C</td>
</tr>
<tr>
<td>Haida et al.</td>
<td>1974</td>
<td>179</td>
<td>$\Delta_{\text{fus}}H$</td>
<td>C</td>
</tr>
</tbody>
</table>

Traceability category: C.
No uncertainty is given for the heat capacity and the enthalpy of fusion.

Osborne (1939): ‘Heat of fusion of ice. A Revision’ [272].
Traceability category: C.
This paper is a revision of the work published by Dickinson et al. [101] and Dickinson/Osborne [102] due to available values being more accurate for the heat capacity of water. In the last
sentence of the last page (p. 646), Osborne makes a statement about the uncertainty of the revised heat capacities. No further explanation for that stated uncertainty is given.


4.7.3. Water: Heat capacities (liquid/solid):

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Quantity</th>
<th>Phase</th>
<th>T / K</th>
<th>Traceability Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dieterici</td>
<td>1905</td>
<td>103</td>
<td>cₚ</td>
<td>lq</td>
<td>273-373</td>
<td>C</td>
</tr>
<tr>
<td>Sage/Lacey</td>
<td>1935</td>
<td>318</td>
<td>cₚ</td>
<td>lq</td>
<td>289-378</td>
<td>C</td>
</tr>
<tr>
<td>Giauque/Stout</td>
<td>1936</td>
<td>155</td>
<td>cₚ</td>
<td>s</td>
<td>16-268</td>
<td>C</td>
</tr>
<tr>
<td>Osborne et al.</td>
<td>1939</td>
<td>272</td>
<td>cₚ</td>
<td>lq</td>
<td>273-373</td>
<td>C</td>
</tr>
<tr>
<td>Flubacher et al.</td>
<td>1960</td>
<td>143</td>
<td>cₚ</td>
<td>s</td>
<td>2-27</td>
<td>C</td>
</tr>
<tr>
<td>Siota et al.</td>
<td>1970</td>
<td>343</td>
<td>cₚ</td>
<td>s/lq</td>
<td>271-305</td>
<td>C</td>
</tr>
<tr>
<td>Pick et al.</td>
<td>1971</td>
<td>285</td>
<td>cₚ</td>
<td>s</td>
<td>80-230</td>
<td>C</td>
</tr>
<tr>
<td>Haida et al.</td>
<td>1974</td>
<td>180</td>
<td>cᵥ</td>
<td>s</td>
<td>13-263</td>
<td>C</td>
</tr>
<tr>
<td>Ernst/Philippi</td>
<td>1990</td>
<td>117</td>
<td>cₚ</td>
<td>lq</td>
<td>298-673</td>
<td>C</td>
</tr>
<tr>
<td>Abdulagatov et al.</td>
<td>1993</td>
<td>1</td>
<td>cᵥ</td>
<td>lq</td>
<td>646-712</td>
<td>C</td>
</tr>
<tr>
<td>Abdulagatov et al.</td>
<td>1997</td>
<td>6</td>
<td>cᵥ</td>
<td>lq</td>
<td>321-576</td>
<td>B</td>
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<tr>
<td>Magee et al.</td>
<td>1998</td>
<td>243</td>
<td>cᵥ</td>
<td>lq</td>
<td>300-420</td>
<td>A</td>
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<tr>
<td>Manya et al.</td>
<td>2011</td>
<td>247</td>
<td>cₚ</td>
<td>lq</td>
<td>298-465</td>
<td>C</td>
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<tr>
<td>He et al.</td>
<td>2015</td>
<td>186</td>
<td>cₚ</td>
<td>lq</td>
<td>395-665</td>
<td>A</td>
</tr>
<tr>
<td>Castro-Gomez et al.</td>
<td>1990</td>
<td>64</td>
<td>ΔH</td>
<td>lq</td>
<td>356-408</td>
<td>B</td>
</tr>
</tbody>
</table>

Dieterici (1905): ‘Über die Flüssigkeitswärme des Wassers und das mechanische Wärmeäquivalent’ [103].
Traceability category: C.

In most of the references for thermophysical properties like the heat capacity this kind of work is considered as 'historical' and should not serve as a source for reference values. Dieterici makes some statements about the uncertainties of the determined heat capacities and about several measurable input quantities. It is not clear how the 'combined' uncertainty for the heat capacity of water is finally calculated.

Sage et al. (1935): See section 4.3.3 ‘Propane: Heat capacities …’.


