

# Calculation of LNG enthalpies and calorific values at different reference conditions

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# Background

- GCV of LNG is required for calculation of LNG energy transferred
- It can be calculated at different reference conditions
- Data required may be obtained from different sources
- In addition;
  - Calculation of GCV at the actual fluid state and its uncertainty are not described in any standard or guideline
- This paper looks at financial impact resulting from:
  - Calculation of LNG GCV at different ref. Conditions
  - Using data from different sources
  - Calculation of GCV at ref. conditions rather than at actual liquid state
  - Associated uncertainty

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## Industry Practice For Calculation of LNG Gcv

Standard	Reference Conditions available		
	GCV <sub>i</sub> mass basis	GCV <sub>i</sub> molar basis	GCV <sub>i</sub> volumetric basis
ISO 6976	0, 15, 20°C and 25°C	0°C, 15°C, 20°C, 25°C and 60°F	various comp/metering conditions
ISO 6578	15°C		15°C
GPA 2145	15°C and 60°F		15°C and 60°F
ASTM 3588		60°F (15.56°C)	60°F (15.56°C)

The GIIGNL handbook refers to use of ISO 6976 and uses 25°C as ref. temp.

# Calculations

LNG Energy transferred:

$$E = \underbrace{(V_{\text{LNG}} \cdot D_{\text{LNG}} \cdot \text{GCV}_{\text{LNG}})}_{\text{-----LNG-----}} - \underbrace{\left[ V_{\text{LNG}} \frac{273.15}{273.15 + T} \times \frac{P}{1.01325} \times \text{GCV}_{\text{Gas}} \right]}_{\text{-----Displaced Gas-----}} \pm E_{\text{Gas to ER}}$$

$\text{GCV}_{\text{LNG}}$  - calculated on the basis of:

Mass:

$$\text{GCV}(\text{mass}) = \frac{\sum X_i M_i \text{GCV}_i(\text{mass})}{\sum X_i M_i}$$

or Molar:

$$\text{GCV}(\text{mass}) = \frac{\sum X_i \text{GCV}_i(\text{mol})}{\sum X_i M_i}$$

$\text{GCV}_{\text{Displaced Gas}}$  (volumetric basis):

$$\text{GCV}(\text{vol}) = \sum Y_i \text{GCV}_i(\text{vol})$$

# Cases Considered

## LNG Test Cases

Component	A	B	C	D	E
	Mole Fraction				
Methane	81.249	85.341	90.068	95.130	97.540
Ethane	8.484	7.898	6.537	1.890	0.460
Propane	4.931	4.729	2.200	1.050	0.530
n-Butane	2.708	0.992	0.284	0.420	0.520
Iso-Butane	0.000	0.854	0.291	0.450	0.490
n-Pentane	0.000	0.089	0.011	0.000	0.000
Iso-Pentane	0.000	0.097	0.010	0.000	0.000
n-Hexane	0.000	0.000	0.000	0.000	0.000
N2	2.628	0.000	0.599	1.060	0.460
MW, g/mol	20.07	19.358	17.902	17.095	16.736
Temperature, °C	-158.150	-158.150	-158.150	-160.780	-161.040
Pressure, bar	2.214	1.172	1.456	1.34	1.16
Ref Density, kg/m <sup>3</sup>	490.8	477.3	454	441.6	434.4

### Example of LNG cargo (value \$27M to \$30M)

<b>Volume of LNG (m<sup>3</sup>)</b>	122034.329
<b>Vapour Temperature (°C)</b>	-140.00
<b>Vapour Pressure (absolute) (Bar)</b>	1.150
<b>Price LNG (USD/MMBTU)</b>	10.00

# Assessment of Financial Impact

- Calculate a reference energy transfer & Cost using
  - Measured LNG density
  - ISO 6976 for GCV of LNG at T= 15°C
  - ISO 6976 for GCV of Displaced gas at T= (15/15)°C