Osborne et al. (1939): ‘Measurements of heat capacity and heat of vaporization of water in the range 0° to 100° C’ [272].
Traceability category: C.
On page 214, Osborne et al. express their intention ‘... to avoid an error of more than 1 part in 5000 in the final results’. This remains the only point in that paper where an uncertainty of the introduced measurement results is mentioned.

Flubacher et al. (1960): ‘Heat Capacity of Ice at Low Temperatures’ [143].
Traceability Category C.
In the temperature range 2 K to 27 K heat capacities were calorimetrically measured. The authors gave a statement of the uncertainties (see abstract: ‘... with an estimated precision varying between ...’) of the determined heat capacities but give no further details how the uncertainty was assessed. In Table I, the heat capacities are reported together with the corresponding temperature. The uncertainties of these temperatures are missing.

Sirota et al. (1970): ‘Experimental investigation of specific heat of water near the fusion line’ [343].
Traceability category: C.
The uncertainty statement on page 93 cannot be reproduced from the information given in the text.

Pick et al. (1971): ‘The Specific Heat of Pure and Doped Ice near 120 K’ [285].
Traceability category: C.
The measurement results are only given in a graph without uncertainties.

Haida et al. (1974): ‘Calorimetric study of the glassy state X. Enthalpy relaxation at the glass-transition temperature of hexagonal ice’ [180].
Traceability category: C.
The paper makes no statement about the uncertainty of the measured heat capacity and enthalpy of fusion, but an uncertainty of the reported entropy is given. Several uncertainties of input quantities are missing, e.g., electrical heating energy and temperature.

Traceability category: B.
On page 273 the authors wrote: ‘The power change in the heater could be determined to ±0.05 per cent’. When we take this statement as the uncertainty of the power measurement it remains an uncertainty statement about an intermediate quantity. The uncertainty of the measured voltage and current, or may be together with a calibrated reference resistor, is not reported. Additionally, there is no uncertainty for the pressure measurement.

Ernst/Philippi (1990): ‘Flow-calorimeter results for the specific heat capacity $c_p$ of water at pressures between 20 and 50 MPA and temperatures between 298.15 and 673.15 K’ [117].
Traceability category: C.
The reported uncertainty for the heat capacity (p. 212) only seems to be a general statement without any model equation and uncertainties of measurable quantities.

Abdulagatov et al. (1993): ‘Isochoric heat capacity of $\{xH_2O+(1-x)KOH\}$ near the critical point of pure water’ [1].
Traceability category: C.
Too many uncertainties of input quantities are missing (current, voltage, sample mass, heat capacity of the empty calorimeter and the correction of working volume).

Abdulagatov et al. (1997): ‘Measurements of the heat capacities at constant volume of H$_2$O and (H$_2$O + KNO$_3$)’ [6].
Traceability category: B.
Isochoric heat capacities $C_V$ were measured with a ‘high-temperature and high-pressure adiabatic nearly constant-volume calorimeter’. On page 1389 the authors explain the applied model equation, a correction to the determined $C_V$ and estimated uncertainties of the input
quantities measured. Only the uncertainty of the heating energy is introduced but not the uncertainties of the measurable quantities voltage, current and time. Uncertainties for the volume of the calorimeter and for the working-volume correction of $C_V$ are also missing.

Traceability category: A.
In section 5 ‘Assessment of Uncertainties’, the authors present a seemingly complete uncertainty budget in a continuous text.

Manya et al. (2011): ‘Specific Heat Capacity of Pure Water at 4.0 MPa between 298.15 and 465.65 K’ [247].
Traceability category: C.
In table 5, the heat capacities are given with uncertainties. It is not clear on which consideration these uncertainties are based on.

He et al. (2015): ‘Measurement of isobaric heat capacity of pure water up to supercritical conditions’ [186].
Traceability category: A.
The paper reports the model equation, table 2 contains all relevant uncertainties and Eq. (4) of the publication explains how the expanded uncertainty is calculated.

4.8. Carbon dioxide:

4.8.1. Carbon dioxide: Standard enthalpy of formation:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Traceability category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jessup</td>
<td>1938</td>
<td>203</td>
<td>C</td>
</tr>
<tr>
<td>Dewey/Harper</td>
<td>1938</td>
<td>100</td>
<td>C</td>
</tr>
<tr>
<td>Prosen/Rossini</td>
<td>1944</td>
<td>294</td>
<td>C</td>
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<td>Lewis et al.</td>
<td>1965</td>
<td>233</td>
<td>C</td>
</tr>
<tr>
<td>Hawtin et al.</td>
<td>1966</td>
<td>183</td>
<td>C</td>
</tr>
</tbody>
</table>

Jessup (1938): ‘Heats of combustion of diamond and of graphite’ [203].
Traceability category: C.
The reported uncertainties are the sum of standard deviations without a detailed uncertainty analysis of the measurement procedure.

Dewey/Harper (1938): ‘Heats of combustion of anthracite cokes and of artificial and natural graphites’ [100].
Traceability category: C.
On page 473, the uncertainty budget is discussed. It consists of tree contributions which are the uncertainty of the used calibration standard (benzoic acid), the standard deviation of the calibration experiments (‘energy equivalent of the calorimeter’) and standard deviation of the combustion experiments (‘heat of combustion’). The standard deviations are the standard deviations of the mean values. Dewey/Harper use in table 1 an equation to calculate the ‘Actual energy equivalent’, but an uncertainty analysis based on that equation is omitted. For the
combustion experiment, an uncertainty analysis of the gravimetrically determined mass of the reaction product would be opportune to produce traceable measurement results.

**Prosen/Rossini (1944):** ‘Some experimental data on the heats of combustion of benzoic acid and carbon (graphite)’ [294].
Traceability category: C.
The overall uncertainty (see page 445) is twice the square root of the sum of the square of standard deviations.

**Lewis et al. (1965):** ‘The heats of combustion of some pyrolytic graphites’ [233].
Traceability category: C.
The bomb calorimeter used was calibrated with benzoic acid but the manufacturer and uncertainty of the energy content of the standard material was not reported.

**Hawtin et al. (1966):** ‘The heats of combustion of graphite, diamond and some non-graphitic carbons’ [183].
Traceability category: C.
The reported uncertainties are calculated on a pure statistical analysis of the measurement results (mean and standard deviation of the mean).

### 4.8.2. Carbon dioxide: Enthalpy of sublimation:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Traceability category</th>
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<tbody>
<tr>
<td>Andrews</td>
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<tr>
<td>Maass et al.</td>
<td>1926</td>
<td>238</td>
<td>C</td>
</tr>
<tr>
<td>Giauque/Egan</td>
<td>1937</td>
<td>156</td>
<td>C</td>
</tr>
<tr>
<td>Ambrose</td>
<td>1956</td>
<td>15</td>
<td>C</td>
</tr>
<tr>
<td>Bryson et al.</td>
<td>1974</td>
<td>59</td>
<td>C</td>
</tr>
</tbody>
</table>

**Andrews (1925):** ‘The heat of sublimation of carbon dioxide’ [19].
Traceability category: C.
In the summary on page 1602, the origin of the reported uncertainty is not comprehensive.

**Maass et al. (1926):** ‘Some Thermal Constants of Solid and Liquid Carbon Dioxide’ [238].
Traceability category: C.
No uncertainty statement is given in the publication.

**Giauque/Egan (1937):** ‘Carbon dioxide. The heat capacity and vapor pressure of the solid. The heat of sublimation. Thermodynamic and spectroscopic values of the entropy’ [156].
Traceability category: C.
The heat of sublimation was determined from vapour pressure and from calorimetric experiments. The value from the vapour-pressure measurements has no uncertainty statement and the uncertainty of the calorimetric result is stated and not further evaluated. This is also valid for the heat-capacity measurements of carbon dioxide in the same publication.

**Ambrose (1956):** ‘The vapour pressures and critical temperatures of acetylene and carbon dioxide’ [15].
Traceability category: C.
The enthalpy of sublimation is reported without an uncertainty on page 780.

In table V of the publication an uncertainty value is reported without further discussion.