} **Baseline condition**
- Calculate energy transfer and cost at different ref. conditions (e.g. 25°C).
- Calculate % difference:  
$$\% \text{ Difference} = \frac{\text{Energy Transferred} - \text{Reference Energy Transferred}}{\text{Reference Energy Transferred}}$$

## Results- Using Different Standards- Averaged for the 5 Examples

Using data from 3 standards: GPA2145, ISO6976 and ISO 6578 at ref Temp of:

- 15°C for LNG &
- (15/15)°C for Displaced gas
- Maximum difference in calculated energy transfer is **0.0268%**
- Corresponding cost difference is  $\approx$  **\$8K** for the cargo in question

Using data from 2 standards: GPA2145 and ISO6976 at US ref temp of

- 60°F for LNG &
- (60/60)°F for displaced gas
- Maximum difference in calculated energy transfer is **0.0216%**
- Corresponding cost difference was about **\$6.2K** for the cargo in question

# Results- Continued

Calculations at different reference temperatures using ISO 6976:

		Average over all 5 LNG Examples	
LNG GCV, Reference Temp (°C)	Displaced gas GCV, Ref Temp. comb/ met (°C)	% Difference	Difference in Cost (\$)
<b>0</b>	<b>0/0</b>	<b>0.1382</b>	<b>39,429.99</b>
<b>15</b>	<b>15/15</b>	<b>0</b>	<b>0</b>
<b>20</b>	<b>20/20</b>	<b>-0.0448</b>	<b>-12,794.51</b>
<b>25</b>	<b>25/25</b>	<b>-0.0914</b>	<b>-26,077.36</b>

Baseline condition





## Main Conclusions- First Part

- Differences in calculation of LNG GCV is
  - Not significant when different standards are used at same ref conditions
  - Significant when calculated at different reference conditions
- Conversion to a single reference condition is described in EN ISO 13443:2005
- Industry can adopt this conversion to ensure equitable LNG energy transfer

# Second Part-

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# Calculation of LNG GCV at Liquid state and Standard Conditions