### 4.8.3. Carbon dioxide: Heat capacities (gaseous/solid):

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Quantity</th>
<th>Phase</th>
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<th>Traceability category</th>
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<td>Giauque/Egan</td>
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<td>C</td>
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<tr>
<td>de Groot/Michels</td>
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<td>97</td>
<td>cₚ</td>
<td>g</td>
<td>298-423</td>
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<td>Masi/Petkof</td>
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<td>Michels et al.</td>
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<td>293-333</td>
<td>C</td>
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<td>283-373</td>
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<td>Amirkhanov et al.</td>
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<td>cᵥ</td>
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<tr>
<td>Bishnoi et al.</td>
<td>1971</td>
<td>54</td>
<td>cₚ/cₚ₀</td>
<td>g</td>
<td>312-424</td>
<td>C</td>
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<td>253-323</td>
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<tr>
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<td>1972</td>
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<td>Pececeu/van Dael</td>
<td>1973</td>
<td>279</td>
<td>cₚ</td>
<td>lq</td>
<td>220-290</td>
<td>C</td>
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<td>1980</td>
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<td>cₚ</td>
<td>g</td>
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<td>Abdualgatov et al.</td>
<td>1994a</td>
<td>2</td>
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<td>lq/g</td>
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<td>Abdualgatov et al.</td>
<td>1994b</td>
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<td>107</td>
<td>cₚ</td>
<td>g</td>
<td>323-573</td>
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<td>Liu et al.</td>
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<td>cₚ₀</td>
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<td>Ishmael et al.</td>
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<td>g</td>
<td>298-423</td>
<td>B</td>
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<table>
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<th>Authors</th>
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<th>Quantity</th>
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<th>T / K</th>
<th>Traceability category</th>
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<td>Dawe/Snowdon</td>
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<td>93</td>
<td>∆H</td>
<td>g</td>
<td>273-373</td>
<td>C</td>
</tr>
</tbody>
</table>
Eucken/Lüde (1929): See section 4.1.3 ‘Methane: Heat capacities …’.


De Groot/Michels (1948): ‘The Joule-Thomson effect and the specific heat at constant pressure of carbon dioxide’ [97].
Traceability category: C.
The uncertainty of the calculated heat capacities is not assessed.

Masi/Petkof (1952): ‘Heat Capacity of Gaseous Carbon Dioxide’ [248].
Traceability category: C.
A model equation (Eq. 1, p. 182) is given but the reported uncertainties (p. 186) are mere statements without discussion of single uncertainty contributions.

Michels et al. (1952): ‘The specific heat at constant volume of compressed carbon dioxide’ [257].
Traceability category: C.
A few uncertainties of input quantities are discussed by the authors, e.g. ‘… accuracy in the resistance ratios …’ (p. 620), but there is no uncertainty statement for the determined heat capacities.

Wolley (1954): ‘Thermodynamic Functions for Carbon Dioxide in the Ideal Gas State’ [408].
Traceability category: B.
Heat capacities and other thermodynamic quantities are calculated from spectroscopic data. The author reports a kind of uncertainty budget (table 4) for different temperatures. Admittedly, it is difficult to decide if the reported budget is complete or not. The respective model equations would be useful.

Traceability category: C.
The authors report several uncertainties of the measurable input quantities (temperature, voltage, current and mass flow) of the input quantities. It is not clear what could be identified as the final uncertainty statement for the measured enthalpy change and derived heat capacity. It seems that the final uncertainty is estimated from the comparison with tabulated values (p. 438).

Vukalovich/Gureev (1964): ‘An experimental study of the thermal capacity $c_p$ of carbon dioxide’ [386].
Traceability category: C.
The determination of the reported uncertainty is incomprehensible.

Vukalovich et al. (1964): ‘An experimental study of the thermal capacity $c_p$ of carbon dioxide at high pressures’ [387].
Traceability category: C.
Uncertainties of the heat capacities measured by a flow-type adiabatic calorimeter are only claimed without a detailed discussion.

Vukalovich et al. (1965): ‘Experimental study of the thermal capacity $c_p$ of carbon dioxide at high pressures’ [389].
Traceability category: C.
The accuracy of the experimental uncertainties is assessed by the authors, but no complete further analysis of the uncertainty is given.

Traceability category: C.
On the one hand, some uncertainties, e. g. for temperature and mass flow, of the adiabatic-flow calorimeter are discussed and a working equation is presented to determine the heat capacity. On the other hand, the uncertainty for the electrical power is missing.

Traceability category: C.
The publication is a continuation of the preceding year’s work; see Altunin/Kuznetsov [12]. The overall uncertainty is stated, but no further information given (p. 131: ‘The maximum error in experimental data, calculated by the well-known procedure, …’).

Amirkhanov et al. (1970): ‘Experimental determination of specific heat $c_v$ of carbon dioxide’ [16].
Traceability category: C.
On page 103, the authors report uncertainties (‘… errors ranged from 2 to 4% …’) and give an equation including all uncertainty contributions. The single uncertainty contribution of that equation (e. g. sample mass, voltage) is not given in the paper.