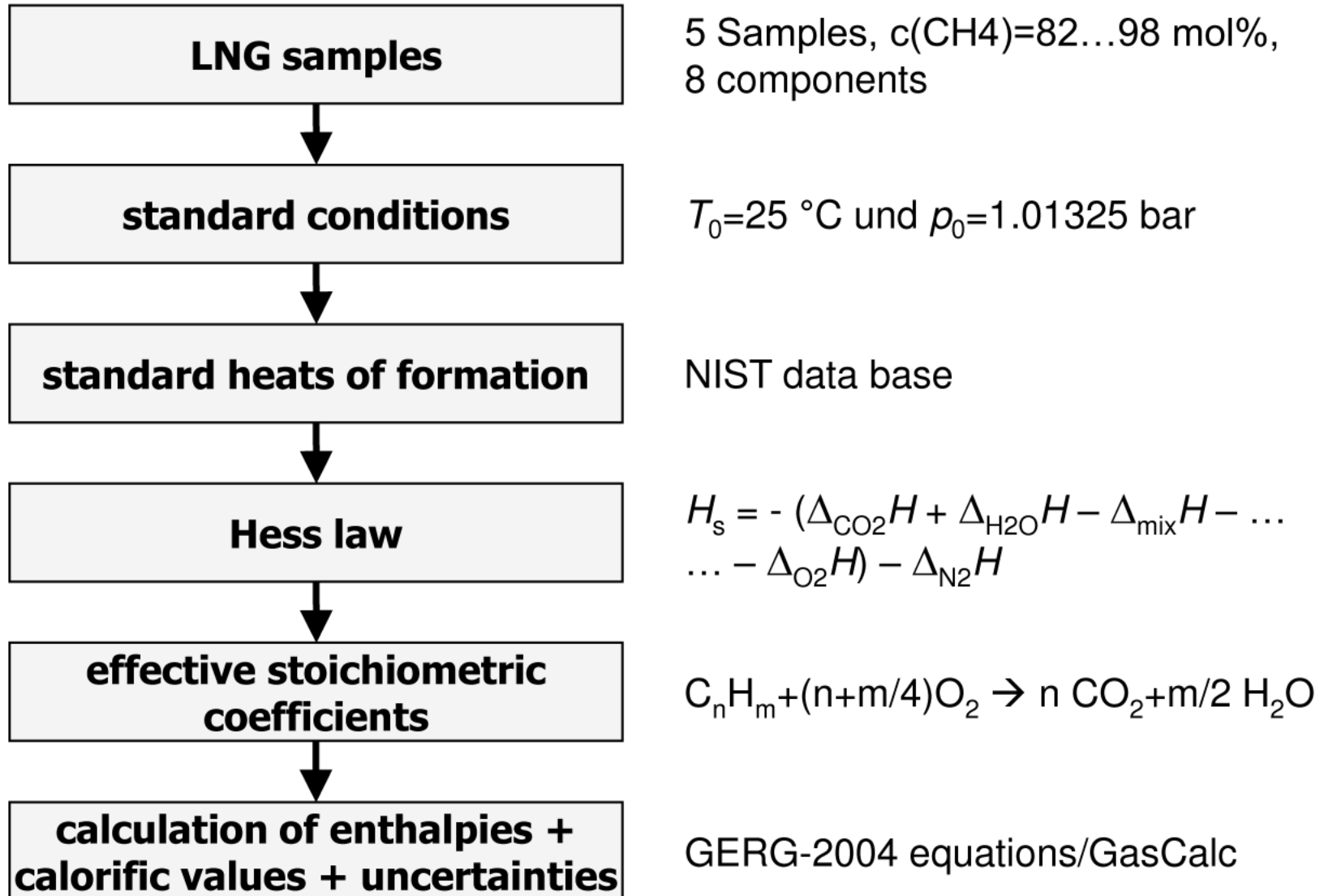
## ToDo:

- Calculation of
  - calorific values and
  - enthalpies of formation
  
- Liquid state and standard conditions ( $T, p, x_i$ )
  
- Difference in enthalpies and calorific values
  
- Uncertainty budget

# Calculation of Enthalpies ... boring?

- LNG:  
**difference in enthalpy** between liquid and gaseous state
- Someone has to pay for the energy difference
- LNG terminal:
  - 200 tank ships per year with a
  - shipload of 150000 m<sup>3</sup>
- ... and the question is ...  
Using or loosing **100 M€/year** ...

# Calculation method – flowchart/overview



# LNG Samples

Gas Samples					
component	A	B	C	D	E
	Mole Fraction				
Methane	81.249	85.341	90.068	95.130	97.540
Ethane	8.484	7.898	6.537	1.890	0.460
Propane	4.931	4.729	2.200	1.050	0.530
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N2	2.628	0.000	0.599	1.060	0.460
Sum / %	100	100	100	100	100
Temperature / °C	-158.150	-158.150	-158.150	-160.780	-161.040
pressure / bar	2.214	1.172	1.456	1.34	1.16

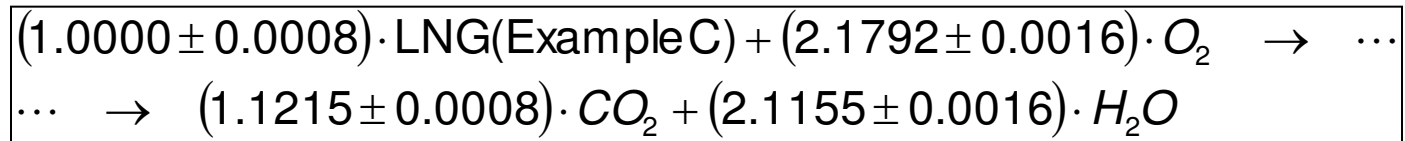
# Calculation Method – Details – Part 1

1. Choice of the **LNG samples** (see table)
2. Specification of the **standard conditions**  
( $T_0=25\text{ °C}$  und  $p_0=1.01325\text{ bar}$ )
  1. Tabulated standard **heats of formation** (NIST online data base) as reference values for calculation of absolute values of enthalpies
  2. Exception **methane**:  
enthalpy (and uncertainty!) aligned with its calorific value given in ISO6976 (total: 74.54 kJ/mol  $\approx$  Pittam/Pilcher, literature data differ by 300 J/mol)
5. Ansatz for calorific value according to **Hess's law**:

$$H_s = -[\Delta_{\text{CO}_2}H + \Delta_{\text{H}_2\text{O}}H - \Delta_{\text{mix}}H - \Delta_{\text{O}_2}H] - \Delta_{\text{N}_2}H$$

## Calculation Method – Details – Part 2

6. Calculation **effective stoichiometric coefficients**  $a$ ,  $b$ ,  $c$  und  $d$  based on the composition of the LNG sample; this means reducing 7 reaction equations ( $C_nH_m + (n+m/4)O_2 \rightarrow n CO_2 + m/2 H_2O$ ) to one equation



6. Calculation **enthalpy of LNG** sample:

$$\boxed{\Delta_{\text{mix}} H = a \cdot (\Delta_{\text{mix}} h(T, p) + \Delta_{\text{mix}} H^\circ)}$$

- $\Delta_{\text{mix}} h(T, p)$ : temperature and pressure dependent change of the LNG enthalpy; calculated with the GERG-2004 equations implemented in the software GasCalc
- $\Delta_{\text{mix}} H^\circ$ : LNG standard enthalpy of formation



# Calculation Method – Details – Part 3

## 8. Calculation **enthalpy water/water ice**:

$$\Delta_{\text{H}_2\text{O}}H = c \cdot \left( \Delta_{\text{H}_2\text{O}}H^\circ + \Delta_{\text{H}_2\text{O}}H(T_0 \rightarrow T_{\text{fus}}) + \Delta_{\text{fus,H}_2\text{O}}H + \int_{T_{\text{fus}}}^T c_p(\text{H}_2\text{O}, s) dT \right)$$

- $\Delta_{\text{H}_2\text{O}}H^\circ$ : standard enthalpy of water
- $\Delta_{\text{H}_2\text{O}}H(T_0 \rightarrow T_{\text{fus}})$ : enthalpy change from reference conditions to the melting temperature  $T_{\text{fus}}$
- $\Delta_{\text{fus,H}_2\text{O}}H$ : water ice heat of fusion
- $\Delta_{\text{H}_2\text{O}}h(T_{\text{fus}} \rightarrow T)$ : change of enthalpy from melting temperature to temperature  $T$  of the LNG; calculated by the integral of the temperature dependent heat capacity of water ice at constant pressure

# Calculation Method – Details – Part 4

## 9. Calculation **enthalpy of carbon dioxide**:

$$\Delta_{\text{CO}_2}H = d \cdot \left( \Delta_{\text{CO}_2}H^\circ + \Delta_{\text{CO}_2}H(T_0 \rightarrow T_{\text{sub}}) + \Delta_{\text{sub,CO}_2}H + \int_{T_{\text{sub}}}^T c_p(\text{CO}_2, s) dT \right)$$

- $\Delta_{\text{CO}_2}H^\circ$ : standard enthalpy of carbon dioxide
- $\Delta_{\text{CO}_2}H(T_0 \rightarrow T_{\text{sub}})$ : enthalpy change from 25 °C to -78.5 °C (down to -56 °C with GERG-2004 equations and then linearly extrapolated to -78.5 °C)
- $\Delta_{\text{sub,CO}_2}H$ : sublimation heat at -78.5 °C and 1.01325 bar
- $\Delta_{\text{CO}_2}h(T_{\text{sub}} \rightarrow T)$ : change of enthalpy from -78.5 °C to LNG temperature  $T$ ; calculated by the integral of the temperature dependent heat capacity of carbon dioxide at constant pressure.

# Calculation Method – Details – Part 5

## 8. Calculation **enthalpy oxygen**:

$$\Delta_{\text{O}_2} H = b \cdot \Delta_{\text{O}_2} h(T, p)$$

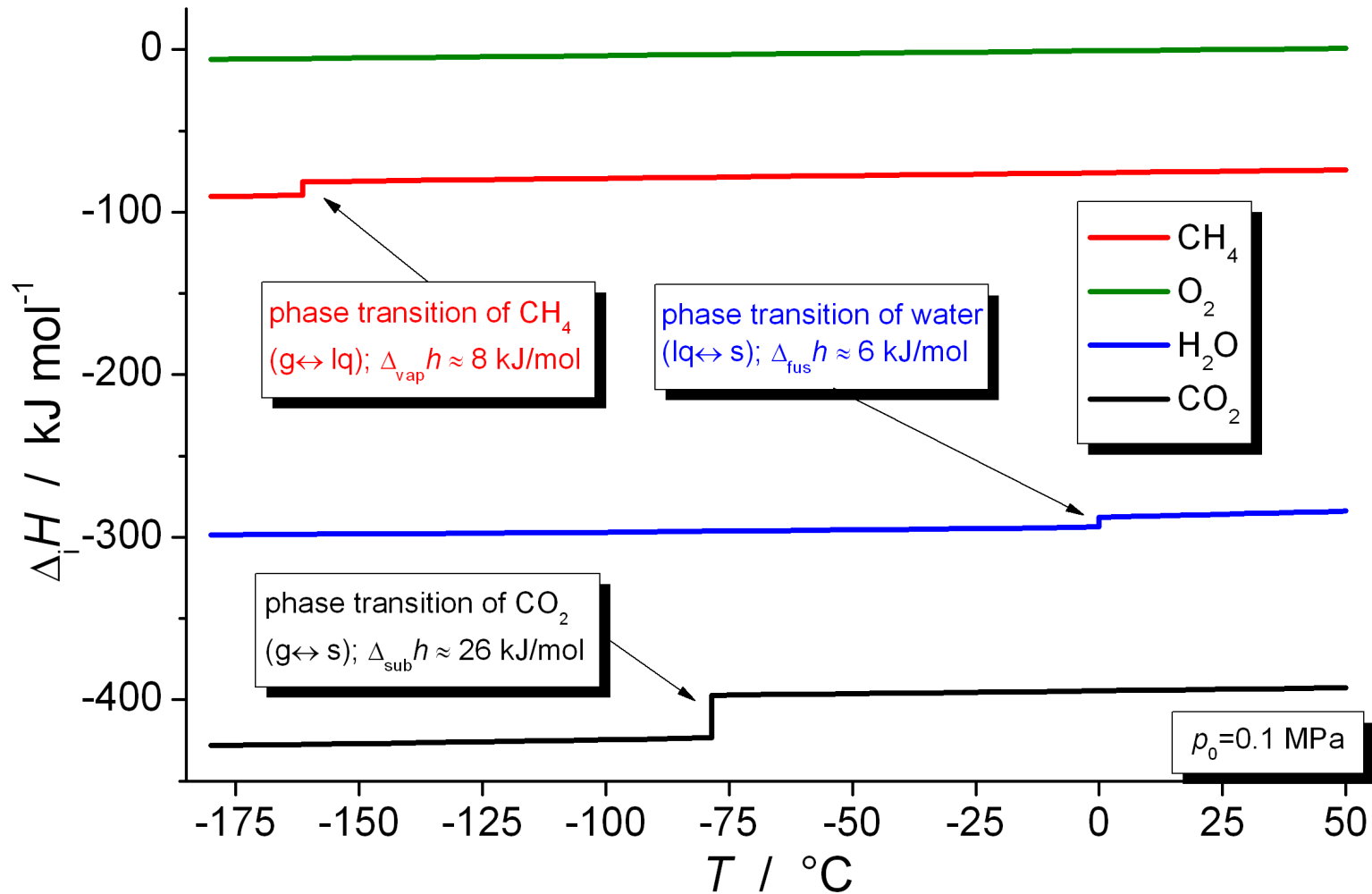
- NIST12-Database