Amirkhanov et al. (1971): ‘Isochoric specific heat-capacity of carbon dioxide’ [17].
Traceability category: C.
The overall uncertainty for the heat capacity is only stated generally without a complete uncertainty budget.

Traceability category: C.
The authors determined the ratio of the isobaric heat capacities at low and higher temperatures for two mixtures of Carbon Dioxide and Methane (14 and 42 mol%) with a heat exchanger method. On page 661, several uncertainties are reported (temperature, pressure etc.), but no working equation and sensitivity coefficients are mentioned. Therefore, the uncertainty of the experimental results is not verifiable.

Altunin/Kuznetsvo (1972): ‘Isobaric specific heat of gaseous carbon dioxide near the saturation line’ [14].
Traceability category: C.
This is the second successor paper of Altunin/Kuznetsov [13]. Apparently, there is no uncertainty statement for the resulting heat capacity. For an assessment of the paper we take into account the two preceding publications [12,13].

Bishnoi et al. (1972): ‘Experimental Heat Capacities of Nitrogen-Carbon Dioxide Mixtures at Elevated Pressures’ [55].
Traceability category: C.
The uncertainty is pure claims without further details, e. g. sensitivity coefficients and uncertainties of input measurements.


Pecceu/Van Dael (1973): ‘Ultrasonic velocity in liquid carbon dioxide’ [279].
Traceability category: C.
Isobaric heat capacities are derived from speed-of-sound measurements and an uncertainty of 4% is claimed without a detailed discussion.

Saegus et al. (1980): ‘Measurements of the Isobaric Specific Heat Capacity of Gaseous Carbon Dioxide from 245 K to 345 K up to 3.7 MPa’ [315].
Traceability category: A.
The authors give an apparently complete uncertainty budget of their measurements, explain it in a continuous text and report where the measurement devices were calibrated.

Magee/Ely (1986): ‘Specific Heats ($C_V$) of Saturated and Compressed Liquid and Vapor Carbon Dioxide’ [244].
Traceability category: B.
Several uncertainty sources are discussed but some uncertainties are from intermediate values. E. g., the applied energy $Q$ is an intermediate quantity where the uncertainties of the simultaneously measured voltage and current are not given. Also, the amount of sample $N$ is an intermediate quantity where the uncertainty contributions from equation of state, pressure and temperature, which are applied to calculate $N$, are not reported.

Traceability Category: C.
Many uncertainties of input measurements are missing, e. g. uncertainties of the mass of the sample, current, voltage, corrections connected with a non-strict isochoric process and heat capacity of the empty calorimeter.

Traceability category: C.
The publication seems to contain some results of Abdulagatov et al. [2] and additional newer experimental results. The authors report an overall uncertainty for the heat capacity measured and give a model equation. Numerical values for the sensitivity coefficients and the uncertainty for the sample mass are missing. Only the uncertainty of the intermediate quantity $Q$ (energy released in the calorimeter) is presented and not the measurable quantities voltage and current according to the authors second model equation on page 1032 ($\Delta Q=I/U\Delta t$).

Dordain et al. (1994): ‘Measurements of isobaric heat capacities of gases from 323.15 to 573.15 K up to 30 MPa’ [107].
Traceability category: C.
The statement ‘accuracy of the method was estimated between 2% and 4%’ (p. 3263) is not supported by a detailed uncertainty analysis.

Traceability category: C.
At page 439, the author refers the discussion of uncertainties to his own publication in the year 1991 [241]. Magee’s fine work in the year 1991 is close to traceability category A, but the difference of 4 years between the two published works should make necessary a recalibration of measurement devices. These circumstances make the reporting of new or changed uncertainty values inevitable.

Liu et al. (2014): ‘Speed of Sound Measurements Using a Cylindrical Resonator for Gaseous Carbon Dioxide and Propene’ [236].
Traceability Category: B
If we assume the uncertainty of the speed of sound as a given quantity, the uncertainties of fitting working equation (5) (see paper) are still required for a transparent assessment of the uncertainty of the ideal heat capacities and, therefore, full traceability is not achieved.