## 10. Calculation **enthalpy of nitrogen**:

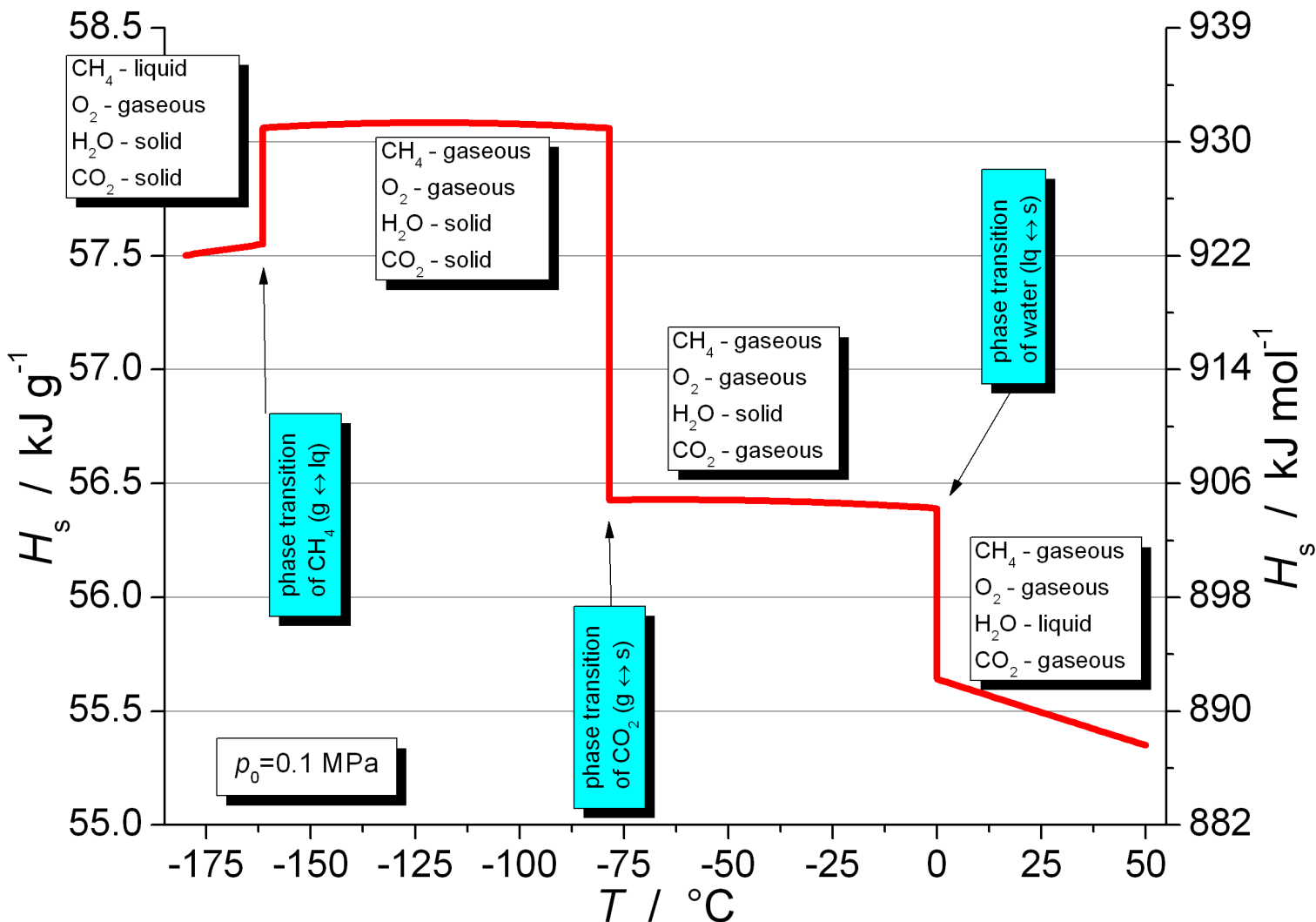
$$\Delta_{\text{N}_2} H = x_{\text{N}_2} \cdot (\Delta_{\text{N}_2} h(T, p) + \Delta_{\text{vap}, \text{N}_2} H)$$

- NIST12-Database
- correction term because it changes the total enthalpy of the LNG mixture but
- is a non-combustible component and
- includes the evaporation heat  $\Delta_{\text{vap}, \text{N}_2} H$  of the dissolved nitrogen

# Changes in the Enthalpies of Methane, Oxygen, Water and Carbon Dioxide



# Calorific Value of Methane – Temperature Dependence



# Results for Enthalpies and Calorific Values

Example	Methane	A	B	C	D	E	E (Composition-analysis 3x better)		
$T =$	-160	-158.15	-158.15	-158.15	-160.78	-161.04	-161.04	°C	
$p =$	2	2.214	1.172	1.456	1.34	1.16	1.16	bar	
<b>Enthalpy</b> $T_0=25\text{ °C},$ $p_0=1.01325\text{ bar}$	$H_{\text{mix}} =$	-74540 ± 1080	-76252 ± 879	-77863 ± 923	-75704 ± 974	-74730 ± 1028	-74963 ± 1054	-74963 ± 1045	J/mol
	$U_{\text{rel}} =$	-4646 ± 67 1.45 %	-3799 ± 44 1.15 %	-4022 ± 48 1.19 %	-4229 ± 54 1.29 %	-4371 ± 60 1.38 %	-4479 ± 63 1.41 %	-4479 ± 62 1.39 %	J/g
<b>Enthalpy</b> $(T,p)$	$H_{\text{mix}} =$	-89051 ± 1128	-93085 ± 950	-94542 ± 991	-91331 ± 1032	-89857 ± 1081	-89929 ± 1105	-89929 ± 1088	J/mol
	$U_{\text{rel}} =$	-5551 ± 70 1.27 %	-4638 ± 47 1.02 %	-4884 ± 51 1.05 %	-5102 ± 58 1.13 %	-5256 ± 63 1.20 %	-5373 ± 66 1.23 %	-5373 ± 65 1.21 %	J/g
<b>Difference of Enthalpy</b> $T-T_0, p-p_0$	$\Delta_{\text{mix}}H =$	-14511 ± 303	-16833 ± 346	-16679 ± 344	-15626 ± 323	-15127 ± 314	-14966 ± 312	-14966 ± 301	J/mol
	$U_{\text{rel}} =$	-905 ± 19 2.09 %	-839 ± 17 2.05 %	-862 ± 18 2.06 %	-873 ± 18 2.07 %	-885 ± 18 2.08 %	-894 ± 19 2.08 %	-894 ± 18 2.01 %	J/g
<b>Calorific Value</b> $T_0=25\text{ °C},$ $p_0=1.01325\text{ bar}$	$H_s =$	890628 ± 1353	1043373 ± 1121	1047887 ± 1171	970271 ± 1226	925044 ± 1289	916675 ± 1320	916675 ± 1088	J/mol
	$U_{\text{rel}} =$	55515 ± 84 0.15 %	51986 ± 56 0.11 %	54131 ± 60 0.11 %	54198 ± 68 0.13 %	54110 ± 75 0.14 %	54772 ± 79 0.14 %	54772 ± 65 0.12 %	J/g
<b>Calorific Value</b> $(T,p)$	$H_s =$	923553 ± 2064	1082837 ± 1779	1087650 ± 1843	1006676 ± 1901	959486 ± 1979	950774 ± 2022	950774 ± 1318	J/mol
	$U_{\text{rel}} =$	57567 ± 129 0.22 %	53952 ± 89 0.16 %	56185 ± 95 0.17 %	56231 ± 106 0.19 %	56125 ± 116 0.21 %	56809 ± 121 0.21 %	56809 ± 79 0.14 %	J/g
<b>Difference of Calorific Value</b> $T-T_0, p-p_0$	$\Delta H_s =$	-32925 ± 936	-39464 ± 905	-39762 ± 920	-36405 ± 910	-34442 ± 919	-34099 ± 930	-34099 ± 601	J/mol
	$U_{\text{rel}} =$	-2052 ± 58 2.84 %	-1966 ± 45 2.29 %	-2054 ± 48 2.31 %	-2034 ± 51 2.50 %	-2015 ± 54 2.67 %	-2037 ± 56 2.73 %	-2037 ± 36 1.76 %	J/g