Ishmael et al. (2016): ‘Isobaric heat capacity ($c_p$) measurements of supercritical fluids using flow calorimetry: equipment design and experimental validation with carbon dioxide, methanol, and carbon dioxide-methanol mixtures’ [199].
Traceability category: B.
The publication reports an overview of the uncertainties of the input quantities (table 1). A model equation is not given and for the heater power the uncertainty is not further resolved (intermediate quantity) down to the measured electrical quantities.

4.9. Oxygen:

4.9.1. Oxygen: Heat of vaporisation:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>( T / K )</th>
<th>Traceability category</th>
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<tr>
<td>Barschall</td>
<td>1911</td>
<td>40</td>
<td>C</td>
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<td>Witt</td>
<td>1912</td>
<td>406</td>
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<td>Keesom</td>
<td>1914</td>
<td>205</td>
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<td>Eucken</td>
<td>1916</td>
<td>124</td>
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<td>1929</td>
<td>153</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>Clusius/Konnertz</td>
<td>1949</td>
<td>73</td>
<td>90</td>
<td>C</td>
</tr>
<tr>
<td>Furukawa/McCoskey</td>
<td>1953</td>
<td>150</td>
<td>68-91</td>
<td>C</td>
</tr>
</tbody>
</table>


Barschall (1911): ‘Über die Verdampfungswärme des Sauerstoffes’ [40].
Traceability category: C.
On page 347, Barschall gives a list of the input quantities and their values in order to calculate heat of vaporisation investigated by his introduced experimental set up. Most of the uncertainties of Barschall’s list are missing.


Keesom (1914): ‘The heat of vaporisation of hydrogen’ [205].
Traceability category: C.
As a test of the method the heat of vaporisation of oxygen is also determined in the publication. Keesom compared his results with other investigators but reported no uncertainty.


Giauque/Johnston (1929): ‘The heat capacity of oxygen from 12 °K to its boiling point and its heat of vaporization. The entropy from spectroscopic data’ [153].
Traceability category: B.
The authors discuss several uncertainty sources but report only relative uncertainties and no sensitivity coefficients.

Clusius/Konnertz (1949): ‘VI. Kalorimetrische Messungen der Verdampfungswärme des Sauerstoffs bei normalen Druck sowie des Äthylens und Propylens unterhalb und oberhalb vom Atmosphärendruck’ [73].
Traceability category: C.
Some uncertainties of the measurable input quantities are given (e.g. temperature) but no model equation is reported and the stated uncertainty of the heat of evaporation could not be reproduced from the published work.


4.9.2. Oxygen: Heat capacity:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Reference</th>
<th>Quantity Phase</th>
<th>T / K</th>
<th>Traceability category</th>
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</thead>
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<tr>
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<td>$c_p$</td>
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<td>90/195/259/294</td>
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<td>Shilling/Partington</td>
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<td>s/lq/g</td>
<td>10-73</td>
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<td>127</td>
<td>$c_p$</td>
<td>g</td>
<td>303-479</td>
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<td>1929</td>
<td>153</td>
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<td>s/lq</td>
<td>12-90</td>
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<td>Hoge</td>
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<td>s/lq</td>
<td>126-162</td>
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<td>Masi/Petkof</td>
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<td>248</td>
<td>$c_p$</td>
<td>g</td>
<td>243-363</td>
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<td>Fagerstroem et al.</td>
<td>1969</td>
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<td>$c_p$</td>
<td>s</td>
<td>1-71</td>
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Scheel/Heuse (1913): See section 4.6.2 ‘Nitrogen: Heat capacity …’.


Shilling/Partington (1928): See section 4.6.2 ‘Nitrogen: heat capacity’.

Clusius (1929): See section 4.1.3 ‘Methane: Heat capacities …’.

Eucken/Lüde (1929): See section 4.1.3 ‘Methane: Heat capacities …’.


Traceability category: C

For the vapour-pressure measurements, Hoge makes statements on the uncertainties of pressure, temperature and mentions a negligible influence of the sample purity. In the part of the paper where heat capacity measurements in the critical region are discussed (p. 336 ff), uncertainty statements about, e.g. sample mass, electrical energy (voltage, current and time) and a combined uncertainty of the determined heat capacity are missing.

Masi/Petkof (1952): see section 4.8.3 ‘Carbon Dioxide: Heat capacities …’.

Traceability category: C

No uncertainty statement for the reported specific heat is given.
5. Summary

The conclusions of this report are part of the ‘Guideline on the traceability of energy and enthalpy calculations (Task D4.4.3)’.
References
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