All uncertainties are given with an expansion factor of  $k=2$ .

# Uncertainty Calculations

Principles:

- **Model equations:** see previous slides
- **Uncertainties** from:
  - literature (e.g. LNG Custody Transfer Handbook 3rd ed.)
  - NIST data base
  - estimated ...
  - traceability not checked

- **Sensitivity coefficients:** differential calculus or numerical

- **Total uncertainty:**

$$u^2(y) = \sum_k u_i^2(y) + \sum_k \sum_{l \neq k} r(z_k, z_l) \cdot u_k(y) \cdot u_l(y)$$

- **Correlations:**

- differences in enthalpies and calorific values have common uncertainty sources
- stoichiometric reaction equation

# Calorific value – Main (relative) uncertainty contributions (in %)

Uncertainty contributions due to:	u(x), k=1 (approx.)	component	LNG-Examples						E + Analysis 3 times better
			Methane	A	B	C	D	E	
Temperature	± 0.5 °C	all	0.154	0.288	0.270	0.217	0.181	0.170	0.401
Pressure	± 30 mbar	LNG, O <sub>2</sub>	0.001	0.001	0.001	0.001	0.001	0.001	0.002
Melting and Sublimation heats	± 72/40/56 J/mol	H <sub>2</sub> O/CO <sub>2</sub> /N <sub>2</sub>	1.853	3.820	3.551	2.745	2.245	2.092	4.923
Changes of enthalpies without phase transitions	± 1 %	all	5.270	9.288	8.647	7.125	6.136	5.785	13.609
Enthalpies of formation	± 500 J/mol	LNG	27.291	24.325	25.003	26.122	26.869	27.065	62.800
	± 20/65 J/mol	H <sub>2</sub> O/CO <sub>2</sub>	0.547	1.066	0.997	0.786	0.651	0.610	1.436
Concentration (without correlations)	± 0.09 % or 10 ppm <sup>1</sup>	all	41.546	39.235	39.680	40.461	40.994	41.240	10.798
Concentration (caused by correlations)		all (-N <sub>2</sub> )	23.338	21.978	21.851	22.543	22.923	23.037	6.032
Sum			100.000	100.000	100.000	100.000	100.000	100.000	100.000

1) 10 ppm is the lowest detection limit in case of concentration c=0 for a LNG component.



# Conclusions

- **Uncertainties** ( $k=2$ ) in the liquid state:
  - Enthalpies: 1.0 – 1.3 %
  - Calorific values: 0.14 – 0.22 %
  
- Main uncertainty contributions:
  - **Enthalpy of formation** of the pure components
  - **Composition analysis** of the LNG
  
- Enthalpy difference approx. **900 J/g** between standard conditions and liquid state
  
- Neglecting the LNG **cooling potential**:
  - effective loss of energy (by the regassification process)
  - up to 500 k€ per tank ship (2.5 €/kWh, 150000 m<sup>3</sup> cargo capacity and density 450 kg/m<sup>3</sup>)